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# Coupled techniques for arsenic speciation in food and drinking water: A Review

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## Abstract

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 $ngl^{-1}$ to high $mgl^{-1}$ 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, and atomic fluorescence spectrometry, atomic emission spectrometry are also widely used and covered in this review.

## 1.1 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, it 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 and inorganic arsenic between <0.014 to 117 mg/ kg [13]. In fish, the As contents varies according to the species of fish concerned; average concentrations vary between 5 and 100 mg/kg [11], although conger and dogfish may contain elevated values of 100 to 250 mg As/ kg. In flat fish the values vary between 10 to 60 mg/ kg [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] . Rattananachongkiat et al [15] in their study of arsenic speciation in sardines, demonstrated that among 95% of As extracted (5.8 mg/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 and more than 5000 µg/l have been reported. The WHO recommended threshold value for As in drinking water is 10 µg/l [16]. However, freshwater usually contains less than 10 µg/l and frequently less than 1.0 µg/l 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. It has 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 As/l 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. Baseline concentrations of arsenic in unpolluted surface water and groundwater typically range between 1-10 µg/l [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 and can lead to skin cancer [22.]

## 1.2 Chemistry of arsenic

Arsenic is a metalloid which ranks 20$^{th}$ in natural abundance and 12$^{th}$ in the human body [25]. It has been uses 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 are 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 and arsenide), 0 (arsenic), and –III (arsine). 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. Table 1 shows the molecular formulae of some common organic arsenic compounds [21].

**Table 1 Some arsenic compounds of environmental interest[21].**

| Name | formula or structure |
|---|---|
| Arsenious acid | $H_3AsO_3$ |
| Arsenic acid | $H_3AsO_4$ |
| Methyl arsine | $CH_3AsH_2$ |
| Dimethylarsine | $(CH_3)_2AsH$ |
| Trimethylarsine | $(CH_3)_3As$ |
| Monomethylarsonic acid | $CH_3AsO(OH)_2$ |
| Monomethylarsenous acid | $CH_3As(OH)_2$ |
| Dimethylarsinic acid | $(CH_3)_2AsOH$ |
| Dimethylarsenous acid | $(CH_3)_2AsOH$ |
| Trimethylarsinic oxide | TMAO |
| Tetramethylarsonium ion | $TMA^+$ |
| Arsenobetaine | $(CH_3)_3As^+CH_2COO^-$ |
| arsenocholine | $(CH_3)_3As^+CH_2CH_2OH$ |
| Dimethylarsinoylribosides | See structures 1-11 in Fig. 1 |
| Trialklylarsonioribosides | See structures 12,13 in Fig. 1 |
| Dimethylarsonoulribtol | See structure 14 in Fig. 1 |
| Glecerophosphorarsnocholine | See structure 15 in Fig. 1 |
| Glecerophosphorarsenocholine | See structure 16 in Fig. 1 |

