

2015-01-01

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

Sadee, B

<http://hdl.handle.net/10026.1/4806>

10.1039/c4ja00269e

Journal of Analytical Atomic Spectrometry

All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.

Disclaimer: This is a pre-publication version. Readers are recommended to consult the full published version for accuracy and citation. Published in J. Anal. At. Spectrom., 30, 102-118 (2015), doi: 10.1039/c4ja00269e

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

B. A. Sadee, M. E. Foulkes and S. J. Hill

**School of Geography, Earth and Environmental Sciences, University of Plymouth, Plymouth
PL4 8AA, UK**

NOTICE: this is the author's version of a work that was accepted for publication in Journal of Analytical Atomic Spectrometry. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Journal of Analytical Atomic Spectrometry, [VOL 30, (DATE 1st December 2014)] DOI 10.1039/c4ja00269e

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 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, 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 routes¹. 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 As². Routine determination of the As content of a sample can be achieved by measurement of the total As using a quantitative procedure³. Although arsenic has the reputation of being a toxic element, it 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 compounds⁴. The oxidation state of organic forms also changes the toxicity, so that trivalent methylated forms are likely to be more toxic than previously thought⁵. 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 metabolism⁶. These are not considered toxic compounds⁷. Other arsenicals such as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), are less toxic than inorganic arsenic⁴, 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 intake¹². 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/kg¹³. In fish, the As contents varies according to the species of fish concerned; average concentrations vary between 5 and 100 mg/kg¹¹, 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/kg¹⁴. 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 al¹⁵ 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/l¹⁶. 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 water¹⁷. The inorganic As species, As^{III} and As^V, are the predominant species found in water¹⁸⁻²⁰, 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 toxicology²³. 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 skin²⁴. 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 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 fields 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), loellingite (FeAs_2), niccolite (NiAs), cobaltite (CoAsS), tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$), 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 operations contribute high levels of As and other heavy metals which are mobilized in the soil and then accumulated in the food chain

via plants³⁰⁻³². 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 rare³³. 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 compounds²¹.

Table 1 Some arsenic compounds of environmental interest²¹.

Name	formula or structure
Arsenious acid	H_3AsO_3
Arsenic acid	H_3AsO_4
Methyl arsine	CH_3AsH_2
Dimethylarsine	$(\text{CH}_3)_2\text{AsH}$
Trimethylarsine	$(\text{CH}_3)_3\text{As}$
Monomethylarsonic acid	$\text{CH}_3\text{AsO}(\text{OH})_2$
Monomethylarsenous acid	$\text{CH}_3\text{As}(\text{OH})_2$
Dimethylarsinic acid	$(\text{CH}_3)_2\text{AsOH}$
Dimethylarsenous acid	$(\text{CH}_3)_2\text{AsOH}$
Trimethylarsinic oxide	TMAO
Tetramethylarsonium ion	TMA^+
Arsenobetaine	$(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{COO}^-$
arsenocholine	$(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CH}_2\text{OH}$
Dimethylarsinoylribosides	See structures 1-11 in Fig. 1
Trialkylarsonioribosides	See structures 12,13 in Fig. 1
Dimethylarsonoulribitol	See structure 14 in Fig. 1
Glycerophosphorarsnocholine	See structure 15 in Fig. 1
Glycerophosphorarsenocholine	See structure 16 in Fig. 1

