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Coupled techniques for arsenic speciation in food and drinking water: a review

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Arsenic is ubiquitous in nature appearing in various chemical forms. The toxicity, environmental mobility and accumulation of As in living organisms depends on the form in which the element exists, thus requiring techniques which can identify specific forms whilst retaining their integrity during extraction and pre-treatment prior to measurement. Both organic and inorganic arsenic species may be present in food staples of both terrestrial and marine origin as well as natural waters, at sub ng l^{-1} to high mg l^{-1} levels. In this review, the speciation steps (sample preparation, species speciation and detection) most commonly used for the determination of As in food are described. High performance liquid chromatography separation with plasma source mass spectrometry is often the technique of choice due to its versatility, robustness and good detection limits. However, detection systems such as atomic absorption spectroscopy, atomic fluorescence spectrometry, and atomic emission spectrometry are also widely used and covered in this review together with some less utilised techniques.

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1. Introduction

Elemental speciation is well established as an important discipline in analytical chemistry. Arsenic is a ubiquitous element in the environment having been introduced *via* both natural and anthropogenic routes.[1] It can be found in the atmosphere, the pedosphere, the hydrosphere and the biosphere. In addition to the biological mechanisms, including microbiological processes, physico-chemical processes such as oxido-reduction, precipitation/solubilisation, and adsorption/desorption determine the biogeochemical behaviour of As.[2] Routine determination of the As content of a sample can be achieved by measurement of the total As using a quantitative procedure.[3] Although arsenic has the reputation of being a toxic element, is also well established that its toxicity critically depends on the chemical form in which it exists and that inorganic species, arsenite (As^{III}) and arsenate (As^{V}), are classified as more toxic than organo arsenic compounds.[4] The oxidation state of organic forms also changes the toxicity, so that trivalent methylated forms are likely to be more toxic than previously thought.[5] Arsenobetaine (AsB) is the major As species in fish and other seafood, and arsenocholine (AsC) is considered as a precursor of AsB, which is the end product of marine arsenic metabolism.[6] These are not considered toxic compounds.[7] Other arsenicals such as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), are less toxic than inorganic arsenic,[4] and together with trimethylarsine oxide are often found in marine organisms, together with many arsenosugars and arsenic containing lipids in the case of marine algae and seaweed.[8,9]

The accumulation of arsenic by plants and fauna of marine origin is relatively high compared to other food sources,[10,11] therefore, many arsenic speciation studies have focused on these types of food. Even though the majority of ingested arsenic (75%) is contributed by fish and shellfish, it generally represents only a small percentage (2%) of the daily dietary intake.[12] Seaweeds used in human foods have a total arsenic content of between 0.031–149 mg kg^{-1} and inorganic arsenic between <0.014 to 117 mg kg^{-1}.[13] In fish, the As contents varies according to the species of fish concerned; average concentrations vary between 5 and 100 mg kg^{-1},[11] although conger and dogfish may contain elevated values of 100 to 250 mg As per kg. In flat fish the values vary between 10 to 60 mg kg^{-1}.[14] Nevertheless it has been confirmed that these elevated concentrations in seafood cause little risk to health, since almost 80–90 % of arsenic is in the organic form (AsB, AsC, arsenosugars, and arsenolipids).[7] Rattanachongkiat *et al.*[15] in their study of arsenic speciation in sardines, demonstrated that among 95% of As extracted (5.8 mg per kg dry weight), 77% was AsB, 17% DMA and 6% inorganic arsenic.

Because of its widespread nature, arsenic exists in all natural waters and concentrations of arsenic between <0.5 μg l^{-1} and more than 5000 μg l^{-1} have been reported. The WHO recommended threshold value for As in drinking water is 10 μg l^{-1}.[16] However, freshwater usually contains less than 10 μg l^{-1} and frequently less than 1.0 μg l^{-1} of arsenic. In some cases, much higher concentrations in groundwater have been monitored. In such areas, often more than 10% of wells are affected (sometimes up to 90%), with arsenic levels exceeding 50 μg l^{-1}. It has

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been reported that some countries such as Argentina, Chile, Mexico, China, and Hungary and more recently in West Bengal (India), Bangladesh and Vietnam have high levels of As in ground water.[17] The inorganic As species, As^{III} and As^{V}, are the predominant species found in water,[18–20] although the concentration of each species varies. A study of thermal waters in New Zealand for example,[21] found concentrations up to 8.5 mg l^{-1} As with the trivalent As form being the dominant species and contributing up to 90% of total As. The concentration of arsenic in seawater is less than 2.0 μg l^{-1}. Baseline concentrations of arsenic in unpolluted surface water and groundwater typically range between 1–10 μg l^{-1}.[21] The weathering and dissolution of arsenic-bearing rocks, minerals and ores also lead to occurrence of arsenic in water,[22] and the arsenic cycle through the groundwater compartment has an important impact on human toxicology.[23] It has been concluded by the International Agency for Research on Cancer that there is sufficient evidence in humans to suggest that arsenic in drinking-water causes cancers of the urinary bladder, lung and skin.[24] According to a study that has been conducted in West Bengal, 94% of those people exposed to high levels of arsenic in drinking water had leukomelanosis and hyperkeratosis which can lead to skin cancer.[22]

1.1 Chemistry of arsenic

Arsenic is a metalloid which ranks 20th in natural abundance and 12th in the human body.[25] It has been used as a medicine, and it has also been utilized in various field such as electronics, agriculture, livestock, metallurgy, industry,[21] pesticides,[26] and fertilizers.[27] More than 245 minerals contain arsenic, the most important arsenic bearing minerals being orpiment (As_2S_3), realgar (AsS), mispickel (FeAsS), loelling-ite ($FeAs_2$), niccolite (NiAs), cobaltite (CoAsS), tennantite ($Cu_{12}As_4S_{13}$), and enargite (Cu_3AsS_4).[28] The origins of high arsenic concentrations in the environment are through volcanic eruption and other natural processes, and human activities such as the disposal of industrial waste chemicals, the smelting of arsenic bearing minerals, the burning of fossil fuels, and the application of arsenic compounds in many products over the past hundred years.[29] Mining operation contribute high level of As and other heavy metals which are mobilized in the soil and then accumulated in the food chain *via* plants.[30–32] Arsenic exists in four oxidation states, +V (arsenate), +III (arsenite), 0 (arsenic), and −III (arsine and arsenide). The most common species in nature are the two highest oxidation states, while the two lowest are rare.[33] Apart from arsenite, arsenate and their methylated derivatives, there are also other compounds such as "fish arsenic" (arsenobetaine and arsenocholine), and arsenosugars; all of which are compounds of environmental interest. Fig. 1 shows examples of some common arsenic compounds.