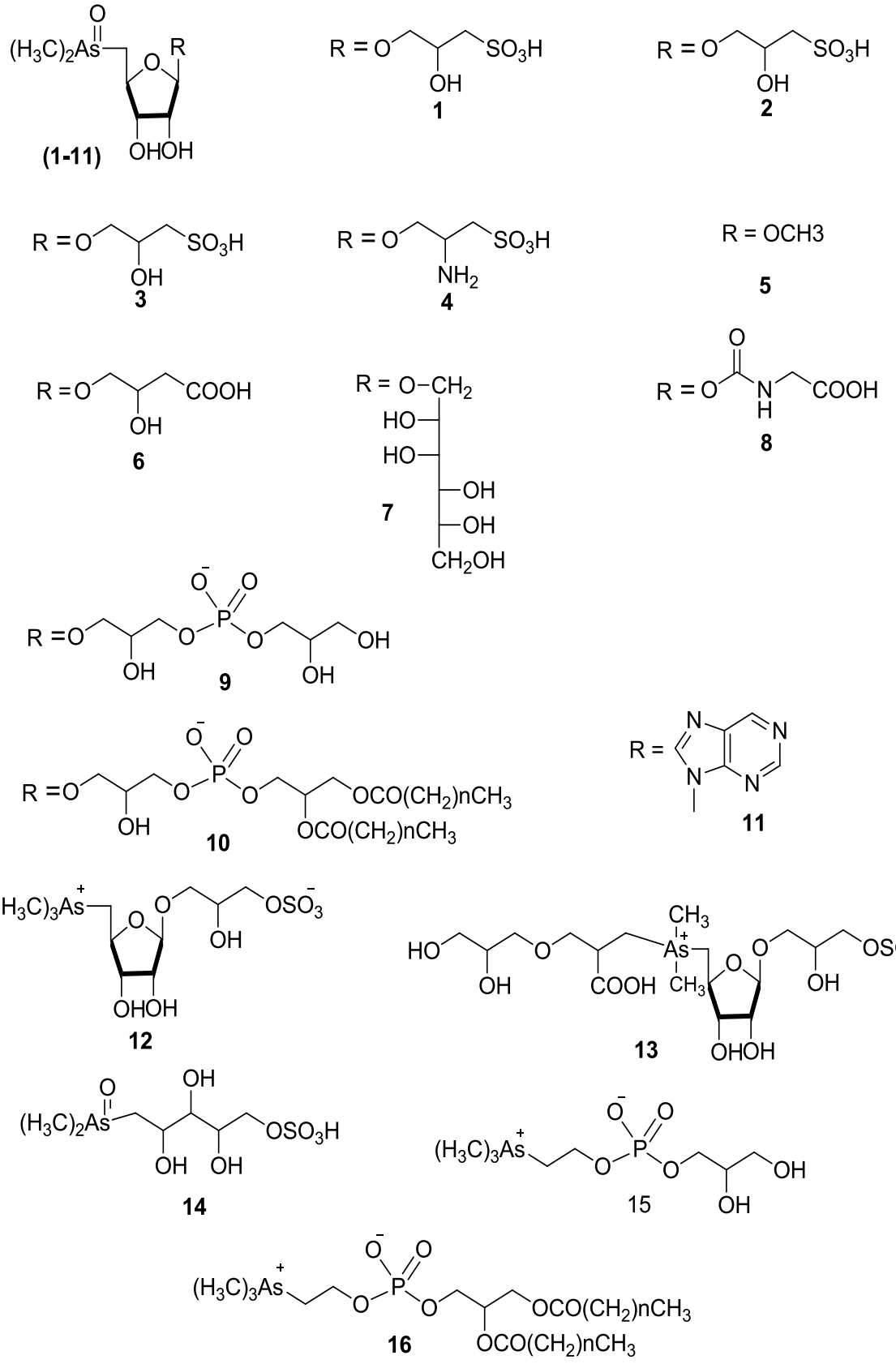


**Fig. 1 Examples of structures of arsenosugars and arsenolipids, 1-16 of Table 1**

## 1.3 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 (LD50) values in rat for some arsenical species are illustrated in Table 2. 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].

**Table 2 Lethal dose $LD_{50}$ values of arsenic species in rat [34, 39, 40].**

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

## 1.4 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 estimated 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.

## 1.5 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/kg/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/kg body-weight/day. In the United State, it is estimated that the average adult intake is 3.2 µg/day, with a range of 1-20 µg/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/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 [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 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 and 36-218 µg/kg, 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/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 present in aquatic organisms, as well as arsenosugars in marine algae and seaweed[34, 62-64]. Table 3 shows the total As and inorganic As concentrations in 20 different food stuffs in the UK[47].

**Table 3 The concentration (mg/kg) of inorganic and total arsenic in the 20 food groups of the 2006 UK Total Diet Study [47].**

| Food group | Inorganic arsenic mg/kg | Total arsenic mg/kg |
|---|---|---|
| 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 |

## 1.6 Arsenic in ground water

The levels of As in uncontaminated groundwater usually range from 1-2 µg/l [21]. The predominant arsenic species in ground water is arsenate while arsenite is a minor As species[65, 66]. In some contaminated areas the concentrations of As in ground water can reach as high as hundreds of µg/l as summarized in Table 4. Ground water As contamination has already been demonstrated in 20 countries around the world [67]. Millions of people in As-contaminated ground water areas drink water with As concentration ≥ 50 µg/l [17, 67], i.e. significantly higher than the World Health Organization (WHO) maximum permissible limit in drinking water which is 50 µg/l and the recommended value is 10 µg/l [68].

**Table 4 Arsenic concentration in ground water in different countries**

| Location | Sampling period | Arsenic source | Concentration µg/l | Reference |
|---|---|---|---|---|
| Laos PDR | 2008 | Tube-well water | <0.05-278 | [69] |
| Kandal, Cambodia | Not mentioned | Aquifer, wells | 15-1300 | [70] |
| | | Shallow wells | 0-1000 | |
| South Vietnam | 2007 | | <1.0-850 | [71] |
| West Bengal, India | 2000 | Hand tube well | 21-176 | [72] |
| | | Shallow tube well on agriculture land | 40-182 | |
| Michigan, USA | 1997 | Shallow groundwater | 0.5-278 | [73] |
| Baseline, UK | Not mentioned | Groundwater | <0.5-10 | [17] |
| Southwest, England | Not mentioned | Groundwater (mining area) | <1.0-80 | [74] |
| Southern Thailand | Not mentioned | Shallow groundwater (mining contaminated) | 1.25-5114 | [75] |