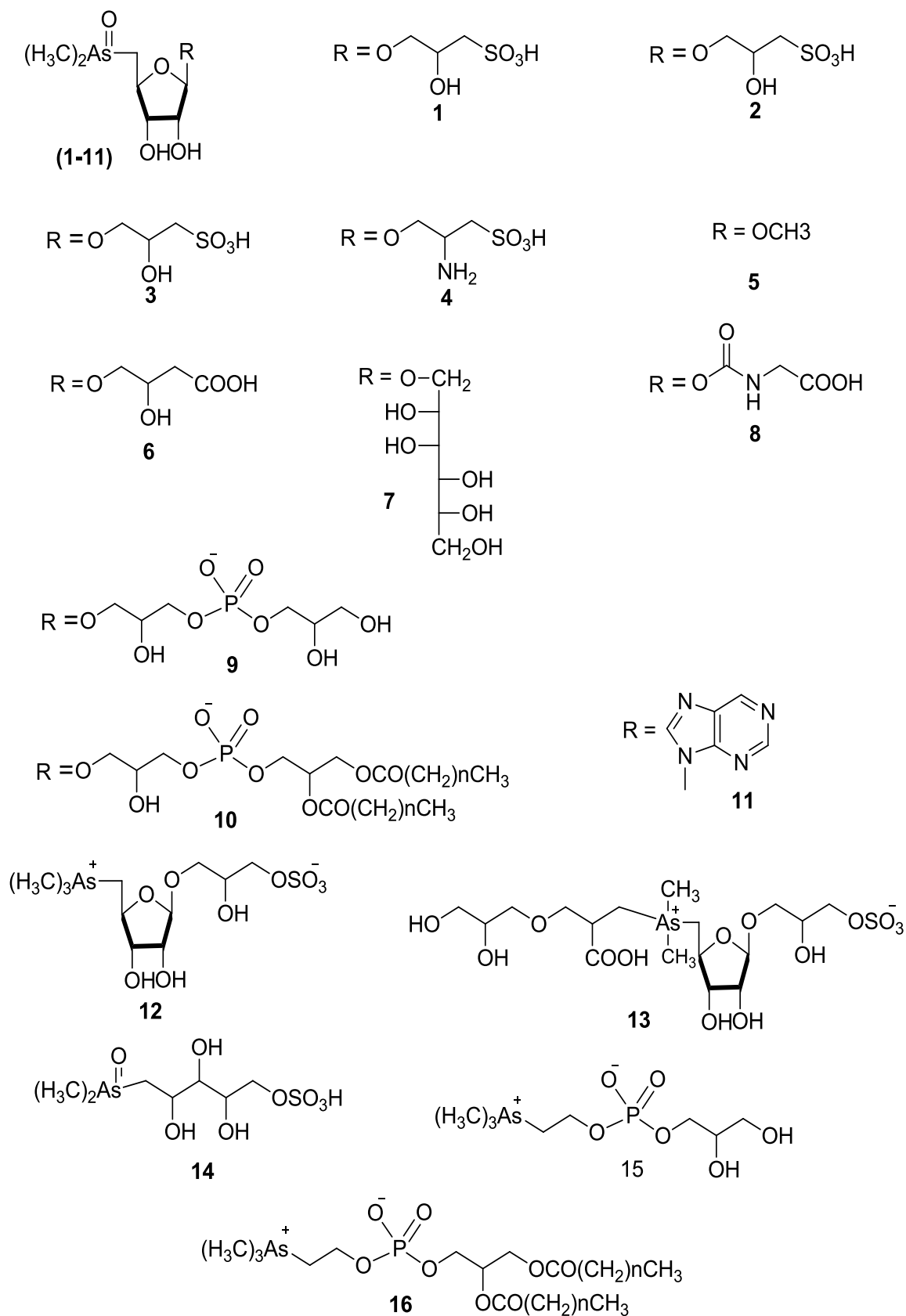


Fig. 1 Examples of structures of arsenosugars and arsenolipids, 1-16 of Table 1

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 arsenite³⁶. To humans, trivalent arsenic is about 60 times more toxic than the oxidized pentavalent state, because the arsenite can react with sulfhydryl groups, whereas the arsenate does not³⁷. 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 LD₅₀ 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 urine⁴¹. 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 1900s⁴⁴. 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 food⁴⁶. Estimates of inorganic As in diet are varied. In the UK, according to the survey by Rose et al⁴⁷ it has been found that the amount of inorganic As consumed by an adult is 0.03-0.09 µg/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/day⁴⁸. Similar estimates have been observed in children diet⁴⁹. 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 estimates⁴⁵. 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 weight⁵⁰. 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/kg⁵¹. 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 countries⁵³ 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 al⁵⁶ 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 seafood⁶¹. 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 UK⁴⁷.

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 $\mu\text{g/l}$ 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 $\mu\text{g/l}$ as summarized in Table 4. Ground water As contamination has already been demonstrated in 20 countries around the world⁶⁷. Millions of people in As-contaminated ground water areas drink water with As concentration $\geq 50 \mu\text{g/l}$ ^{17, 67}, i.e. significantly higher than the World Health Organization (WHO) maximum permissible limit in drinking water which is 50 $\mu\text{g/l}$ and the recommended value is 10 $\mu\text{g/l}$ ⁶⁸.

Table 4 Arsenic concentration in ground water in different countries

Location	Sampling period	Arsenic source	Concentration $\mu\text{g/l}$	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 extraction⁸¹ liquid-liquid extraction⁷⁹, 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 Soxhlet⁸⁴, sonication⁸⁵, 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 speciation⁸⁹. 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 process⁹⁴. McKiernan et al⁹⁵ 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 extraction⁹¹, and As^{III} and As^V have been quantified from plant material by using microwave-assisted extraction¹¹⁷. 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 extraction¹¹⁸. 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 matrices⁷³.

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 species⁸⁸. These drawbacks have been tackled by combining enzymatic treatment with ultrasonic probe sonication in more recent studies¹¹⁶.

Supercritical fluid extraction (SFE) has some favourable characteristics which make it attractive as an extraction technique, including the low viscosity and diffusion coefficients¹²¹. However, it has not found widespread use for speciation studies due to its low extraction efficiency for highly polar or ionic compounds¹²². The addition of complexing agents and/ or modifiers may partly address these problems and enhance extraction efficiencies¹²⁰.

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 samples¹²³. 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 observed¹²⁴.

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 characteristic¹²¹.

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 utilized¹²⁷. 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 used¹³⁰. 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-MS¹³¹. 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 analysis¹³².

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 characteristics 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 species¹³³. A wide range of inorganic and organic As species can be separated by this technique¹³⁴. Several element-selective detectors have been coupled with CE including both ICP-AES and ICP-MS^{135,136}. Yang et al¹³⁷ 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 MS¹². Narrow-bore-HPLC column coupled with ICP-MS has been used by Wangkarn and

Pergontis¹³⁹ 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 extracts¹⁴³ and raw vegetable¹⁴⁴.