1.2 Toxicity

Toxicity of arsenic in humans depends on chemical speciation and the oxidation state of the As.[34,35] It is considered that the toxicity of As increases in the order of arsenobetaine; arsenosugar, dimethylarsinic acid; monomethylarsonic acid, arsenate and arsenite.[36] To humans, trivalent arsenic is about 60 times more toxic than the oxidized pentavalent state, because the arsenite can react with sulfydryl groups, whereas the arsenate does not.[37] Inorganic As compounds are about 100 times more toxic than organic As compounds (DMA and MMA).[38] The 50% lethal dose (LD_{50}) values in rat for some arsenical species are illustrated in Table 1. It can be seen from the table that As^{III} is more toxic by a factor of between 200 and 300 times than arsenocholine and trimethylarsine oxide, respectively while trimethylated compounds are virtually non-toxic.[34,39]

1.3 Toxicity in food

The most toxic As species in food are inorganic As, As^{III} and As^{V}, followed by organic arsenic such as MMA^{V}, DMA^{V} and TMA^{+} which are considered less toxic. However, some organic As species found in food as major or constituent like AsB, AC, TMAO, and arsenosugers are considered harmless. Trivalent methylated species such as MMA^{III} and DMA^{V} have been detected in the human urine.[41] These methylated arsenicals are more toxic than inorganic forms[42,43] but they have not been found in any foodstuffs possibly because of lack of a suitable extraction method.

1.4 Arsenic in the diet

Today, inorganic As is not intentionally used as a preservative added to food as it was in the late 1800s and early 1900s.[44] It is, however, well known that the diet contains mainly inorganic and organic As compounds.[44,45] The WHO has established a provisional maximum tolerable daily intake (PMTDI) of 2.1 μg inorganic As per kg per day body weight to cover risks from both water and food, although these guidelines are not for a specific food.[46] Estimates of inorganic As in diet are varied. In the UK, according to the survey by Rose *et al.*[47] it has been found that the amount of inorganic As consumed by an adult is 0.03–0.09 pg per kg body-weight per day. In the United State, it is estimated that the average adult intake is 3.2 μg per day, with a range of 1–20 μg per day.[48] Similar estimates have been observed in children diet.[49] Recently, a higher intake level has been estimated by the European Food Safety Authority (EFSA). However, simplifying assumptions which are related to the ratio of inorganic As to total As in food are used to determine these estimates.[45] It has been reported by EFSA that the national As exposure from food and water across 19 European countries utilizing lower bound and upper bound concentrations have been measured to be in the range 0.13–0.56 μg per kg body weight.[50] It has also been shown that some of our foodstuffs are contaminated with As. Most foodstuffs contain organic arsenic compounds at a total concentration of less than 1 mg kg^{-1}.[51] Rice can contain a relatively high amount of As.[52,53] Rice provides 70% of energy of daily food intake of over half of the world's population especially in Asian developing countries[53] and can accumulate typically between 100–400 μg kg^{-1} As.[11,54,55] The arsenic species determined in rice include As^{III}, MMA, DMA and As^{V}.[56,57] Raber *et al.*[56] have demonstrated that inorganic As and total As of 10 rice sample was 25–171 μg kg^{-1}

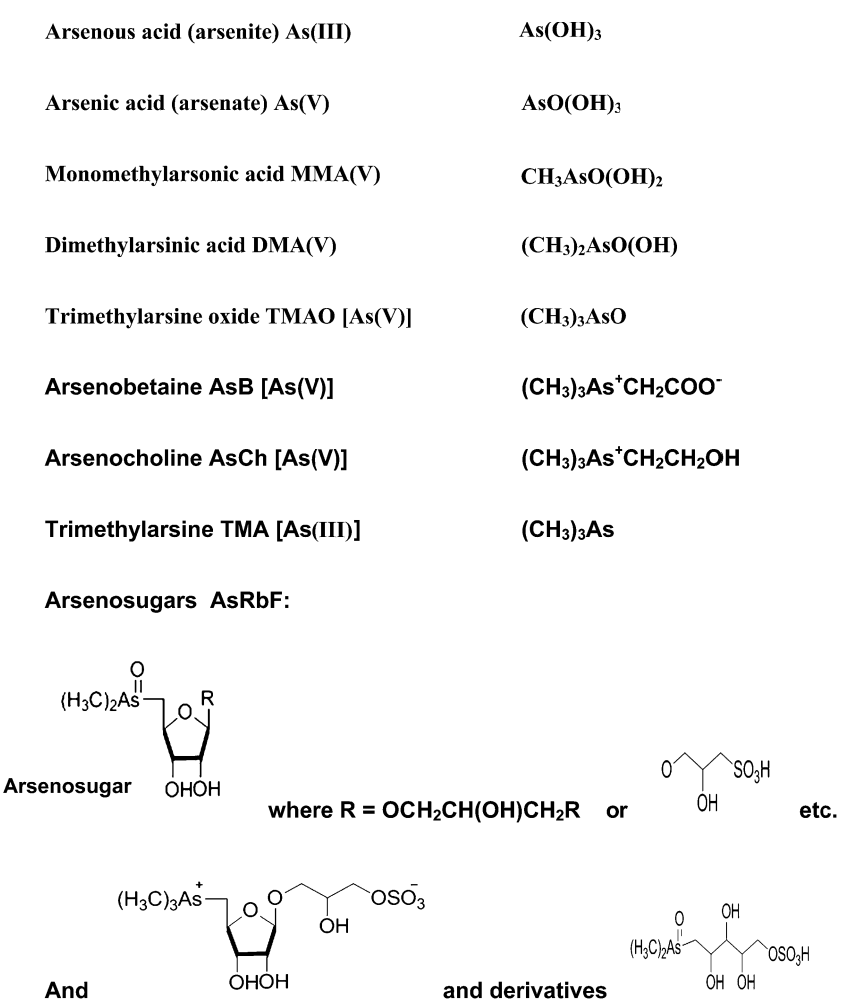

Fig. 1 Examples of some common arsenic species.

Table 1 Lethal dose LD_{50} values of arsenic species in rat[34,39,40]

Arsenic species	Dose (mg kg^{-1})
Arsine	3.0
As^{III}	14.0
As^{V}	20.0
TMA^{+}	890
MMA	700–1800
DMA	700–2600
AsB	>10 000
AsC	6500

and 36–218 μg kg^{-1}, respectively. When the diet is not rice-based wheat will be the major contributor to the consumption of inorganic As. It has been found the total As concentration in wheat samples ranged between 8.6–166 μg per kg dry weight and about 91–95% of the As was found to be in inorganic form, while the rest was mainly DMA.[56,58] However, seafood is the main source of As in diet,[3,59,60] with AsB being the major species in fish and seafood.[61] Other arsenic species such as As^{III}, As^{V}, AsC, MMA, DMA, TMAO and arsenic containing lipids are also

Table 2 The concentration (mg kg^{-1}) of inorganic and total arsenic in the 20 food groups of the 2006 UK Total Diet Study[47]