## 1.7 Methods to speciation arsenic in food

### 1.7.1 Sampling and sampling 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 [76]. During these procedures problems may result from losses during sampling, unrepresentative samples, contamination, inter conversion between species, inefficient extraction of the analyte, and the possibility of precipitation and wall effects from the sample container [77-79]. The possible risk of a redox interconversion of inorganic As forms to other species can be minimized using microwave-assisted extraction[78]. 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 [80].

### 1.7.2 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[81] liquid-liquid extraction[79], solid phase extraction (SPE) [82] and solid phase microextraction (SPME) [83]. Solid sample preparation generally includes milling, grinding, freeze drying or sieving following by some forms of extraction. Enhanced techniques such as soxhlet[84], sonication[85], pressurized liquid extraction (PLE)[86], microwave-assisted extraction (MWA)[87] and supercritical fluid extraction (SFE) [88] 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.

#### 1.7.2.1 Solvents

Numerous extraction methods have been utilized for total, total inorganic and full As speciation [89]. The extraction is most often achieved via water, methanol, methanol-water solvent systems or infrequently acetonitrile-water [90, 91], 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 [92, 93]. A trypsin digestion procedure may be performed on fish samples, and AsB is not decomposed by this process [94]. McKiernan et al [95] 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.

**Table 4 Extraction procedures for determining arsenicals species in food.**

| Extraction process | | | | | | |
|---|---|---|---|---|---|---|
| Extraction solution | Shaking/mixing | Sonication | MW-assisted heating | Sub/ supercritical fluid | PLE | Soxhlet |
| Water | 96, 97, 98, 99, 100, 101, 102 | 97, 93, 100 | 97, 100, 103 | 100, 104 | 99, 105, 40 | 100 |
| Methanol | | 106 | 106 | | 105, 40 | 106, 100 |
| Methanol/water mixture | 96, 97, 98, 99, 100 | 97, 93, 105, 18, 106, 100 | 107, 97, 108, 18, 100, 109 | | 99, 105, 40, 110 | 106 |
| $HNO_3$/Methanol mixture | | 111 | | | | |
| $HNO_3$ | | | 112, 113 | | | |
| Ionic extractants | 96, 98, 105, 100 | 97, 93, 18, 57, 100, 62 | 97, 57, 100 | | | |
| Enzymes | 93, 105, 15, 114,115 | 18, 116, 101 | | | | |
| Others | | 18 | | 100 | | |

### 1.7.2.2 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. As species have been removed from fish using microwave-assisted extraction [91], and $As^{III}$ and $As^{V}$ have been quantified from plant material by using microwave-assisted extraction [117]. Another enhanced extraction techniques 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 [118]. 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 40kHz may often be used to extract from solids faster than by using classical methods[88, 119]. Insoluble arsenic fractions such 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[88]. These drawbacks have been tackled by combining enzymatic treatment with ultrasonic probe sonication in more recent studies[116].

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[120].

Pressurized liquid extraction (PLE) is another automated approach which can provide fast extractions using low solvent volumes and avoiding filtration [121, 122]. This method has been reported for As speciation in marine biological materials including mussels and fish samples[123]. 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[124].

Microwave assisted extraction (MAE) 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[121],[126] This approach has found widespread application in speciation studies for As. Optimisation of MAE 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[121].

### 1.7.3 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 [125, 126]. 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 [127]. Since there is sometimes a requirement for the separation of anions and cations of As in a single run, column-switching systems, which involve a combination of anion-exchange and reversed-phase separation, have been developed [128,129].

Different chromatographic conditions have been used for arsenic speciation in various matrices (Table 5).

The coupling of gas chromatography (GC) with ICP-MS has also been used[130]. 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 [131]. 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 [132].

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 [133]. A wide range of inorganic and organic As species can be separated by this technique [134]. Several element-selective detector have been coupled with CE including both ICP-AES and ICP-MS [135,136] . Yang et al [137] 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.

Micro-scale separation has become a popular technique due to the improved separation efficiency, reduced analysis time and reduction in sample consumption[12, 138]. Micro-bore and narrow-bore have been coupled with ICP-MS as a result of their compatibility with ionisation sources of MS [12]. Narrow-bore-HPLC column coupled with ICP-MS has been used by Wangkarn and

Pergontis [139] 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)[140,141, 142] , plant extracts[143] and raw vegetable [144].