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 Bangladesh alone¹⁴⁵. As is present predominately as As^{III} and As^{V} in water¹⁸. 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 As¹⁴⁶. 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 μ l	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) ₂ CO 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 ₄ H ₂ PO ₄ , 10 mM NH ₄ NO ₃ , pH 6.3.		25	As ^{III} : 0.10 As ^V : 0.10 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 ₄ H ₂ PO ₄ , pH 5.6, 40 °C.	10	20	As ^{III} : 1.3, As ^V : 1.3 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, 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 ₂ PO 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	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 ₂ PO ₄ ⁻ , pH 6.0.		-	As ^{III} : 0.015, MMA: 0.06, DMA: 0.06, As ^V : 0.06	116
Rice	As ^{III} , As ^V , MMA, DMA	HPLC-HG-AFS	A Hamilton PRP-X 100 anion-exchange column (250 mm \times 4.1 mm I.D. 10 μ m); mobile phase, 15 mM phosphate buffer, pH 6.	-		Not called	64
Rice	As ^{III} As ^V	FI-HG-AAS				As ^{III} : 13.0 As ^V : 13.0	149
Rice and rice flour	As ^{III} , total inorganic arsenic(t-iAs)	ET-AAS		-	-	As ^{III} : 9.75 t-iAs: 15.05	57

Table 5 continued

Matrix	Species	Technique	Chromatographic conditions	Time of separation minute	Amount of sample μ l	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 (<i>Sinapis alba</i>)	As ^{III} , As ^V , DMA and MMA	HPLC-ICP-MS	Anion exchange column PRP-X100; mobile phase, 0.M Na ₂ HPO ₄ (80%), 0.01 M NaH ₂ PO 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 dihydrophosphate, 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) ₂ CO ₃ ; pH 8.5: mobile phase B: 50 mM (NH ₄) ₂ CO ₃	30	200	As ^{III} : 0.089, DMA: 0.034, MMA: 0.063, As ^V : 0.19	152
<i>Xerocomus badius</i> (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 ₂ HPO ₄ and 5 mM KH ₂ PO ₄ .2H ₂ O), B-Second analytical system: Column, Zorbax SAX, mobile phase, phosphate buffer (100 mM Na ₂ HPO ₄ and 10 mM KH ₂ PO ₄ .2H ₂ O).	-	-	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 ₂ O; B: 50 mM (NH ₄) ₂ HPO 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 $\text{NH}_4\text{H}_2\text{PO}_4$, 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} 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 $(\text{NH}_4)_2\text{HPO}_4$, 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 $\text{NH}_4\text{H}_2\text{PO}_4$, pH 10.0, B: 50 mM $\text{NH}_4\text{H}_2\text{PO}_4$.	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 $\text{H}_2\text{PO}_4/\text{HPO}_4$, pH 6.0)	-	-	As^{III} : 0.1, As^{V} : 0.6, MMA: 0.3, DMA: 0.2	161
Ground water	As^{III} 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 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, Arseniosugar SO_3 ,	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 $(\text{NH}_4)_2\text{HPO}_4$ – $(\text{NH}_4)_2\text{HPO}_4$, 2% CH_3CN , pH 6.5; mobile phase B, 100 mM $(\text{NH}_4)_2\text{HPO}_4$, 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 tetrabutylammoniumphosphate–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 TM 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	166
Dorm 2, fish	AsB, DMA, MMA, As^{III} and As^{V}	HPLC-ICP-MS	Hamilton PRP-X100 column; mobile Phase, A: 15 mM $(\text{NH}_4)_2\text{CO}_3$, 2% MeOH, pH 9 : B: 50 mM $(\text{NH}_4)_2\text{CO}_3$, 2% MeOH, pH 9.	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, pH 9; 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 ₂ SO ₄ , pH 10-10.5; B: 50 mM Na ₂ SO ₄ , pH 10-10.5 (fish and crustacean). Hamilton PRP-X100 anion exchange column; mobile phase, A: H ₃ PO ₄ , pH 7.5; B: 50 mM, pH 6 (Sediment).	15	100 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 ₄ H ₂ PO ₄ , pH 5.6; 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 Corp, USA); mobile phase, A: 0.4 mM nitric acid, pH 3.3; B: 50 mM nitric, 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	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 nitric 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 °C.	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-SugPO ₄ , Thio-As-SugPO ₄ .	HPLC-ICP-MS	Hamilton PRP-X100 anion exchange column; mobile phase, 20 mM NH ₄ H ₂ PO 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% methanol, pH 3.	19	–	Not called	170
Bivalve mollusks		HPLC-ICP-MS	Hamilton PRP-X100 column; mobile phase, A: 20 mM (NH ₄) ₂ HPO ₄ , pH 6.0; B: 20 mM (NH ₄) ₂ CO 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 ₄ NO ₃ ; B: 60 mM NH ₄ NO ₃ , pH8.65. Hamilton PRP-X200 cation-exchange column; mobile phase, 20 mM pyridine (C ₅ H ₅ N)/pH 2.7, formic acid (CH ₂ O 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 DMA : 2.0, MMA: 1.9 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 DMA : 0.1, MMA: 0.1, 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: 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.

