Chapter

Arsenic Speciation Techniques in Soil Water and Plant: An Overview

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Abstract

There are more than 100 different arsenic with different characteristics in the soil-water-plant ecosystem. The identification and quantification of individual arsenic species is essential for understanding the distribution, environmental fate and behavior, metabolism and toxicity of arsenic. Due to the hazardous nature of arsenic, people have a high interest in the measurement of arsenic species. The reaction of the formation of arsenic speciation in the soil-water-plant environment is briefly studied. There is little information on methods used to quantify arsenic forms and species in contaminated soil, water and plant. The purpose of this article is to understand the available sample pretreatment, extraction, separation, detection and method validation techniques for arsenic speciation analysis of arsenic species in soil, water and plant. The performances of various sample preparation and extraction processes, as well as effective separation techniques, that contribute greatly to excellent sensitivity and selectivity in arsenic speciation when coupling with suitable detection mode, and method validity are discussed. The outlines of arsenic speciation techniques are discussed in view of the importance to the completeness and accuracy of analytical data in the soil-water-plant samples. To develop cheap, fast, sensitive, and reproducible techniques with low detection limits, still needed to confine research on arsenic speciation present in environmental matrices.

Keywords: Arsenic speciation, extraction, separation, detection, techniques, soil water and plant

1. Introduction

Arsenic (As) is a geogenic toxic metalloid found ubiquitously in environmental systems such as lithosphere (earth crusts, soil, rock, and sediment), hydrosphere (surface water, aquifers, deep wells, and oceans), atmosphere and biosphere (food chain and ecosystems) [1]. Arsenic is considered as the 12th most abundant elements in the earth's crust. Elevated arsenic having been introduced in the ecosystem either by natural routes involve in weathering and other biogeochemical processes or via anthropogenic activities, including mining, and smelting, excessive agricultural utilization of As-based fertilizers and pesticides and irrigation with As-laden groundwater [2–4]. This problem becomes serious concern because once arsenic is released in the soil and water resources, it is bioaccumulated by the terrestrial and aquatic biota, and subsequently enters in the human or animal food chain [5, 6]. In highly arsenic contaminated ($\geq$0.01 mg L^{-1}) area, the migration of arsenic from soil to water and plant is a serious problem, becoming a major threat to sustainable agriculture practices and food security [7, 8]. Empirical data shows that the

concentration of arsenic in contaminated soils lies between 10 mg kg^{-1} and as high as 30,000 mg/kg [9]. In addition, the reported concentrations of arsenic in all natural waters is between <0.5 μg L^{-1} and more than 5000 μg L^{-1}, although maximum permissible contaminant total As limits in drinking water by WHO is 10 μg L^{-1} [1, 10]. Moreover, considering toxicity, the Joint Food and Agriculture Organization and the World Health Organization (FAO/ WHO) Expert Committee on Food Additives proposed that the maximum inorganic arsenic content in food such as polished rice is 0.2 mg kg^{-1} [11–13]. Thus, exposure to arsenic (As) in soil-water-plant becomes global public health and the environment concern due to the wide distribution in ecosystem and its close association with numerous adverse effects.

There are more than 100 different arsenic compounds in the soil-water-plant ecosystem [14, 15]. It is well known that the toxicity, bioavailability, physiological and metabolic processes and mobility of arsenic vary greatly depending on the chemical species and oxidative states rather than its total content [16, 17]. Arsenic (As) speciation analysis may specify not only the determination of total As contents but also considering its specific ionic forms in the aqueous solution and the sequential extracted As related to various mineral phases [18]. According to the IUPAC recommendations, "speciation of an element" is defined as "the distribution of an element amongst defined chemical species in a system" rather than fractionation. While speciation analysis is defined as "analytical activity of measuring the quantities of one or more individual chemical species in a sample" [19].