Food group	Inorganic arsenic mg kg^{-1}	Total arsenic mg kg^{-1}
Bread	<0.01	<0.005
Miscellaneous cereal	0.012	0.018
Carcase meat	<0.01	0.006
Offal	<0.01	0.008
Meat products	<0.01	0.005
Poultry	<0.01	0.022
Fish	0.015	3.99
Oils and fats	<0.01	<0.005
Eggs	<0.01	<0.003
Sugars and preserves	<0.01	0.005
Green vegetable	<0.01	0.004
Potatoes	<0.01	0.005
Other vegetables	<0.01	0.005
Canned vegetables	<0.01	0.005
Fresh fruit	<0.01	0.001
Fruit products	<0.01	0.001
Beverages	<0.01	0.003
Milk	<0.01	<0.001
Dairy produce	<0.01	<0.003
Nuts	<0.01	0.007

Table 3 Arsenic concentration in ground water in different countries

Location	Sampling period	Arsenic source	Concentration μg l^{-1}	Reference
Laos PDR	2008	Tube-well water	<0.05–278	71
Kandal, Cambodia	Not mentioned	Aquifer, wells	15–1300	72
		Shallow wells	0–1000	
South Vietnam	2007		<1.0–850	73
West Bengal, India	2000	Hand tube well	21–176	74
		Shallow tube well on agriculture land	40–182	
Michigan, USA	1997	Shallow groundwater	0.5–278	75
Baseline, UK	Not mentioned	Groundwater	<0.5–10	17
Southwest, England	Not mentioned	Groundwater (mining area)	<1.0–80	76
Southern Thailand	Not mentioned	Shallow groundwater (mining contaminated)	1.25–5114	77

present in aquatic organisms, as well as arsenosugars in marine algae and seaweed.[34,62–64] Table 2 shows the total As and inorganic As concentrations reported in 20 different food stuffs in the UK from a study by Rose *et al.*[47]

1.5 Arsenic in natural waters

Human exposure to elevated As is often associated with drinking water. Drinking water contaminated with As is a major global concern, with over 100 million people affected, including up to 57 million in Bangladesh alone.[65] As is present predominately as As^{III} and As^{V} in water.[18] A clear link between elevated As exposure *via* drinking water and the prevalence of skin, lung, and bladder cancer has been reported based on epidemiological studies of populations exposed to high levels of As.[66]

The levels of As in uncontaminated groundwater usually range from 1–2 μg l^{-1}.[21] The predominant arsenic species in ground water is As^{V} while As^{III} is a minor As species.[67,68] In some contaminated areas the concentrations of As in ground water can reach as high as hundreds of μg l^{-1} as summarized in Table 3. Contamination of ground water by As has already been demonstrated in 20 countries around the world.[69] Millions of people in As-contaminated ground water areas drink water with As concentration ≥50 μg l^{-1},[17,69] *i.e.* significantly higher than the World Health Organization (WHO) maximum permissible limit in drinking water which is 50 μg l^{-1} and the recommended value is 10 μg l^{-1}.[70] Various analytical techniques have been used to measure As in drinking water, some of which are included in Table 5.

2. Methods to speciate arsenic in food

2.1 Sampling and sample pre-treatment for speciation

Maintaining the concentration and chemical structure of the original species during the sample preparation and extraction steps are critical requirements for obtaining information on accurate As speciation.[78] During these procedures problems may result from losses during sampling, unrepresentative samples,[79] contamination, inter conversion between species, inefficient extraction of the analyte, and the possibility of precipitation and wall effects from the sample container.[80–82] The possible risk of a redox interconversion of inorganic As forms to other species can be minimized using microwave-assisted extraction.[81] Microorganisms can participate in a range of element transformations including a change in valence (*i.e.* oxidation/reduction) or chemical form (*i.e.* solid, liquid and gas).[83] It is well-known that many microorganisms (bacteria, fungi and yeast) have ability of biomethylate arsenic and both volatile (*e.g.*, methylarsines) and nonvolatile (*e.g.*, methylarsonic acid and dimethylarsinic acid) compounds are formed.[84] Biological sample should be kept at low temperatures as bacteria can degrade the integrity of the sample. Drying is often used for the stabilization of samples particularly freeze-drying or lyophilisation which tend to reduce analyte loss.[85]

2.2 Extraction

Sample extraction is one of the crucial steps in the analysis of food samples. It is important to avoid chemical transformation of the species during the extraction process, and to ensure the full extraction of each species. Extraction procedures employ a range of approaches including solid–liquid extraction[86] liquid–liquid extraction,[82] solid phase extraction (SPE)[87] and solid phase microextraction (SPME).[88] Solid sample preparation generally includes milling, grinding, freeze drying or sieving following by some forms of extraction. Enhanced techniques such as soxhlet,[89] sonication,[90] pressurized liquid extraction (PLE),[91] microwave-assisted extraction (MWA)[92] and supercritical fluid extraction (SFE)[93] have also been utilized for the determination of As in food, although as discussed below, some of these approaches may be problematic for some matrices.

2.2.1 Solvents. Numerous extraction methods have been utilized for total, total inorganic and full As speciation.[94] The extraction is most often achieved *via* water, methanol, methanol–water solvent systems and sometimes, although infrequently, by acetonitrile–water,[95,96] and sequential extractions are common. Some food stuffs have also been treated with enzymes; α-amylase has been used with freeze-dried apple samples. The cellulose in freeze-dried apple samples is broken down by α-amylase and extraction yields of arsenic species are improved; this treatment may be followed by extraction with acetonitrile–water.[97,98] A trypsin digestion procedure may be performed on fish samples, and AsB is not decomposed by this

Table 4 Extraction procedures for determining arsenical species in food

Extraction process						
Extraction solution	Shaking/mixing	Sonication	MW-assisted heating	Sub/supercritical fluid	PLE	Soxhlet
Water	10 and 101–109	10, 98, 103, 106 and 110	10, 103, 106 and 111–113	106 and 114	40, 105 and 115	10 and 106
Methanol	10 and 116	10, 117 and 118	10 and 117		115 and 40	10, 106 and 117
Methanol–water mixture	10, 101, 101, 103–106 and 119	10, 18, 98, 103, 106, 115, 117 and 119	10, 18, 92, 103, 106, 120, 121 and 121–124	125	40, 105, 115 and 126–129	10 and 117
Ionic extractants	101, 104, 104, 106 and 115	18, 57, 62, 98, 103, 106 and 130	57, 92, 103, 103, 106, 131 and 132	102		
Enzymes	15, 98, 115, 133 and 134	18, 107 and 135		136		
Others	10, 119, 137 and 138	10, 18, 62 and 139–142	10, 92, 143 and 144	102, 106 and 145–148	128 and 149–151	10

process.[99] McKiernan *et al.*[100] used a sequential extraction to extract As species from fish tissue; fats and lipids were removed from the mixture using acetone and then the As species extracted by water–methanol 150 : 150 (v/v). A summary of research papers focusing on extraction methods for arsenic species in food is shown in Table 4.