Reference

1. S. W. Al Rmalli, P. I. Haris, C. F. Harrington and M. Ayub, *Science of The Total Environment*, 2005, **337**, 23-30.
2. D. Lièvremon, P. N. Bertin and M.-C. Lett, *Biochimie*, 2009, **91**, 1229-1237.
3. K. J. Lamble and S. J. Hill, *Analytica Chimica Acta*, 1996, **334**, 261-270.
4. E. Sanz, R. Muñoz-Olivas and C. Cámara, *Journal of Chromatography A*, 2005, **1097**, 1-8.
5. M. F. Hughes, *Toxicology Letters*, 2002, **133**, 1-16.
6. A. Moreda-Piñeiro, E. Peña-Vázquez, P. Hermelo-Herbello, P. Bermejo-Barrera, J. Moreda-Piñeiro, E. Alonso-Rodríguez, S. Muniategui-Lorenzo, P. n. López-Mahía and D. o. Prada-Rodríguez, *Analytical Chemistry*, 2008, **80**, 9272-9278.
7. W. Goessler, W. Maher, K. Irgolic, D. Kuehnelt, C. Schlagenhaufen and T. Kaise, *Fresenius' journal of analytical chemistry*, 1997, **359**, 434-437.
8. T. Watanabe and S. Hirano, *Arch Toxicol*, 2012, 1-11.
9. J. Moreda-Piñeiro, E. Alonso-Rodríguez, V. Romarís-Hortas, A. Moreda-Piñeiro, P. López-Mahía, S. Muniategui-Lorenzo, D. Prada-Rodríguez and P. Bermejo-Barrera, *Food chemistry*, 2012, **130**, 552-560.
10. C.-g. Yuan, G.-b. Jiang and B. He, *Journal of Analytical Atomic Spectrometry*, 2005, **20**, 103-110.
11. K. A. Francesconi, *Pure and Applied Chemistry*, 2010, **82**, 373-381.
12. S. McSheehy, J. Szpunar, R. Morabito and P. Quevauviller, *TrAC Trends in Analytical Chemistry*, 2003, **22**, 191-209.
13. C. Almela, M. Jesús Clemente, D. Vélez and R. Montoro, *Food and Chemical Toxicology*, 2006, **44**, 1901-1908.
14. L. Benramdane, F. Bressolle and J. Vallon, *Journal of Chromatographic Science*, 1999, **37**, 330-344.
15. S. Rattanachongkiat, G. E. Millward and M. E. Foulkes, *Journal of Environmental Monitoring*, 2004, **6**, 254-261.
16. K. Morita and E. Kaneko, *Analytical sciences*, 2006, **22**, 1085-1090.
17. P. L. Smedley and D. G. Kinniburgh, *Applied Geochemistry*, 2002, **17**, 517-568.
18. L. S. Milstein, A. Essader, C. Murrell, E. D. Pellizzari, R. A. Fernando, J. H. Raymer and O. Akinbo, *Journal of Agricultural and Food Chemistry*, 2003, **51**, 4180-4184.
19. J. M. Ballantyne and J. N. Moore, *Geochimica et Cosmochimica Acta*, 1988, **52**, 475-483.
20. T. Yokoyama, Y. Takahashi and T. Tarutani, *Chemical geology*, 1993, **103**, 103-111.
21. V. K. Sharma and M. Sohn, *Environment International*, 2009, **35**, 743-759.
22. B. Petrusevski, S. Sharma, J. C. Schippers and K. Shordt, *Delft: IRC International Water and Sanitation Centre*, 2007, **17**.
23. J. K. Nag, V. Balaram, R. Rubio, J. Albertí and A. K. Das, *Journal of Trace Elements in Medicine and Biology*, 1996, **10**, 20-24.
24. W. Anders, R. Bull, K. Cantor, D. Chakraborti, C. Chen, A. DeAngelo, D. DeMarini, C. Ferreccio, S. Fukushima and T. Gebel, *Some drinking-water disinfectants and contaminants, including arsenic*, World Health Organization, 2004.
25. B. K. Mandal and K. T. Suzuki, *Talanta*, 2002, **58**, 201-235.
26. G. X. Sun, P. N. Williams, A. M. Carey, Y. G. Zhu, C. Deacon, A. Raab, J. Feldmann, R. M. Islam and A. A. Meharg, *Environmental science & technology*, 2008, **42**, 7542-7546.
27. P. Thomas, J. K. Finnie and J. G. Williams, *Journal of Analytical Atomic Spectrometry*, 1997, **12**, 1367-1372.
28. J. Matschullat, *Science of The Total Environment*, 2000, **249**, 297-312.
29. M. Bissen and F. H. Frimmel, *Acta hydrochimica et hydrobiologica*, 2003, **31**, 9-18.
30. E. Moreno-Jiménez, R. Manzano, E. Esteban and J. Peñalosa, *Journal of Soils and Sediments*, 2010, **10**, 301-312.