Arsenic exists multiple oxidation states (+III, +V, 0, –III) and various inorganic and organic chemical species. In environmental assessment, it is far from enough to know the total arsenic content in actual samples, because the toxicity of As element is predestined by distinct arsenical species [20]. Generally speaking, trivalent arsenic compounds are usually more toxic than pentavalent arsenic compounds [4] and inorganic species are more toxic than the organic ones. Again, trivalent organic arsenicals can be more toxic than trivalent inorganic arsenicals [21]. The United States Environmental Protection Agency (USEPA) priority pollutants list represents inorganic As is the first category of toxins [22], classified as Group I carcinogens based on human epidemiological data. In addition, the organic species toxicity usually decreases with the increase of methylation. For example, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are less toxic, arsenobetaine (AsB), arsenocholine (AsC) and other arsenosugars are even considered non- toxic [21]. However, in certain environments, such as in aquatic biomass, AsB can be converted into toxic inorganic arsenicals and enter the food chain [23, 24]. Depending on the source, metals or metalloids may enter the environment, where they may be transformed into another compound. Therefore, As speciation is essential for understanding its distribution, transformation in the environment, toxicity, metabolism, bioavailability and health effects in the natural system [15].

There is a huge difference between the toxicity and distribution of the arsenic species observed in the environment, which heights the importance of detecting and quantifying a single compound. Recently, various techniques have been developed to figure out arsenic species in environmental and biological samples, including soil, water and plants. The establishment of the new arsenic speciation analysis program not only improves our understanding of arsenic biogeochemistry, toxicity and metabolism but also provides a lot of information about exposure biomarkers and arsenic cycling in the natural environment. However, it is still a challenge to completely isolate the target arsenic compound from background interference [25]. Therefore, a quick and simple method is needed to analyze the arsenic species in different matrices. In addition, optimizing the extraction of target arsenic is also crucial for accurate quantification [26]. Determining the exact species of arsenic in biological and environmental samples helps to more accurately assess the

environmental impact and health risks caused by arsenic exposure. Appropriate sample pretreatment techniques are necessary to reduce the influence of matrix, to enrich the target species and/or separation of As species for accurate identification. The newly developed As speciation protocols must achieve suitable detection mode, excellent selectivity and sensitivity in various environmental and biological species. Various non-chromatographic and chromatographic methods are involved in the selective separation of the arsenic species.

To date, several study on overall arsenic speciation analysis have been done [15, 27, 28]. Nevertheless, there is still a big knowledge gap in the speciation of arsenic. This overview includes arsenic speciation analysis, species detection systems, key extraction/separation techniques and mechanisms used in the accuracy assessment of speciation methods, and focuses on important strategies for specific arsenic speciation. This study will provide sentinels on comprehensively discuss in the latest developments in arsenic speciation analysis and challenges for further research.

2. Reactions of arsenic speciation on environment

Arsenic is introduced into the environment either naturally or anthropogenically; once released, it cannot be degraded or destroyed. The environmental transformation of arsenic depends on the availability of arsenic in the geological source, as well as their oxidation state, speciation and other environmental factors [29, 30]. There are different forms of arsenic containing mineral in the Earth's crust. For example, 60% are in arsenate form, 20% are in the form of sulfides and sulfonates, and the remaining 20% are in the form of arsenites, arsenides, silicates, oxides, and elemental As [31]. In the soil and water environments, As can exist in four different oxidation states (As^{3+}, As^{5+}, As^{0} and As^{3-}), in inorganic as well as in organic forms [4]. The most widespread arsenic species detected in the environment and biological systems are shown in **Table 1**.

In natural environment, inorganic arsenic contains two oxygen anions, arsenite As (III) and arsenate As (V) but there are many organic arsenic compounds including monomethyl arsonic acid (MMA) and dimethyl arsinic acid (DMA) is the most common. According to intake and mobility, the toxicity of arsenic compounds decreases in the following sequential order: arsines > inorganic arsenites > organic trivalent compounds (arsenoxides), inorganic arsenates > organic pentavalent compounds > arsonium compounds > elemental arsenic. Arsenobetaine and arsenocholine are considered nontoxic [4]. At the same time, arsenic species exhibit various reaction behaviors and metabolic transformations in soil-water and plant ecosystems. For arsenic risk assessment of environmental samples and detection of appropriate speciation analysis, it is necessary to understand the main forms and metabolic transformations of arsenic compounds.