2.2.2 Extraction systems. Common extraction methods including mixing/shaking, sonication, microwave-assisted heating and accelerated solvent extraction are presented in Table 4. The preservation of the organoarsenic species is the main requirements of a successful extraction procedure prior to speciation analysis. Thermal and microwave heating have been used for As speciation analysis, following optimization of the microwave conditions. The direct energy of the microwave can be managed using the programming options (controlled power, time, temperature, and/or pressure) of modern commercial instruments. Arsenic species have been removed from fish using microwave-assisted extraction,[96] and As^{III} and As^{V} have been quantified from plant material by using microwave-assisted extraction.[152] Another enhanced extraction technique is pressurized liquid extraction or accelerated solvent extraction. Here the applied temperature, and raised pressure, maintain the solvent below its boiling point, to facilitate safe and rapid extraction.[153] Most instrumental systems can be programmed at various temperature and heating/static times for the solvent within the sample cell. Supercritical fluid extraction has also been used to extract arsenic species from different food matrices.[73]

Ultrasound probe sonication can be used to aid the removal of the analyte from the sample matrix. A standard ultrasonic bath operating at a frequency of 40 kHz may often be used to extract from solids faster than by using classical methods.[93,154] Insoluble arsenic fractions such as protein bound arsenic and/or lipid arsenic have traditionally been little researched due to the absence of a suitable analytical methods and difficulties of a total recovery of species.[93] These drawbacks have been tackled by combining enzymatic treatment with ultrasonic probe sonication in more recent studies.[135]

Supercritical fluid extraction (SFE) has some favourable characteristics which make it attractive as an extraction technique, including the low viscosity and diffusion coefficients.[121] However, it has not found widespread use for speciation studies due to is low extraction efficiency for highly polar or ionic compounds.[122] The addition of complexing agents and/or modifiers may partly address these problems and enhance extraction efficiencies.[155]

Pressurized liquid extraction (PLE) is another automated approach which can provide fast extractions using low solvent volumes and avoiding filtration.[156,157] This method has been reported for As speciation in marine biological materials including mussels and fish samples.[124] However, PLE is not without its problems for speciation studies since dispersion of the sample in an inert medium is a fundamental step. When this dispersal is not homogenous a large reduction in extraction efficiency will be observed.[128]

Microwave digestion is a viable replacement to conventional techniques for many matrices, offering acceptable and reproducible efficiencies, together with a reduction in extraction times, low solvent volumes, and the opportunity of fast and multiple extraction.[126,156] This approach has found widespread application in speciation studies for As. Optimisation is straight forward because of the low number of parameters involved, such as choice of solvent, solvent volume, temperature, extraction time, power and matrix characteristic.[156]

2.3 Methods of separation

Liquid chromatography (LC) is a method often used for arsenic speciation in food. It provides separation of both inorganic and organic forms of As. The coupling of ICP-MS, ICP-AES and HG-AAS with liquid chromatography has also been widely used for arsenic speciation, since LC offers good separation of many arsenic species using a simple interface for real time measurement.[158,159] Arsenical species have been separated using several techniques including anion-exchange HPLC with either isocratic or gradient-step elution or cation-exchange HPLC with isocratic elution. Ion-pair HPLC has also been utilized.[160] Since

Table 5 Arsenic in food and natural water

Matrix	Species	Technique	Separation conditions	Time of separation minute	Amount of sample μl	Detection limits (ng ml^{-1})	References
Rice	As^{III}, As^{V}, DMA and MMA	HPLC-ICP-MS	PEEK PRP-X100 anion exchange column; mobile phase, 20 mM ammonium phosphate buffer, pH 4.5, 40 °C	—	40	Not given	131
Rice	As^{III}, As^{V}, DMA	HPLC-ICP-MS	Waters IC-Pak anion HR column; mobile phase, 10 mM $(NH_4)_2CO_3$, pH 10, Dionex AS7 & AG7 column; mobile phase, 12.5 mM HNO_3, pH 1.8, Hamilton PRP-X100 column; mobile phase, 10 mM $NH_4H_2PO_4$, 10 mM NH_4NO_3, pH 6.3	—	25	As^{III}: 0.10, As^{V}: 0.10, DMA: 0.13	115
Rice	As^{III}, As^{V}, DMA and MMA	HPLC-ICP-MS	PRP-X100 anion-exchange column (Hamilton); mobile phase, 20 mM $NH_4H_2PO_4$, pH 5.6, 40 °C	10	20	As^{III}: 1.3, As^{V}: 1.3 DMA: 1.3, MMA: 1.3	234
Rice	As^{III}, As^{V}, DMA, MMA	HPLC-ICP-MS	Column X-Select (Charged Surface Hybrid; CSH) C18; mobile phase, 7.5 mM tetrabutylammonium hydroxide, 10 mM ammonium phosphate monobasic, 5% methanol, pH 8.25	9	25	As^{III}: 0.1, As^{V}: 0.2, DMA: 0.1, MMA: 0.2	134
Rice, straw	AsB, As^{III}, DMA, MMA, As^{V}	HPLC-ICP-MS	Hamilton PRP-X100 anion exchange column; mobile phase, 10 mM HPO_4^{2-}/$H_2PO_4^{-}$, 2% (v/v) methanol, pH 8.5	11	100	AsB: 0.0136, As^{III}: 0.0196, DMA: 0.0127, MMA: 0.0143, As^{V}: 0.0194	235
Rice	As^{III}, MMA, DMA As^{V}	HPLC-HG-AAS	PRP-X100 analytical and guard anion-exchange column (Hamilton, Reno, NV, USA); mobile phase, 10 mM HPO_4^{2-}/H_2PO^{4-}, pH 6.0	—	—	As^{III}: 0.015, MMA0.06, DMA: 0.06, As^{V}: 0.06	135
Rice	As^{III}, As^{V}, MMA, DMA	HPLC-HG-AFS	Hamilton PRP-X 100 anion-exchange column (250 mm × 4.1 mm I.D. 10 μm); mobile phase, 15 mM phosphate buffer, pH 6	—	—	Not given	64
Plant	As^{III}, As^{V} DMA, MA and TMAO	HPLC-ICP-MS	Cation exchange: ZORBAX 300-SCX column; mobile phase, 20 mM pyridine, pH 2.6, anion exchange: PRP-X100 column; mobile phase, 20 mM $NH_4H_2PO_4$, pH 6, anion exchange: PRP-X100 column; mobile phase, 20 mM NH_4HHCO_3, pH 10.3	7–12	20	Not given	236
Plant	As^{III}, As^{V}, DMA and MMA	HPLC-ICP-MS	Hamilton PRP-X100 anion-exchange column; mobile phase, 30 and 100 mM TRIS acetate buffer, pH 7	13	200	Not given	237
White mustard (*Sinapis alba*)	As^{III}, As^{V}, DMA and MMA	HPLC-ICP-MS	Anion exchange column PRP-X100; mobile phase, 0.01 M Na_2HPO_4 (80%), 0.01 M NaH_2PO_4 (20%), pH 6	—	100	Not given	238
Carrots	As^{III}, As^{V}, MMA, DMA, AsB	HPLC-ICP-MS	Column, Waters IC-Pak Anion HR; mobile phase, 10 mM ammonium carbonate, pH 10	7	20	As^{III}: 0.15, As^{V}: 0.11, MMA: 0.13, DMA: 0.24, AsB: 0.14	40