31. E. Hozhina, A. Khramov, P. Gerasimov and A. Kumarkov, *Journal of Geochemical Exploration*, 2001, **74**, 153-162.
32. A. M. Murciego, A. G. Sánchez, M. González, E. P. Gil, C. T. Gordillo, J. C. Fernández and T. B. Triguero, *Environmental Pollution*, 2007, **145**, 15-21.
33. R. S. Oremland and J. F. Stolz, *Trends in Microbiology*, 2005, **13**, 45-49.
34. W. Li, C. Wei, C. Zhang, M. Van Hulle, R. Cornelis and X. Zhang, *Food and Chemical Toxicology*, 2003, **41**, 1103-1110.
35. B. K. Mandal, K. T. Suzuki, K. Anzai, K. Yamaguchi and Y. Sei, *Journal of Chromatography B*, 2008, **874**, 64-76.
36. M. Van Hulle, C. Zhang, X. Zhang and R. Cornelis, *Analyst*, 2002, **127**, 634-640.
37. J. F. Ferguson and J. Gavis, *Water Research*, 1972, **6**, 1259-1274.
38. H. Guo, D. Stüben, Z. Berner and Q. Yu, *Applied Geochemistry*, 2009, **24**, 657-663.
39. O. Muñoz, D. Vélez and R. Montoro, *Analyst*, 1999, **124**, 601-607.
40. N. P. Vela, D. T. Heitkemper and K. R. Stewart, *Analyst*, 2001, **126**, 1011-1017.
41. X. C. Le, X. Lu, M. Ma, W. R. Cullen, H. V. Aposhian and B. Zheng, *Analytical Chemistry*, 2000, **72**, 5172-5177.
42. S. Suzuki, L. L. Arnold, K. L. Pennington, B. Chen, H. Naranmandura, X. C. Le and S. M. Cohen, *Toxicology and Applied Pharmacology*, 2010, **244**, 99-105.
43. A. McKnight-Whitford, B. Chen, H. Naranmandura, C. Zhu and X. C. Le, *Environmental science & technology*, 2010, **44**, 5875-5880.
44. A. H. BUCK, *The American Journal of the Medical Sciences*, 1904, **123**, 162.
45. M. F. Hughes, B. D. Beck, Y. Chen, A. S. Lewis and D. J. Thomas, *Toxicological Sciences*, 2011, **123**, 305-332.
46. A. A. Meharg and A. Raab, *Environmental science & technology*, 2010, **44**, 4395-4399.
47. M. Rose, M. Baxter, N. Brereton and C. Baskaran, *Food Additives & Contaminants: Part A*, 2010, **27**, 1380-1404.
48. R. A. Schoof, L. J. Yost, J. Eickhoff, E. A. Crecelius, D. W. Cragin, D. M. Meacher and D. B. Menzel, *Food and Chemical Toxicology*, 1999, **37**, 839-846.
49. L. J. Yost, S. H. Tao, S. K. Egan, L. M. Barraaj, K. M. Smith, J. S. Tsuji, Y. W. Lowney, R. A. Schoof and N. J. Rachman, *Human and Ecological Risk Assessment: An International Journal*, 2004, **10**, 473-483.
50. European Food Safety Authority (EFSA).. 7, (2009), **7**, 1351.
51. J. Laizu, *Bangladesh Journal of Pharmacology*, 2007, **2**, 88-94.
52. A. H. Ackerman, P. A. Creed, A. N. Parks, M. W. Fricke, C. A. Schwegel, J. T. Creed, D. T. Heitkemper and N. P. Vela, *Environmental science & technology*, 2005, **39**, 5241-5246.
53. S. Torres-Escribano, M. Leal, D. Vélez and R. Montoro, *Environmental science & technology*, 2008, **42**, 3867-3872.
54. Y.-G. Zhu, G.-X. Sun, M. Lei, M. Teng, Y.-X. Liu, N.-C. Chen, L.-H. Wang, A. Carey, C. Deacon and A. Raab, *Environmental science & technology*, 2008, **42**, 5008-5013.
55. B. P. Jackson, V. F. Taylor, M. R. Karagas, T. Punshon and K. L. Cottingham, *Environ Health Perspect*, 2012, **120**.
56. G. Raber, N. Stock, P. Hanel, M. Murko, J. Navratilova and K. A. Francesconi, *Food Chemistry*, 2012, **134**, 524-532.
57. I. N. Pasiyas, N. S. Thomaidis and E. A. Piperaki, *Microchemical Journal*, 2013, **108**, 1-6.
58. M. D'Amato, F. Aureli, S. Ciardullo, A. Raggi and F. Cubadda, *Journal of Analytical Atomic Spectrometry*, 2011, **26**, 207-213.
59. I. B. Karadjova, P. K. Petrov, I. Serafimovski, T. Stafilov and D. L. Tsalev, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2007, **62**, 258-268.
60. J. M. Llobet, G. Falcó, C. Casas, A. Teixidó and J. L. Domingo, *Journal of Agricultural and Food Chemistry*, 2002, **51**, 838-842.