2.1 Arsenic speciation in soil

The various species or chemical forms of As in soil include- free ionic forms, precipitated as solids, adsorbed on soil organic or inorganic constituents, exchangeable, and structural constituent of primary and secondary minerals [32, 33]. There are both inorganic and organic forms (species) of arsenic in the soil. The most common inorganic species are arsenate (AsV) and arsenite (AsIII), while the most common organic species are monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). The order of toxicity of arsenic species is AsIII > AsV > MMA > DMA [34]. In general, minor amount of naturally occurring arsenic in soil exists as a form of amorphous iron and aluminum oxides.

Name	Abbreviation	Chemical structure
Inorganic form		
Arsenite (Arsenous acid)	As (III)	H_3AsO_3, H_2AsO^{3-}, $HAsO_3^{2-}$, AsO_3^{3-}
Arsenate (arsenic acid)	As (V)	H_3AsO_4, $H_2AsO_4^{-}$, $HAsO_4^{2-}$, AsO_4^{3-}
Organic form		
Monomethylarsenic acid	MMA	$CH_3AsO(OH)_2$
Monomethylarsonic acid	MMA(V)	$CH_3AsO(OH)_2$
Monomethylarsonous acid	MMA(III)	$CH_3As(OH)_2$
Dimethylarsinic acid	DMA (V)	$(CH_3)_2AsO(OH)$
Dimethylarsinous acid	DMA (III)	$(CH_3)_2AsOH$
Dimethylarsinoyl ethanol	DMAE	$(CH_3)_2AsOCH_2\ CH_2OH$
Trimethylarsine oxide	TMAO	$(CH_3)_3AsO$
Trimethylarsoniopropionate	TMAP	$(CH_3)_3As^+CH_2CH_2COO^-$
Tetramethylarsonium ion	TETRA, TMA	$(CH_3)_4As^+$
Arsenobetaine	AsB	$(CH_3)_3As^+CH_2COOH$
Arsenobetaine 2	AsB-2	$(CH_3)_3As^+CH_2CH_2COO^-$
Arsenocholine	AsC	$(CH_3)_3As^+CH_2CH_2OH$
Trimethylarsine	TMA (III)	$(CH_3)_3As$
Arsines	AsH_3, $MeAsH_2$, Me_2AsH	$(CH_3)_xAsH_{3-x}$ (x = 0–3)
Ethylmethylarsines	Et_xAsMe_{3-x}	$(CH_3CH_2)_xAs\ (CH_3)_{3-x}$ (x = 0–3)
Dimethylarsinyolacetic acid	DMAA	$(CH_3)_2AsOCH_2\ COOH$
Phenylarsine oxide	PAO	C_6H_5AsO
Phenylarsonic acid	PAA	$C_6H_5AsO(OH)_2$
Arsenosugars $C_7H_{14}AsO_3CH_2CH(OH)CH_2R$		
Arsenosugar 1 (glycerol sugar)	—	R = OH
Arsenosugar 2 (phosphate sugar)	—	$R = OP(O)(O^-)OCH_2CH(OH)CH_2OH$
Arsenosugar 3 (sulphonate sugar)	—	$R = SO_3^-$
Arsenosugar 4 (sulphate sugar)	—	$R = OSO_3^-$

Table 1.
Arsenic species commonly identified in the environment and biological systems.