Table 5 (*Contd.*)

Matrix	Species	Technique	Separation conditions	Time of separation minute	Amount of sample μl	Detection limits (ng ml^{-1})	References
Fruit and vegetable	As^{III}, As^{V}, DMA and MMA	HPLC-ICP-MS	PRP-X100 anion exchange column; mobile phase, ammonia phosphate buffer (6.6 mM ammonium dihydrophosphate, 6.6 mM ammonium nitrate), pH 6.2	—	100	Not given	132
Apple	As^{III}, DMA, MMA, As^{V}	HPLC-ICP-MS	Hamilton PRP-X100 anion exchange column with mobile phase A: 12.5 mM $(NH_4)_2CO_3$; pH 8.5: Mobile phase B: 50 mM $(NH_4)_2CO_3$	30	200	As^{III}: 0.089, DMA: 0.034, MMA: 0.063, As^{V}: 0.19	239
Xerocomus badius (Mushroom)	As^{III}, As^{V}, and DMA	HPLC-HG-AAS	A-First analytical system: Column Supelco LC SAX-1; mobile phase, phosphate buffer (50 mM Na_2HPO_4 and 5 mM $KH_2PO_4 \cdot 2H_2O$), B-Second analytical system: Column, Zorbax SAX, mobile phase, phosphate buffer (100 mM Na_2HPO_4 and 10 mM $KH_2PO_4 \cdot 2H_2O$)	—	—	Not given	240
Plant (bean, rice, hot pepper)	As^{III}, As^{V}, and DMA	HPLC-HG-AFS	Hamilton PRP-X100 anion-exchange column; mobile phase, 5 mM ammonium phosphate buffers, pH 4.7 for 4.1 min; 30 mM at pH 8.0 for 6.0 min; 5 mM at pH 4.7 again for 10 min, in order to equilibrate the column before the following analysis)	21	100	As^{III}: 1.5, DMA: 2.4, MMA: 2.1, As^{V}: 1.8	103
Feed additive	As^{III}, As^{V}, DMA, MMA, Roxarsone (ROX) and *p*-arsanilic acid (ASA)	HPLC-ICP-MS	PRP-X100 anion exchange chromatographic column (Hamilton, USA); ZORBAX Eclipse XDB-C18 chromatographic column (Agilent, USA); mobile phase, A: H_2O; B: 50 mM $(NH_4)_2HPO_4$, pH 6.0	20	15–25	As^{III}: 0.04, As^{V}: 0.15 DMA: 0.24, MMA: 0.36, ROX: 0.5, ASA: 0.092	241
Algae and freshwater plant	Glycerol-arsenosugar (gly-sug), As^{III}, As^{V}, DMA and MMA	HPLC-ICP-MS	PRP-X100 (Hamilton, USA) column; mobile phase, 20 mM $NH_4H_2PO_4$, and Zorbax SCX300 (Agilent, Germany) column; mobile phase, 20 mM pyridine	10	20	As^{III}: 2, As^{V}: 8, MMA: 5, DMA: 3, gly-sug: 15	108
Seaweed	AsB, As^{III}, As^{V}, DMA, ribose-OH, ribose-PO_4, ribose-SO_3	HPLC-ICP-MS	Anion-exchange Hamilton PRP-X100 anion-exchange; mobile phase, 20 mM NH_4HCO_3, pH 9.0, 1% MeOH	25	50	Not given	62
Clams and seaweed	As^{III}, As^{V}	HPLC-HG-AAS	Hamilton PRP-X100 anion exchange column; mobile phase, 20 mM ammonium phosphate pH 6	—	—	Not given	53
Porphyra	As^{III}, As^{V}, MMA, DMA and AsB	HPLC-(UV)-HG-AFS	Hamilton PRP-X100 anion exchange column; mobile phase, 3 mM $(NH_4)_2HPO_4$, pH 8.7	—	—	As^{III}: 2.7, As^{V}: 8.3 MMA: 2.1, DMA: 1.8 AsB: 2.1	242

Table 5 (*Contd.*)

Matrix	Species	Technique	Separation conditions	Time of separation minute	Amount of sample μl	Detection limits (ng ml^{-1})	References
Ground water	As^{III}, As^{V}, DMA and MMA	HPLC-ICP-MS	Strong cation exchange (SCX); strong anion exchange (SAX) cartridge; mobile phase, 1 M HNO_3 for DMA, and 5 ml of 80 mM acetic acid, 5 ml of 1 M HNO_3.	—	—	As^{III}: 0.12, As^{V}: 0.02, MMA: 0.02, DMA: 0.03	243
Water	AsB, As^{III}, As^{V}, MMA and DMA.	HPLC-ICP-MS	Column, Dionex AS7 anion-exchange; mobile phase, A: 2.5 mM $NH_4H_2PO_4$, pH 10.0, B: 50 mM $NH_4H_2PO_4$	30	20	AsB: 0.024, As^{III}: 0.017 As^{V}: 0.026, MA: 0.026, DMA: 0.023	244
Fresh water and seawater	AsB, As^{III}, DMA, MMA and As^{V}	HPLC-HG-AAS	Anion exchange column (Hamilton, Reno, NV, USA); mobile phase, 25 mM phosphate, pH 5.8	—	—	AsB: 0.3, As^{III}: 0.08 DMA: 0.1, MMA: 0.1, As^{V}: 0.3	214
Fresh water	As^{III}, MMA, DMA As^{V}	HPLC-HG-AAS	Anionic column (Hamilton PRP-X100), mobile phase (17 mM $H_2PO_4^-$/HPO_4, pH 6.0)	—	—	As^{III}: 0.1, As^{V}: 0.6, MMA: 0.3, DMA: 0.2	245
Ground water	As^{III}, As^{V}	HPLC-HG-AAS	Anion-exchange column Supelco LC-SAX1 and thermostatted by column oven (CTO-10ASvp); mobile phase phosphate buffer (50 mM Na_2HPO_4, 5 mM, KH_2PO_4; pH 5.4)	—	—	As^{III}: 7.8, As^{V}: 12.0	246
Fresh water	As^{III}, MMA, DMA, As^{V}	HPLC-HG-AFS	Hamilton PRP-X100 anion exchange column; mobile phase A; $NH_4H_2PO_4$/$(NH_4)_2HPO_4$) 5 mM, pH 4.8, mobile phase B: $NH_4H_2PO_4$/$(NH_4)_2HPO_4$) 30 mM, pH 8.0	20	100	As^{III}: 0.05, As^{V}: 0.06, MMA: 0.07, DMA: 0.05	247
Algae, fish tissue and shellfish	Inorganic arsenic, DMA, AsB, Arseniosugar PO_4, Arseninosugar OH, Arsinosugar SO3	HPLC-ICP-MS	Cation exchange Dionex Ionpac CS-10 column; mobile phase, 5 mM pyridinium, pH 2, anion exchange Hamilton PRP-X100 column; mobile phase, 20 mM NH_4HCO_3, pH 10.3	—	50	—	34
Fish and sediment	AsB, AsC, DMA, MMA, As^{III} and As^{V}	HPLC-ICP-MS	Hamilton PRPX-100 column; mobile phase A, 10 mM $NH_4H_2PO_4$–$(NH_4)_2HPO_4$, 2% CH_3CN, pH 6.5; mobile phase B, 100 mM $(NH_4)_2HPO_4$, pH 7.95	10	20	AsC: 0.5, AsB: 0.5, As^{III}: 0.5, DMA: 1.0, MMA: 1.0 As^{V}: 1.5	248
Fish, mussel	AsB, AsC, DMA, MMA, As^{III} and As^{V}	HPLC-ICP-MS	Column, Hamilton PRP-1; mobile phase, 0.5 mM tetrabutylammoniumphosphate–4 mM phosphate buffer, pH 9.	9	20	AsC: 9, AsB: 6, As^{III}: 6, As^{V}: 25, MMA: 22, DMA: 10	249
Dogfish	AsB, DMA, MMA, As^{III} and As^{V}	HPLC-ICP-MS	Anion-pairing column, 10 μm PRP-1; mobile phase, 0.5 mM tetrabutylammonium hydroxide,5% methanol, pH 7, anion-exchange column, PRPX-100 (Hamilton); mobile phase, 8 mM phosphate buffer, pH 7; cation-pairing column PRP-1 (Hamilton); mobile phase, 5% methanol, 2.5% acetic acid and 50 mM sodium dodecylsulphate, pH 2.5	9	200	AsB: 5.0, As^{III}: 1.0	250