61. A. Moreda-Piñeiro, J. Moreda-Piñeiro, P. Herbello-Hermelo, P. Bermejo-Barrera, S. Muniategui-Lorenzo, P. López-Mahía and D. Prada-Rodríguez, *Journal of Chromatography A*, 2011, **1218**, 6970-6980.
62. C. García Sartal, M. d. C. Barciela-Alonso and P. Bermejo-Barrera, *Microchemical Journal*, 2012, **105**, 65-71.
63. A. Terol, F. Ardini, M. Grotti and J. L. Todolí, *Journal of Chromatography A*, 2012, **1262**, 70-76.
64. S. Musil, Á. H. Pétursdóttir, A. Raab, H. Gunnlaugsdóttir, E. Krupp and J. r. Feldmann, *Analytical Chemistry*, 2014, **86**, 993-999.
65. G. W. Page, *Environmental science & technology*, 1981, **15**, 1475-1481.
66. F. Robertson, *Environ Geochem Health*, 1989, **11**, 171-185.
67. D. Chakraborti, M. M. Rahman, K. Paul, U. K. Chowdhury, M. K. Sengupta, D. Lodh, C. R. Chanda, K. C. Saha and S. C. Mukherjee, *Talanta*, 2002, **58**, 3-22.
68. A. H. Smith and M. M. H. Smith, *Toxicology*, 2004, **198**, 39-44.
69. P. Chanpiwat, S. Sthiannopkao, K. H. Cho, K.-W. Kim, V. San, B. Suvanthong and C. Vongthavady, *Environmental Pollution*, 2011, **159**, 567-576.
70. B. D. Kocar, M. L. Polizzotto, S. G. Benner, S. C. Ying, M. Ung, K. Ouch, S. Samreth, B. Suy, K. Phan, M. Sampson and S. Fendorf, *Applied Geochemistry*, 2008, **23**, 3059-3071.
71. J. Buschmann, M. Berg, C. Stengel, L. Winkel, M. L. Sampson, P. T. K. Trang and P. H. Viet, *Environment International*, 2008, **34**, 756-764.
72. T. Roychowdhury, H. Tokunaga and M. Ando, *Science of The Total Environment*, 2003, **308**, 15-35.
73. M.-J. Kim, J. Nriagu and S. Haack, *Environmental Pollution*, 2002, **120**, 379-390.
74. D. K. Nordstrom, *Science(Washington)*, 2002, **296**, 2143-2145.
75. M. Williams, F. Fordyce, A. Pajitprapapon and P. Charoenchaisri, *Geo*, 1996, **27**, 16-33.
76. C. B'Hymer and J. A. Caruso, *Journal of Chromatography A*, 2004, **1045**, 1-13.
77. J. Moreda-Piñeiro, E. Alonso-Rodríguez, A. Moreda-Piñeiro, C. Moscoso-Pérez, S. Muniategui-Lorenzo, P. López-Mahía, D. Prada-Rodríguez and P. Bermejo-Barrera, *Analytica chimica acta*, 2010, **679**, 63-73.
78. M. Montperrus, Y. Bohari, M. Bueno, A. Astruc and M. Astruc, *Applied Organometallic Chemistry*, 2002, **16**, 347-354.
79. S. HonorÚáHansen, *Journal of Analytical Atomic Spectrometry*, 1993, **8**, 1075-1084.
80. Z. Mester and R. Sturgeon, *Sample preparation for trace element analysis*, Elsevier Amsterdam, 2003.
81. S. Van Herreweghe, R. Swennen, C. Vandecasteele and V. Cappuyns, *Environmental Pollution*, 2003, **122**, 323-342.
82. J. A. Baig, T. G. Kazi, A. Q. Shah, M. B. Arain, H. I. Afridi, G. A. Kandhro and S. Khan, *Analytica Chimica Acta*, 2009, **651**, 57-63.
83. J. Wu, Z. Mester and J. Pawliszyn, *Analytica Chimica Acta*, 2000, **424**, 211-222.
84. K. A. Mir, A. Rutter, I. Koch, P. Smith, K. J. Reimer and J. S. Poland, *Talanta*, 2007, **72**, 1507-1518.
85. I. Pizarro, M. Gómez, C. Cámara and M. Palacios, *Analytica Chimica Acta*, 2003, **495**, 85-98.
86. R. Carabias-Martínez, E. Rodríguez-Gonzalo, P. Revilla-Ruiz and J. Hernández-Méndez, *Journal of Chromatography A*, 2005, **1089**, 1-17.
87. S. Foster, W. Maher, F. Krikowa and S. Apte, *Talanta*, 2007, **71**, 537-549.
88. C. Dietz, J. Sanz, E. Sanz, R. Munoz-Olivas and C. Cámara, *Journal of Chromatography A*, 2007, **1153**, 114-129.
89. D. T. Heitkemper, N. P. Vela, K. R. Stewart and C. S. Westphal, *J. Anal. At. Spectrom.*, 2001, **16**, 299-306.
90. J. A. Caruso, D. T. Heitkemper and C. B'Hymer, *Analyst*, 2001, **126**, 136-140.
91. K. L. Ackley, C. B'Hymer, K. L. Sutton and J. A. Caruso, *Journal of Analytical Atomic Spectrometry*, 1999, **14**, 845-850.