Arsenic can be transformed in the soils through various mechanisms, such as oxidation, reduction, adsorption, dissolution, precipitation, and volatilization. The inorganic species of As, As(III) and As(V), are present in different forms (e.g., fully protonated As acids or arsenous acid) [35]. The main and thermodynamically stable forms of As(V/III) in soil may include $H_2AsO_4^-$, $HAsO_4^{2-}$ and H_3AsO_3. The existence of different As forms in soil largely depends on the texture, organic matter, pH value and redox potential of the surrounding environment. Arsenic exists in aerobic soil (oxidized conditions) in the form of arsenate (As^V) and is rapidly adsorbed on clay minerals and Fe/Mn oxides/hydroxides [2]. However, in reducing soil environment such as paddy fields, the arsenite (AsIII) form of arsenic dominates and its

solubility, mobility, and toxicity are about 60 times that of As(V) [2]. In addition, under anaerobic conditions in the presence of sulfides, arsenic may precipitate in the form of arsenic sulfide and release excess arsenic into the environment [36]. Anaerobic bacteria degrade into less toxic volatile forms, such as dimethyl arsenic acid (DMAA) and monomethyl arsenic acid (MMAA) [37]. The oxidation and reduction of arsenic species takes place biologically and chemically in soil and water [38]. In addition, higher concentrations of arsenic were observed in alluvial soils and organic soils, while lower concentrations of arsenic were found in sandy soils [39]. Clay played a leading role in arsenic fixation. Arsenate is mainly adsorbed on clay particles in soils with neutral pH. Soil pH plays a major role in the types of arsenic compounds present in the soil. Under acidic conditions, arsenic tends to form compounds with aluminum and iron ($AlAsO_4$, FeAsO4), whereas under alkaline conditions (limestone soils) Under acidic conditions, arsenic tends to form compounds with aluminum and iron.

Arsenate exists in the form of oxygen anions at neutral pH, while arsenite has a neutral charge at pH 7.0. It leads to the formation of $Ca_3(AsO_4)_2$, $Mn_3(AsO_4)_2$, $AlAsO_4$ and $FeAsO_4$ [40]. However, when the pH value is higher than 8.5, as the pH value increases, the adsorption capacity of As^V decreases, while the case of As^{III} is the opposite. But at pH around 4, the adsorption for As^V on FeOOH is maximum, whereas for As^{III} the optimum pH is 7–8.5 [41]. Arsenic is more soluble under high or low pH values. In reducing environment, as arsenate is reduced to arsenite, it binds less strongly to the hydroxide solids, which increase the bioavailability of arsenic [42]. On the contrary, due to the larger arsenic sorption affinity, organic matter has formed organo-arsenic complex and reduced the solubility of arsenic in the soil [43]. Naturally, arsenic can be released into the soil environment through the hydrolysis and oxidation process of primary sulfide mineral (i.e arsenopyrite) and absorbed by ferric hydroxide. Meanwhile, the retention and mobilization of arsenic in soil is largely controlled by Ferric hydroxide. Such as iron oxides has stronger arsenic adsorption capacity than manganese oxides. Moreover, Phosphate plays significant role in absorption of arsenic from contaminant soil. Williams et al. [44] reported that in iron oxides dominated acidic soil, approximately 60% of the adsorbed pentavalent arsenic and 70% of the trivalent arsenic were displaced by H_2PO_4. Soil microbial activities can affect the adsorption/desorption, solubility, bioavailability, mobility and soil–plant transfer of arsenic by changing the chemical speciation of As in soil [45, 46]. Due to the action of microorganisms or the past use of methylated arsenic compounds, dimethyl sulfoxide, or sodium salts of MMA and DMA as pesticides, methylated As species, (i.e MMA and DMA) might be accumulate in soil [45]. Microorganisms in soil may interconvert As species As^V and As^{III} and further transform into MMA and DMA.

2.2 Arsenic speciation in water

The presence of arsenic in water is either dissolved or in particulate form. Arsenic pollution in groundwater mainly occurs due to release of geothermal water, desorption and reductive dissolution of iron oxides and oxidation of sulfide minerals [37]. High levels of arsenic in groundwater have been observed in many countries, such as more than 3000 μg L^{-1} because As has been released geogenically either by oxidation of arsenopyrite, or by reductive dissolution of arsenic rich ferrous oxyhydroxides in reducing aquifer environment [47, 48]. The most common forms of arsenic in natural waters are arsenite and arsenate. However, the main species found in natural water are forms of inorganic arsenic, namely H_2AsO_4-, H_3AsO_3, $HAsO_4^-$ and $As_3O_4^{3-}$. The change in the arsenic solubility in sulfidic water promotes the formation of amorphous metal-sulfide complex thioaresenic