Table 5 (*Contd.*)

Matrix	Species	Technique	Separation conditions	Time of separation minute	Amount of sample μl	Detection limits (ng ml^{-1})	References
Fish tissues	AsB, As^{III}, DMA, MMA and As^{V}	HPLC-ICP-MS	Metrosep™ Anion Dual 3 column; mobile phase, A: 5 mM NH_4NO_3: B: 50 mM NH_4NO_3, 2% (v/v) methanol, pH 8.7	12	100	AsB: 22, As^{III}: 15 DMA: 16, MMA: 14 As^{V}: 17	251
Dorm 2, fish	AsB, DMA, MMA, As^{III} and As^{V}	HPLC-ICP-MS	Hamilton PRP-X100 column; mobile Phase, A: 15 mM $(NH_4)_2CO_3$, 2% MeOH, pH 9: B: 50 mM $(NH_4)_2CO_3$, 2% MeOH, pH 9	22	200	AsB: 0.003, As^{III}: 0.01, DMA: 0.004, MMA: 0.003	252
Fish, molluscs and crustaceans	AsB, As^{III}, DMA, MMA and As^{V}	HPLC-ICP-MS	A Hamilton PRPX-100 column, mobile phase, A: 60 mM ammonium carbonate, pH 9, B: H_2O	15	60	Not given	111
Fish tissue, DORM-2	AsB, DMA, MMA, As^{III} and As^{V}	HPLC-ICP-MS	Dionex Ionpac AS4A4 column; mobile Phase, A: 0.4 mM HNO_3, pH 3.4: B: 50 mM HNO_3, pH 1.3	—	100	AsB: 0.042, As^{III}: 0.066, As^{V}: 0.045, MMA: 0.059, DMA: 0.044	253
Fish and oyster	AsB, AsC, As^{III}, As^{V}, DMA, MMA	CE-ICP-MS	15 mM Tris solution containing 15 mM SDS (pH 9.0) was used as the electrophoretic buffer and the applied voltage was set at 122 kV	0.2	0.02	0.3–0.5	254
Fish, crustacean	AsB, As^{III}, As^{V}, DMA, MMA	HPLC-ICP-MS	Hamilton PRP-X100 anion exchange column; mobile phase, A: 5.0 mM Na_2SO_4, pH 10–10.5; B: 50 mM Na_2SO_4, pH 10–10.5 (fish and crustacean), Hamilton PRP-X100 anion exchange column; mobile phase, A: H_3PO_4, pH 7.5: B: 50 mM, pH 6 (sediment)	15	100	Not given	15
Marine organisms	Arsenosugar glycerol, arsenosugar phosphate, arsenosugar sulfonate and arsenosugar sulfate	HPLC-ICP-MS	ZirChrom-SAX column; mobile phase, 1 mM $NH_4H_2PO_4$, pH 5.6, Hypercarb (Thermo Electron Corporation, Runcorn UK) column; mobile phase, 13.8 mM nitric acid, 2% (v/v) MeOH, pH 8	20	20	1.5–2.0	63
Seafood	As^{III}, MMA, DMA, As^{V}, AsB, AC, TMA^{+} and TMAO	HPLC-ICP-MS	An IonPac AG4 guard column and an IonPac AS4A analytical column (both from Dionex Corpn, USA); mobile phase, A: 0.4 mM HNO_3, pH 3.3; B: 50 mM HNO_3, pH 1.3	15	100	As^{III}: 0.03, MMA: 0.05, DMA: 0.05, As^{V}: 1.6, AsB: 0.08, AC: 0.14, TMA^{+}: 0.09, TMAO: 0.13	255
Seafood	AsB, AsC, As^{III}, DMA, MMA and As^{V}	HPLC-ICP-MS	IonPac AS7 anion exchange column; mobile phase, A: 1.0 mM HNO_3, 1% (v/v) methanol, pH 2.9: B: 80 mM HNO_3, 1% (v/v), pH 1.3	9.5	50	AsB: 8.5, AsC: 6.7 As^{III}: 5.4, DMA: 10.7 MMA: 10.8, As^{V}: 6.2	80
Oyster tissue	DMA, MMA, As^{V}, oxo-arsenosugars: O-PO_4, S-Gly and S-PO_4	HPLC-ICP-MS	Hamilton PRP-X100 column; mobile phase, A: 20 mM phosphate buffer, pH 5.6; B: 20 mM phosphate, pH 5.6, MeOH50% (v/v), 40 °C	25	10	Not given	239

Table 5 (*Contd.*)