92. J. Mattusch, M. Cimpean and R. Wennrich, *International Journal of Environmental Analytical Chemistry*, 2006, **86**, 629-640.
93. J. A. Caruso, D. T. Heitkemper and C. B'Hymer, *Analyst*, 2001, **126**, 136-140.
94. S. Branch, L. Ebdon and P. O'Neill, *Journal of Analytical Atomic Spectrometry*, 1994, **9**, 33-37.
95. J. W. McKiernan, J. T. Creed, C. A. Brockhoff, J. A. Caruso and R. M. Lorenzana, *Journal of Analytical Atomic Spectrometry*, 1999, **14**, 607-613.
96. B. He, Y. Fang, G. Jiang and Z. Ni, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2002, **57**, 1705-1711.
97. Y. Bohari, G. Lobos, H. Pinochet, F. Pannier, A. Astruc and M. Potin-Gautier, *Journal of Environmental Monitoring*, 2002, **4**, 596-602.
98. D. Kuehnelt, K. J. Irgolic and W. Goessler, *Applied Organometallic Chemistry*, 2001, **15**, 445-456.
99. A.-C. Schmidt, W. Reisser, J. Mattusch, P. Popp and R. Wennrich, *Journal of Chromatography A*, 2000, **889**, 83-91.
100. J. A. Brisbin and J. A. Caruso, *Analyst*, 2002, **127**, 921-929.
101. V. G. Mihucz, E. Tatár, I. Virág, C. Zang, Y. Jao and G. Záray, *Food chemistry*, 2007, **105**, 1718-1725.
102. A. Pell, A. Márquez, J. F. López-Sánchez, R. Rubio, M. Barbero, S. Stegen, F. Queirolo and P. Díaz-Palma, *Chemosphere*, 2013, **90**, 556-564.
103. A. Ruttens, A. Blanpain, L. De Temmerman and N. Waegeneers, *Journal of Geochemical Exploration*, 2012, **121**, 55-61.
104. J. A. Brisbin, C. B'Hymer and J. A. Caruso, *Talanta*, 2002, **58**, 133-145.
105. D. T. Heitkemper, N. P. Vela, K. R. Stewart and C. S. Westphal, *Journal of Analytical Atomic Spectrometry*, 2001, **16**, 299-306.
106. J. Gomez-Ariza, D. Sanchez-Rodas, I. Giraldez and E. Morales, *Analyst*, 2000, **125**, 401-407.
107. M. Vilanó and R. Rubio, *Applied Organometallic Chemistry*, 2001, **15**, 658-666.
108. R. Tukai, W. A. Maher, I. J. McNaught and M. J. Ellwood, *Analytica Chimica Acta*, 2002, **457**, 173-185.
109. C. M. Santos, M. A. Nunes, I. S. Barbosa, G. L. Santos, M. C. Peso-Aguiar, M. G. Korn, E. M. Flores and V. L. Dressler, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2013, **86**, 108-114.
110. P. A. Gallagher, J. A. Shoemaker, X. Wei, C. A. Brockhoff-Schwegel and J. T. Creed, *Fresenius' journal of analytical chemistry*, 2001, **369**, 71-80.
111. B. Batista, L. Nacano, S. De Souza and F. Barbosa Jr, *Food Additives & Contaminants: Part A*, 2012, **29**, 780-788.
112. W. Maher, S. Foster, F. Krikowa, E. Donner and E. Lombi, *Environmental science & technology*, 2013, **47**, 5821-5827.
113. G. Norton, C. Deacon, A. Mestrot, J. Feldmann, P. Jenkins, C. Baskaran and A. A. Meharg, *Environmental science & technology*, 2013, **47**, 6164-6172.
114. S. Branch, L. Ebdon and P. O'Neill, *J. Anal. At. Spectrom.*, 1994, **9**, 33-37.
115. S. Nookabkaew, N. Rangkadilok, C. Mahidol, G. Promsuk and J. Satayavivad, *Journal of Agricultural and Food Chemistry*, 2013, **61**, 6991-6998.
116. E. Sanz, R. Muñoz-Olivas and C. Cámara, *Analytica Chimica Acta*, 2005, **535**, 227-235.
117. M. Quaghebeur, Z. Rengel and M. Smirk, *Journal of Analytical Atomic Spectrometry*, 2003, **18**, 128-134.
118. C. Dietz, J. Sanz, E. Sanz, R. Muñoz-Olivas and C. Cámara, *Journal of Chromatography A*, 2007, **1153**, 114-129.
119. P. Bermejo, J. Capelo, A. Mota, Y. Madrid and C. Cámara, *TrAC Trends in Analytical Chemistry*, 2004, **23**, 654-663.
120. S. Babel and D. del Mundo Dacera, *Waste Management*, 2006, **26**, 988-1004.
121. C. Sparr Eskilsson and E. Björklund, *Journal of Chromatography A*, 2000, **902**, 227-250.

122. E. Björklund, T. Nilsson and S. Bøwadt, *TrAC Trends in Analytical Chemistry*, 2000, **19**, 434-445.
123. M. Mato-Fernández, J. Otero-Rey, J. Moreda-Pineiro, E. Alonso-Rodríguez, P. López-Mahía, S. Muniategui-Lorenzo and D. Prada-Rodríguez, *Talanta*, 2007, **71**, 515-520.
124. P. A. Gallagher, S. Murray, X. Wei, C. A. Schwegel and J. T. Creed, *Journal of Analytical Atomic Spectrometry*, 2002, **17**, 581-586.
125. K. Whaley-Martin, I. Koch and K. Reimer, *Science of The Total Environment*, 2013, **456**, 148-153.
126. K. L. Linge, *Geostandards and Geoanalytical Research*, 2006, **30**, 157-174.
127. M. Kumaresan and P. Riyazuddin, *Curr Sci*, 2001, **80**, 837-846.
128. M. Kumaresan and P. Riyazuddin, *CURRENT SCIENCE-BANGALORE*, 2001, **80**, 837-846.
129. A. Taboada-de la Calzada, M. C. Villa-Lojo, E. Beceiro-González, E. Alonso-Rodríguez and D. Prada-Rodríguez, *TrAC Trends in Analytical Chemistry*, 1998, **17**, 167-175.
130. Z. Mester and J. Pawliszyn, *Journal of Chromatography A*, 2000, **873**, 129-135.
131. B. Bouyssiere, J. Szpunar and R. Lobinski, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2002, **57**, 805-828.
132. R. Łobiński and F. C. Adams, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 1997, **52**, 1865-1903.
133. X.-B. Yin, X.-P. Yan, Y. Jiang and X.-W. He, *Analytical Chemistry*, 2002, **74**, 3720-3725.
134. R. Naidu, J. Smith, R. G. McLaren, D. Stevens, M. Sumner and P. Jackson, *Soil Science Society of America Journal*, 2000, **64**, 122-128.
135. B. Deng and W.-T. Chan, *Journal of Chromatography A*, 2000, **891**, 139-148.
136. Q. Tu, J. Qvarnström and W. Frech, *Analyst*, 2000, **125**, 705-710.
137. G. Yang, J. Xu, J. Zheng, X. Xu, W. Wang, L. Xu, G. Chen and F. Fu, *Talanta*, 2009, **78**, 471-476.
138. V. Tanboonchuy, N. Grisdanurak and C.-H. Liao, *Journal of Hazardous Materials*, 2012, **205**, 40-46.
139. S. Wangkarn and S. A. Pergantis, *J. Anal. At. Spectrom.*, 2000, **15**, 627-633.
140. H. Heng-Bin, L. Yan-Bing, M. Shi-Fen and N. Zhe-Ming, *J. Anal. At. Spectrom.*, 1993, **8**, 1085-1090.
141. M. Storelli and G. Marcotrigiano, *Food Additives & Contaminants*, 2000, **17**, 763-768.
142. M. Storelli, R. G. Stuffer and G. Marcotrigiano, *Food Additives & Contaminants*, 2002, **19**, 715-720.
143. K. Bluemlein, A. Raab and J. Feldmann, *Analytical and bioanalytical chemistry*, 2009, **393**, 357-366.
144. O. Muñoz, O. P. Diaz, I. Leyton, N. Nuñez, V. Devesa, M. A. Súñer, D. Vélez and R. Montoro, *Journal of Agricultural and Food Chemistry*, 2002, **50**, 642-647.
145. M. Argos, T. Kalra, B. L. Pierce, Y. Chen, F. Parvez, T. Islam, A. Ahmed, R. Hasan, K. Hasan and G. Sarwar, *American Journal of Epidemiology*, 2011, **174**, 185-194.
146. X. C. Le, S. Yalcin and M. Ma, *Environmental science & technology*, 2000, **34**, 2342-2347.
147. J. H. Huang, P. Fecher, G. Ilgen, K. N. Hu and J. Yang, *Food chemistry*, 2012, **130**, 453-459.
148. E. Sanz, R. Muñoz-Olivas, C. Cámara, M. K. Sengupta and S. Ahamed, *Journal of Environmental Science and Health, Part A*, 2007, **42**, 1695-1705.
149. K. L. Linge and K. E. Jarvis, *Geostandards and Geoanalytical Research*, 2009, **33**, 445-467.
150. R. Larios, R. Fernández-Martínez, I. LeHecho and I. Rucandio, *Science of The Total Environment*, 2012, **414**, 600-607.
151. L. Jedynek, J. Kowalska, M. Kossykowska and J. Golimowski, *Microchemical Journal*, 2010, **94**, 125-129.