compounds [49]. Various species of aquatic micro and higher organisms plays important role on biomethylation process of arsenic, which reduces As^{5+} to soluble As^{3+} species [37]. Arsenate is the main form of arsenic in seawater. Dimethyl arsenic acid (DMMA) and methylarsenic acid (MMA) are also present in small amounts in seawater [50]. Moreover, the determination of arsenic in saline waters bear much importance due to gaining knowledge on because salinity induced inorganic arsenic specifically arsenite transformation to arsine gas [51].

2.3 Arsenic speciation in plants

Arsenic is not essential elements for plants development, although very small amounts of As in plants may have a positive effect on plant species. The concentration of As in plants is usually less than 1.0 mg kg^{-1} dry weight (DW) [52]. The mechanism by which plants absorb arsenic varies depending on the chemical form of arsenic.

2.3.1 Transformation of inorganic arsenic species in plants

Plants absorb inorganic arsenic through two mechanisms. The first mechanism involves the use of a high-affinity PO_4 transporter through phosphate (PO_4) transport pathway [53, 54] which uptake As (V) from soil solution and subsequently to aerial parts of the plants [55]. While, the second route for plant roots to absorb arsenic is through the aquaporin channels, which uptake As (III) (silicic acid analog) and methylated As species (MMA and DMA) [56]. In rice root cells, As (III) uses generally Si transporter owing to its similarities with silicic acid. Once in plant cell, As (V) is reduced to As (III) with the help of As reductase, ACR2 [57]. The detoxification of As (III) is achieved by forming complexes with thiol- rich peptides [58]. The form of As in the phloem is considered to be very crucial for the redistribution of As in various tissues in the plant [59].

2.3.2 Organic arsenic species transformation in plant

The methylated arsenic species, such as MMA and DMA, contribute less to the total arsenic in the soil. The organic arsenic substances MMA and DMA have taken up by the intrinsic protein of Oncokin 26. Rabb et al. [60] showed that the absorption efficiency of inorganic As species (AsIII and AsV) in roots is much higher than that of methylated As species (DMA and MMA), but the translocation efficiency of inorganic species in plant stems is much lower than that of methylation As species. The decrease in the As complex formed with ligands (such as glutathione) in the root may be the reason for the better translocation of methylated As species [60]. In rice, As (III) is found to be the most abundant species, followed by DMA. As (V), MMA and two other unidentified As also have found in lower concentrations [61]. A speciation analysis revealed the As (V) as a predominant species in rice straw followed by As (III) and DMA [62]. Meanwhile, in rice grain, As (III) and DMA are the dominant species.

3. Soil, water and plant sample preparation and extraction of arsenic species

3.1 Soil, water and plant sample preparation for arsenic speciation

Sample preparation and storage procedures are considered to be a key prerequisite for maintaining the concentration and chemical structure of the original species

in the sample during the analysis process to obtain accurate As speciation information. Impractical As speciation data may arise due to losses during sampling, unrepresentative samples [63], contamination, mutual conversion between species, inefficient extraction of the analyte, and the possibility of precipitation and wall effects from the sample container [64]. To obtain reliable arsenic speciation data in soil, water and plant samples, two main strategies should be considered. First, determine appropriate species preservation practices to keep the chemical species of interest unchanged throughout the analysis process through avoiding changes in oxidation state, changes caused by microbial activity, and losses caused by volatilization or adsorption. Secondly, the species can be quantitatively converted into appropriate derivatives for further separation, accumulation and quantification [65]. Microbial transformation of arsenical compounds in contaminated samples is observe through a change in valence (i.e.oxidation/reduction) or chemical form (i.e. solid, liquid and gas) and formed biomethylate arsenic and both volatile (e.g., methylarsines) and nonvolatile (e.g., methylarsonic acid and dimethylarsinic acid) compounds [66]. To avoid degradation of arsenic speciation, biological samples should be kept in low temperature. To reduce analyte loss, drying in oven used for the stabilization of samples particularly freeze-drying [67].