Matrix	Species	Technique	Separation conditions	Time of separation minute	Amount of sample μl	Detection limits (ng ml^{-1})	References
Shrimp	AsB, DMA, As^{III}, As^{V}, OXO-As-SugPO_4, Thio-As-SugPO_4	HPLC-ICP-MS	Hamilton PRP-X100 anion exchange column; mobile phase, 20 mM $NH_4H_2PO_4$, pH 6, 40 °C, Cation exchange Supelcosil LC-SCX column, mobile phase, 20 mM pyridine at pH 2, 40 °C, reverse phase chromatography using a Shisheido Capcell PAK C18 MGII; mobile phase, 10 mM sodium 1-butansulfonate, 4 mM tetramethylammonium hydroxide, 4 mM malonic acid, 0.5% MeOH, pH 3	19	—	Not given	256
Bivalve mollusks	AsB, As^{III}, MMA, DMA, As^{V}, *p*-arsanilic acid (*p*-ASA)	HPLC-ICP-MS	Hamilton PRP-X100 column; mobile phase, A: 20 mM $(NH_4)_2HPO_4$, pH 6.0; B: 20 mM $(NH_4)_2CO_3$, pH 8.5	15	200	Not given	123
Edible periwinkles	TMA^{+}, AsB, MMA, glycerol arsenosugar and inorganic As	HPLC-ICP-MS	Hamilton PRP-X100 anion exchange column; gradient mobile phase, A: 4 mM NH_4NO_3; B: 60 mM NH_4NO_3, pH 8.65, Hamilton PRP-X200 cation-exchange column; mobile phase, 20 mM pyridine (C_5H_5N)/pH 2.7, formic acid (CH_2O_2)	8	—	Not given	158
Biological tissues (certified material TORT-1 and fresh bivalve tissues)	AsB, As^{III}, MMA, DMA As^{V}	HPLC-HG-AAS	Column, Hamilton PRP X-100 strong anionic exchange column; mobile phase, phosphate buffers (10 mM and 100 mM at pH 5.8)	—	—	AsB: ND, As^{III}: 1.1, DMA: 2.0, MMA: 1.9, As^{V}: 3.9	257
Biota sample	AsB, As^{III}, DMA, MMA and As^{V}	HPLC-HG-AAS	Anion exchange column (Hamilton, Reno, NV, USA); mobile phase, 25 mM phosphate, pH 5.8	—	—	AsB: 0.3, As^{III}: 0.08 DMA: 0.1, MMA: 0.1, As^{V}: 0.3	117
Marine organism	As^{III}, As^{V}, MMA, DMA and AsB	HPLC-(UV)-HG-AFS	Hamilton PRP X-100 (25 cm × 4.1 mm) column; mobile phase, 25 mM phosphate buffer, pH 5.8	—	—	As^{III} : As^{V} : MMA : DMA : AsB = 0.3	257
Canned cod liver tissue	Triethylarsine (Et_3As), triphenylarsine (Ph_3As)	GC-ICP-MS	Column: HP-5MS (30 mm × 0.25 mm × 0.25 μm), carrier gas: He 2 ml min^{-1}, GC program; A: 40 °C, 10 °C min^{-1} to 60 °C, 30 °C min^{-1} to 250 °C, 40 °C min^{-1} to 280 °C, B: 50 °C, 1 min, 50 °C min^{-1} to 180 °C, 3 °C min^{-1} to 220 °C 1 min, 15 °C min^{-1} to 270 °C 8 min	20	—	Et_3As: 0.00005, Ph_3As: 0.00013	258

there is sometimes a requirement for the separation of anions and cations of As in a single analysis, column-switching systems, which involve a combination of anion-exchange and reversed-phase separation, have been developed.[161,162] The coupling of gas chromatography (GC) with ICP-MS has also been used,[163] for example the detection of a range of As-containing hydrocarbons in commercial fish oils[200] and seafood.[149] Speciation analysis of organometallic compounds in complex environmental and industrial samples have been achieved by combination of capillary GC with ICP-MS to utilise the high resolving power of GC and the sensitivity and specificity of ICP-MS.[164] Using GC speciation can be an attractive technique because of the lack of condensed mobile phase although there is often the need for derivatisation of the analyte prior to analysis.[165]

In recent years, the number of reports on the use of capillary electrophoresis (CE) has continued to grow. CE is an attractive technique for elemental speciation since it has several unique characteristic in comparison with GC or HPLC methods *i.e.* high resolving power, rapid, effectual separations, minimal reagent consumption and the probability of separation with only minor disturbances of the existing equilibrium between different species.[166] A wide range of inorganic and organic As species can be separated by this technique.[167] Several element-selective detector have been coupled with CE including both ICP-AES and ICP-MS.[168,169] Yang *et al.*[170] have analysed seafood using capillary electrophoresis-inductively coupled plasma mass spectrometry. As^{III}, As^{V}, MMA and DMA have been separated and determined in dried *Mya arenaria I* and shrimp within 10 min. CE has also been coupled to ICP-MS to quantify the As species AsB, As^{III}, As^{V}, DMA, MMA in fish.[171]

Micro-scale separation has become a popular technique due to the improved separation efficiency, reduced analysis time and reduction in sample consumption.[12,172] Micro-bore and narrow-bore have been coupled with ICP-MS as a result of their compatibility with MS ionisation sources.[12] Narrow-bore-HPLC column coupled with ICP-MS has been used by Wangkarn and Pergantis[173] to analyse several wines. Arsenite at trace levels was found to be the only arsenic species in the analysed wines.

Separation with off line detection depends on the chemical or physical separation of the element of interest. Particular arsenic species are separated selectively before determination as arsenic; for instance, formation of $AsCl_3$ (reasonably volatile, non-polar) from arsenite which is ultimately separated from other organoarsenicals by distillation or solvent partitioning. Off line detection methods have been applied to the separation and determination of inorganic As (As^{III} and As^{V}) and organic arsenic (MMA and DMA) in fish (skate, hake, albacore, blue fin tuna and blue whiting),[174–176] plant extracts[177] and raw vegetable.[178]

Organoarsenical compounds have also been quantified by HPLC-MS with LODs below (30 ng ml^{-1}) approaching those of HPLC-ICP-MS. HPLC-MS and HPLC-MS-MS are most often used to characterize arsenicals, such as AsB, AsC, arsenosugars in biota like algae,[179] oyster[180] and calms.[181] Different chromatographic conditions have been used for arsenic speciation in various matrices (Table 5).

2.4 Certified reference materials

The use of CRM materials has been reviewed extensively with respect of quality control, method validation, interlaboratory testing, control charting and evaluation of analytical results using a matrix-matched CRM.[182] Several arsenic-containing CRMs have been developed, but most of them are certified for the total-element concentration. Species specific CRM materials are now crucial as a result of the increasing used for species specific measurement.[12] Amongst the CRMs available for As are BCR627 (Tuna fish), BCR 710 (oyster tissue), DORM-2 (dog fish muscle), and SRM 1640 (natural water).[183] Species specific materials include TORT-3 (lobster) and several from the National Metrology Institute of Japan (NMIJ), including CRM 7405 (seaweed) and CRM 7503a (rice flour).