### 1.7.4 Arsenic in natural water.

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 Bangladish alone [145]. 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 [146]. Various analytical techniques have been used to measure As in drinking water, some of which are included in Table 5.

## Table 5 Arsenic in food and natural water

| Matrix | species | Technique | HPLC Conditions | Time of separation minute | Amount of sample µl | Detection limits (ng/ml) | References |
|---|---|---|---|---|---|---|---|
| Rice | $As^{III}$, $As^{V}$, DMA and MMA | HPLC-ICP-MS | A PEEK PRP-X100 anion exchange column; mobile phase, 20 mM ammonium phosphate buffer, pH 4.5, 40 °C | - | 40 | Not called | 112 |
| 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.<br>Dionex AS7 & AG7 column; mobile phase, 12.5 mM $HNO_3$, pH 1.8.<br>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<br>$As^{V}$: 0.10<br>DMA: 0.13 | 105 |
| 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 ºC. | 10 | 20 | $As^{III}$: 1.3, $As^{V}$: 1.3<br>DMA: 1.3, MMA: 1.3 | 147 |
| 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,<br>DMA: 0.1, MMA: 0.2 | 115 |
| 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<br>$As^{III}$: 0.0196<br>DMA: 0.0127<br>MMA: 0.0143<br>$As^{V}$: 0.0194 | 148 |
| 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,<br>DMA: 0.06, AsV: 0.06 | 116 |
| Rice | $As^{III}$, $As^{V}$, MMA, DMA | HPLC-HG-AFS | A 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 called | 64 |
| Rice | As $^{III}$<br>As $^{V}$ | FI-HG-AAS | | | | As $^{III}$ : 13.0<br>As $^{V}$: 13.0 | 149 |
| Rice and rice flour | $As^{III}$, total inorganic arsenic(t-iAs) | ET-AAS | | - | - | $As^{III}$:9.75<br>t-iAs:15.05 | 57 |

Table 5 continued

| Matrix | Species | Technique | Chromatographic conditions | Time of separation minute | Amount of sample µl | Detection limits (ng/ml) | References |
|---|---|---|---|---|---|---|---|
| Plant | $As^{III}$, $As^{V}$, DMA and MMA | HPLC-ICP-MS | A Hamilton PRP-X100 anion-exchange column; mobile phase, 30 and 100 mM TRIS acetate buffer, pH 7. | 13 | 200 | Not called | 150 |
| White mustard (*Sinapis alba*) | $As^{III}$, $As^{V}$, DMA and MMA | HPLC-ICP-MS | Anion exchange column PRP-X100; mobile phase, 0.M $Na_2HPO_4$ (80%), 0.01 M $NaH_2PO_4$ (20%), pH 6. | _ | 100 | Not called | 151 |
| 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 |
| 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 dihydro-phosphate, 6.6 mM ammonium nitrate), pH 6.2. | - | 100 | | 113 |
| 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 | 152 |
| *Xerocomus badius* (Mushroom) | $As^{III}$, $As^{V}$, and DMA. | HPLC-HG-AAS | First analytical system: Column Supelco LC SAX-1; mobile phase, phosphate buffer (50 mM $Na_2HPO_4$ and 5 mM $KH_2PO_4$.2H2O), B-Second analytical system: Column, Zorbax SAX, mobile phase, phosphate buffer (100 mM $Na_2HPO_4$ and 10 mM $KH_2PO_4.2H_2O$). | - | - | Not called | 153 |
| Dietary supplement | $As^{III}$, $As^{V}$ | HG-AAS | | - | | Not called | 154 |
| Edible Zingiberaceous Rhizomes | $As^{III}$, $As^{V}$ | HG-AAS | | - | | Not called | 155 |
| 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 | 156 |

Table 5 continued

| Matrix | Species | Technique | Chromatographic Conditions | Time of separation Minute | Amount of sample µL | Detection limit (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|
| 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 | 102 |
| 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% methanol. | 25 | 50 | Not called | 62 |
| Clams and Seaweed | $As^{III}$<br>$As^{V}$ | HPLC-HG-AAS | Hamilton PRP-X100 anion exchange column; mobile phase, 20 mM ammonium phosphate pH 6. | _ | - | Not called | 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 | 157 |
| Ground water | $As^{III}$, $As^{V}$, DMA and MMA | HPLC-ICP-MS | Varian 500 mg Junior Bond Elut® 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 | 158 |
| 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 | 159 |
| 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 | 160 |
| 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 | 161 |
| Ground water | $As^{III}$<br>$As^{V}$ | HPLC-HG-AAS | Column, 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<br>$As^{V}$ 12.0 | 162 |
| Fresh water | Total As | FI-HG-AAS | | - | - | Not called | 102 |