To avoid arsenic speciation loss during sampling, the soil–plant-water should be collected in polyethylene flip-top bottle/plastic with lock and/or seal lead. Immediately after collection all of the samples should be kept in freezer until sample preparation for analysis. The soil samples were air-dried, gently crushed and sieved through a 2 mm sieve and used for analysis. Meanwhile the plant sample placed in a oven drier at 40°C until constant weight and then grind and sieve the sample and stored in brown glass bottles in a desiccator in order to avoid exposure to light and moisture until required for analysis. Sample preparation for solid samples generally may include procedures such as mincing, freeze drying, milling, grinding, homogenization, and sieving, followed by extraction. For achieving the best extraction efficiency and reproducibility of arsenic speciation in soil and plant sample, the tested sample must dried and homogenized before extraction. Because, particle size plays a crucial role in the extraction efficiency of As [68]. After sampling the fresh plant sample, it should be kept in freezing (−80°C) to avoid species interchange. Moreover, dry and grind plant and soil sample can store at −20°C up to one year [69].

The most reliable method for preserving natural water samples is, therefore, acidification to pH 2, refrigeration and deoxygenation [70]. Preservation of natural water in polypropylene bottles in refrigerator arsenic species in water is stabile under neutral conditions for a period of 4 months [71]. To increases the stability of dissolved As redox species (As (III) and As(V)) of water sample, the samples to be filtered and stored in darkened polythene containers. For longer preservation, water samples are acidified with HCl [72], HNO_3 [73], H_2SO_4 [74] and H_3PO_4 [75], ascorbic acid [76] ethylene diamine tetraacetic acid [65]. Filtering the sample removes most of the colloidal material and microorganisms; acidification prevents oxidation and precipitation of Fe and Mn hydroxides and EDTA sequesters Fe and inhibits precipitation. Using 10 mM H_3PO_4 as a preserving agent combined with keeping samples at 6°C in dark, As species remain stable for 3 months, even with high concentrations of Fe and Mn.

3.2 Extraction procedures for arsenic speciation

The great challenge of As speciation, as it has been highlighted, is to maintain the original characteristics of species during extraction step. Extraction is the first step for speciation of target As species from their matrix (water, soil, sediment,

plant, biological tissue or fluid). Determining an appropriate sample preparation method that provides high extraction efficiency for the arsenic species of interest and prevents inter-conversion between arsenic species can be challenging. To achieve maximum extraction competence of arsenic speciation from solid or liquid matrix, the extraction protocols must have three criteria's, such as (i) the extracting solution must solubilize only the specific form, (ii) reduction of native As (V) to As (III) may not occur during the extraction, and (iii) oxidation of native As (III) to As (V) should not occur [77]. Extraction procedures employ a range of approaches including solid–liquid extraction [78] liquid– liquid extraction, solid phase extraction (SPE) [79] and solid phase microextraction (SPME) [80]. Enhanced techniques such as soxhlet, [69] sonication, [81] pressurized liquid extraction (PLE), [82] microwave-assisted extraction (MWA) [83] and supercritical fluid extraction (SFE) [84] have also been utilized for the determination of As speciation in soil–plant-water sample. Soil-pant-water sample preparation and extraction methods applied for the arsenic speciation analysis are presented in **Table 2**.