3. Methods of detection

3.1 X-ray spectroscopic techniques

X-ray spectroscopic methods are being increasingly used for As speciation analysis. They are most often used for geological samples[184,185] but can also be used for arsenic-rich biological samples.[186,187] The possibility of conducting speciation analysis on solid environmental samples without the need for extraction of the element species has been investigated and a number of X-ray spectroscopic techniques have been used to measure total As and As speciation in different solid environmental and biological samples. However these techniques may have limited application for food analysis, due to the relatively poor detection limits and problems from the high intensity of the X-ray beam modifying the samples.[188,189] XANES and EXAFS have been used for arsenic speciation in biological environmental samples,[190,191] *Daphnia pulex*,[192] plant material,[193,194] seaweed[195] and rice grain.[196]

3.2 Mass spectrometry

MS is the most frequently applied method for identifying and elucidating unknown compounds in foods following speciation. Ionization of the compounds can be achieved by techniques such as ionspray, electrospray, atmospheric pressure chemical ionization (APCI), electron ionization (EI), and fast atom bombardment. Because most As compounds are not volatile, some form of derivatization is require before GC separation. Many As speciation methods are based on conversion of As into the corresponding methylarsine by sodium borohydride, although thioglycolic acid methylester has been used to derivatise methylarsenic to produce lipophilic species,[197] and methyl thioglycolate has been used to derivatize MMA, DMA and inorganic As for extraction into cyclohexane prior to chromatographic separation. Mercaptanes/dimercaptanes or thioglycolic acid methyl esters have also been used to derivatize phenylarsinc compounds before injecting into the GC-MS.[198,199]

3.3 Detection by AAS, AFS and AES

In atomic spectrometry, an excitation source is required to atomise or ionise the analyte of interest. The advantage of these techniques is their inherent sensitive and element specific

detection. Graphite furnace atomic absorption spectroscopy (GFAAS) has found preference over flame AAS for As studies since the sensitivity is greater by a factor of 10–100 times.[201] Both fraction collection and on-line coupling of HPLC with GFAAS have been reported offering detection limit in the range of a few nanogram.[174,202–206]

Due to its low detection limit and high selectivity, hydride generation atomic absorption spectroscopy (HG-AAS) has been traditionally one of the most widely used methods for As speciation.[39,207–210] Hydride generation coupled with AAS is a popular method for determining hydride reducible arsenic compounds such as As^{III}, As^{V}, MMA and DMA. The volatile As species is produced using either by zinc/hydrochloric acid or sodium borohydride/acid mixtures and the volatile As species produced are transported to the detection system with argon gas. By forming arsine gas, the analyte is easily and efficiently separated from its sample matrices and transported to the detection system, sometimes *via* a cryogenic pre-concentration step to obtain better detection limits. However, a number of organo arsenicals, for instance AsB and AC, cannot be detected by this method since they are not able to produce volatile hydrides. In this case, the separation of these species prior to HG-AAS is required followed by conversion of the individual As species *via* photolysis or chemical destruction.[3] As a result of incorporating these techniques, AsB and AC may be determined using hydride generation, although controllable reaction conditions and the reduction of certain interfering elements may be required.[211]

Total As in sea food has been determined by HG-AAS after performing a dry-ashing to the sample.[212] The results in this study were very close to the data achieved by other authors using a range of different methods. HG-AAS has also been widely utilized for the determination of As in water.[213] A summary of publications employing HG-AAS and HPLC coupled with HG-AAS is presented in Table 5.

Coupling atomic fluorescence spectrometry (AFS) with HPLC is now a well-established and useful technique for As speciation. AFS can rival ICP-MS regarding performance criteria such as detection limits, reproducibility, repeatability, and sensitivity for As. AFS also offers low purchase and running cost, shorter warm up times prior to analysis and easy handling.[214] HPLC-(UV)-HG-AFS has been applied to As speciation for the both NRCC-TORT1 reference material and several environmental samples with the detection limits ranging from 0.1 to 0.3 $\mu g\ l^{-1}$.[214]

Finally, atomic emission spectroscopy may be used as an alternative technique for As speciation. Chausseau *et al.*[215] concluded that HPLC-ICP-AES is a reliable technique for As speciation, when very low limit of detections are not required; they reported detection limits better than 10 $\mu g\ l^{-1}$ for As^{III}, and DMA and 20 $\mu g\ l^{-1}$ for As^{V}. The technique can also be used in conjunction with HG, although it should be remembered that not all As species may be determined using this approach.

3.4 Detection by ICP-MS

The merits of ICP-MS are well documented,[216,217] and this approach is now the method of choice in most laboratories for As speciation. The main advantages that the ICP-MS has over the other techniques are its low detection limits, 1–10 pg ml^{-1} range for quadrupole instruments, large linear dynamic range, rapid, multi-element capability for many elements and potential to use isotopic studies (although not As).[218] Despite all of these advantages there some limitations using ICP-MS for As speciation. The use of ICP-MS alone does not provide direct molecular information and it is impossible to identify individual As species without some form of prior separation usually by HPLC.

Interferences can be a problem in ICP-MS, particularly when there is an isobaric overlap due to polyatomic ions formed by combination of two or more atoms. The most significance polyatomic ions are formed from the most abundant isotopes of argon, atmospheric gases, and the solvents or acids used during sample preparation.[219] A major polyatomic interference for As [As is monoisotope m/z 75] is $^{40}As^{35}Cl$. Incomplete dissociation, or recombination in cooler plasma regions may lead to the formation of refractory oxides, especially in the boundary layer around the sampler cone.[220]

These interferences problem can be attenuated in ICP-MS by several methods. Polyatomic interferences can be tackled *via* mathematical correction[221] or by adding another gas such as nitrogen, oxygen, air, helium, and hydrogen to the argon plasma, which can minimise the inherent polyatomic interference. Addition of nitrogen gas to an argon plasma has been found very effective due to an increasing in signal and a decrease in the argon and O-based interferences.[222] However, a more recent approach utilising collision cell technology is now available on commercial instruments for interferences reduction. For As, a reduction in the $^{40}Ar^{35}Cl^{+}$ interference can be achieved using a collision reaction cell including gases such as H_2, O_2, NH_3, CH_4, NO, CO_2 and C_2H_4.[223–225]

Sector field (SF)-ICP-MS is perhaps the ultimate choice for elemental speciation studies due to its sensitivity and ability to resolve isobaric overlaps.[226] Some examples of As speciation studies using this technique include arsenic speciation in xylem sap of cucumber,[227] freshwater fish[228] and fish sample.[228]

3.5 Carbon enhancement of the As signal

Signal enhancement is a well-known phenomenon in inductively plasma mass spectrometry. The addition of carbon to the argon plasma of an ICP-MS causes an increase in the proportion of As atoms that are ionised by the charge transfer effect. This increases the observed counts per second for the As signal at m/z 75.[229–231] Traditionally this has been achieved through the addition of organic solvents to the sample matrix[231] or to the mobile phase[232] to improve sensitivity. Signal enhancement can also be obtained by addition of aqueous solutions of volatile carbon compounds (acetone, methanol, and acetic acid) directly into the thermostatic spray chamber.[233]

4. Conclusion

Arsenic species can accumulate in both plant derived and marine food stuffs. Arsenic exists in food as As^{III} and As^{V},

organic arsenic (such as MMA, DMA) and tetramethylarsonium ion, AC, TMAO, and arsenosugers. Fauna sources such as fish and seafood are well known to contain relatively high concentration of AsB which is not toxic, whereas cereals for example rice, and drinking water may contain inorganic arsenic which may present a risk to health. This review of the literature suggests that appropriate analytical techniques now exists to determine the most common As species in food and waters to ensure that current health guidelines are met.

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