Table 5 continued

| Matrix | Species | Technique | Chromatographic Conditions | Time of separation Minute | Amount of sample µL | Detection limit (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|
| 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 m M $NH_4HCO_3$, 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 $NH_4)H_2PO_4$–$(NH_4)_2HPO_4$, 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 | 163 |
| Fish, mussel | AsB, AsC, DMA, MMA, $As^{III}$ and $As^{V}$. | HPLC-ICP-MS | Column, Hamilton PRP-1; mobile phase, 0.5 mM tetrabutylammon-iumphosphate–4mM phosphate buffer, pH 9. | 9 | 20 | AsC: 9, AsB: 6 $As^{III}$: 6, $As^{V}$: 25 MMA: 22, DMA: 10 | 164 |
| Dogfish | AsB, DMA, MMA, $As^{III}$ and $As^{V}$ | | Anion-pairing column, 10-µm RP-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 50mM sodium dodecylsulphate, pH 2.5. | 9 | 200 | AsB: 5.0 $As^{III}$:1.0 | 165 |
| 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, pH8.7 | 12 | 100 | AsB: 22, $As^{III}$: 15 DMA: 16, MMA: 14 $As^{V}$: 17 | 166 |
| 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, pH9. | 22 | 200 | AsB: 0.003, $As^{III}$: 0.01, DMA: 0.004, MMA: 0.003 | 167 |
| 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, pH9: B:$H_2O$ | 15 | 60 | | 103 |
| 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 | 168 |

Table 5 continued

| Matrix | Species | Technique | Chromatographic Conditions | Time of separation Minute | Amount of sample µL | Detection limit (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|
| 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).<br>Hailton PRP-X100 anion exchange column; mobile phase, A: $H_3PO_4$, pH 7.5: B: 50 mM, pH 6 (Sediment). | 15 | 100<br>20 | Not called | 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;<br>Hypercarb (Thermo Electron Corporation, Runcorn UK) column; mobile phase, 13.8mM nitric acid, 2% (v/v) methanol, pH 8. | 20 | 20 | 1.5-2.0 | 63 |
| Seafood | $As^{III}$, MMA, DMA, $As^{V}$, AsB, AC, $TMA^{+}$ and trimethylarsine oxide (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 nitric acid, pH 3.3; B: 50 mM nitric, pH1.3. | 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 | 169 |
| Seafood | AsB, AsC, $As^{III}$, DMA, MMA and $As^{V}$ | HPLC-ICP-MS | IonPac AS7 anion exchange column; mobile phase, A: 1.0 mM nitric acid, 1 % (v/v) methanol, pH 2.9: B: 80 mM nirtic acid, 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 | 77 |
| 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, methanol 50 % (v/v), 40 ºC. | 25 | 10 | 0.3 for As | 152 |

Table 5 continued

| Matrix | Species | Technique | Chromatographic Conditions | Time of separation Minute | Amount of sample µL | Detection limit (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|
| Shrimp | AsB, DMA, $As^{III}$, $As^{V}$, OXO-As-Sug$PO_4$, Thio-As-Sug$PO_4$. | HPLC-ICP-MS | Hamilton PRP-X100 anion exchange column; mobile phase, 20 mM $NH_4H_2PO_4$, pH 6, 40 ºC.<br>Cation exchange Supelcosil LC-SCX column, mobile phase, 20 mM pyridine at pH 2, 40 ºC.<br>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% methanol, pH 3. | 19 | _ | Not called | 170 |
| Bivalve mollusks | | 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 called | 109 |
| 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 $NH_4NO_3$, pH8.65.<br>Hamilton PRP-X200 cation-exchange column; mobile phase, 20 mM pyridine ($C_5H_5N$)/pH 2.7, formic acid ($CH_2O_2$). | 8 | - | Not called | 125 |
| 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<br>DMA : 2.0, MMA: 1.9<br>$As^{V}$: 3.9 | 171 |
| 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<br>DMA: 0.1, MMA: 0.1,<br>$As^{V}$: 0.3 | 106 |
| 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. | | | AsIII:AsV:MMA:<br>DMA: AsB=0.3 | 171 |
| Fauna | Inorganic arsenic | FI-HG-AAS | | | | $As^{III}$:$As^{V}$= 0.00325 | 172 |

## 1.8 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 compound, whereas cereals for example rice and drinking water may contain inorganic arsenic which may present a risk to health. This review of the literature indicates, that appropriate analytical technique exists to determine the most common As species in food and waters to ensure that current health guidelines are met.

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