152. C. B'Hymer and J. Caruso, *Journal of liquid chromatography & related technologies*, 2002, **25**, 639-653.
153. P. Niedzielski, M. Mleczek, Z. Magdziak, M. Siwulski and L. Kozak, *Food chemistry*, 2013, **141**, 3571-3577.
154. L. García-Rico and L. Tejada-Valenzuela, *Environmental monitoring and assessment*, 2013, **185**, 6111-6117.
155. C. Ubonnuch, S. Ruangwises, W. Gritsanapan and N. Ruangwises, *Evidence-Based Complementary and Alternative Medicine*, 2013, **2013**.
156. X. Liu, W. Zhang, Y. Hu and H. Cheng, *Microchemical Journal*, 2013, **108**, 38-45.
157. C. Zhang, Y. Wang and Y. Ge, *Analytical Letters*, 2013, **46**, 1573-1586.
158. M. Christodoulidou, C. Charalambous, M. Aletrari, P. Nicolaidou Kanari, A. Petronda and N. Ward, *Journal of Hydrology*, 2012, **468**, 94-100.
159. S. N. Ronkart, V. Laurent, P. Carbonnelle, N. Mabon, A. Copin and J.-P. Barthélemy, *Chemosphere*, 2007, **66**, 738-745.
160. J. L. Gómez-Ariza, D. Sánchez-Rodas, I. Giráldez and E. Morales, *Talanta*, 2000, **51**, 257-268.
161. M. Gomez, C. Cámara, M. Palacios and A. Lopez-Gonzalvez, *Fresenius' journal of analytical chemistry*, 1997, **357**, 844-849.
162. P. Niedzielski, *Analytica Chimica Acta*, 2005, **551**, 199-206.
163. C. Demesmay, M. Olle and M. Porthault, *Fresenius' journal of analytical chemistry*, 1994, **348**, 205-210.
164. P. Thomas and K. Sniatecki, *Journal of Analytical Atomic Spectrometry*, 1995, **10**, 615-618.
165. D. Beauchemin, K. Siu, J. W. McLaren and S. S. Berman, *J. Anal. At. Spectrom.*, 1989, **4**, 285-289.
166. L. H. Reyes, J. L. G. Mar, G. M. M. Rahman, B. Seybert, T. Fahrenholz and H. M. S. Kingston, *Talanta*, 2009, **78**, 983-990.
167. R.-Y. Wang, Y.-L. Hsu, L.-F. Chang and S.-J. Jiang, *Analytica Chimica Acta*, 2007, **590**, 239-244.
168. S. Karthikeyan, S. Hirata and C. S. Iyer, *International Journal of Environmental Analytical Chemistry*, 2004, **84**, 573-582.
169. S. Karthikeyan and S. Hirata, *Applied Organometallic Chemistry*, 2004, **18**, 323-330.
170. V. F. Taylor, B. P. Jackson, M. R. Siegfried, J. Navratilova, K. A. Francesconi, J. Kirshtein and M. Voytek, *Environmental Chemistry*, 2012, **9**, 130-138.
171. J. L. Gómez-Ariza, D. Sánchez-Rodas, R. Beltrán and I. Giráldez, *International Journal of Environmental Analytical Chemistry*, 1999, **74**, 203-213.
172. M. Suner, V. Devesa, O. Munoz, F. Lopez, R. Montoro, A. Arias and J. Blasco, *The Science of the Total Environment*, 1999, **242**, 261-270.