3.2.1 Solvent extraction

The solvent extraction technique is often used to determine organic arsenic compounds, especially arsenic compounds in biological samples. The extraction of arsenic substances is usually achieved through mild extraction solvents (ie water, methanol, methanol–water solvent system) and/or rarely uses acetonitrile-water and sequential extraction [15, 103]. Methanol/water mixture 1/1 (v/v) is widely used for the quantification of water-soluble As compounds in environmental samples, followed by centrifugation and filtration [104], while methanol-chloroform or hexane is used in non-polar species [15]. Moreover, extraction with water–methanol (1:1vv^{-1}) had offered easy oxidation of As (III) in basic medium such as soil and the best efficiency was achieved after 20 min of extraction [105]. Extraction efficiency of arsenic species in soil–plant-water samples varied according with the changing the ratio of methanol– water solvent. Nevertheless, the methanol:water extraction solvent ratio of 1:1 provides the best processing and extraction efficiency for the extraction of arsenic species from plant samples, while 1 M phosphoric acid is suitable for soil samples [15]. At the same time, Rahman et al., [98] noticed that addition of extracting agent $NH_4H_2PO_4$ in edible part of spinach had shown similar extraction efficiency of As (III) and As (V) by water, 50% vv^{-1}water/methanol solution on shaking and microwave techniques. However, As(III) was extracted twice as much by the protein extract, indicating that it is a good extractor. Zheng and Hintelmann [106] pointed out that methanol/water mixture is an effective extractant for organic species, and its efficiency for inorganic species drops sharply. The solvent extraction reagent, tetramethylammonium hydroxide (TMAH) in alkaline medium, is also useful for the determination of AB, DMA and inorganic arsenic form a wide variety of biological matrices. In addition, sequential extraction procedure using different solvents (i.e $(NH_4)_2SO_4$, $(NH)_4H_2PO_4$, NH_4-oxalate buffer, KOH and hot water) can effectively extract organic and inorganic arsenic species, namely arsenous acid, arsenic acid, monomethylarsonic acid, dimethylarsinic acid, arsenobetaine, trimethylarsine oxide and glycerol-ribose in both soil and plant [107, 108]. Larios et al. [109] found that orthophosphoric acid followed by graphite block heating at 90°C for 60 min was provided the best conditions for As speciation in plants grown in contaminated environment. The applied extraction solvent led to an extraction efficiency of 80% for samples without species interconversion and recovery of 95% for leaves As speciation of Arsenic (V), As (III), DMA and MMA.

Matrix	Arsenic species	Sample preparation/extraction	Extraction solution	Detection	References
Soil	AS total, AS^{III}, AS^{V}	Shaking/mixing	10 M HCl	HGAAS; XRF	[85]
Soil	AS total, AS^{III}, AS^{V}	Shaking/mixing	10 mM phosphate	HPLC	[86]
Soil	AS total, AS^{III}, AS^{V}	Micro wave heating + Shaking	1 M H_3PO_4 + 0.5 M ascorbic acid (C6H8O6)	LC=UV- HG- AFS	[87]
Soil	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}	Ultrasonic, shaking, Microwave heat	500 mM Phosphate solution	HPLC-HG-AFS	[88]
Soil	AS^{III}, AS^{V}	Filtration. Shaking and water bath heat	[BMIM] [PF6]	IL-LLME-ETAAS	[89]
Soil	AS total	Microwave heat	HNO_3 + $HClO_4$+ H_2SO_4	HGAAS	[90]
Soil	AS total, AS^{III}, AS^{V}	Microwave heat	1 M H_3PO_4 + 0.1–1 M ascorbic acid	LC–HG–AFS	[91]
Soil	AS^{III}, AS^{V}	Shaking/mixing	2.5 mM CaCl2	LC–HG–AFS	[21]
Soil	AS^{V}	Shaking/mixing	1 M HCl	XRF	[92]
Soil and plant (chickpea)	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}	Shaking/mixing	Buffer solution (1.5 mM NaH_2PO_4+ 0.2 mM Na_2EDTA + 3 mM $NaNO_3$,+ 10 mM CH_3COONa + 1% C_2H_5OH; pH 6.0)	ICP-MS	[93]
Plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}	Shaking/mixing	0.3 M H_3PO_4	HPLC-ICP-MS	[94]
Plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}	Shaking/mixing	1% HCOOH	HPLC-ICP-MS-ESI-MS	[95]
Plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}	Sonication	2 mM NaH_2PO_4 + 0.2 mM Na_2EDTA (pH 6.0)	HPLC-ICP-MS-ESI-MS.	[95]
Soil and plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}, AsC	Shaking/mixing + sonication	CH3OH/H2O 1 + 1 v/v	HPLC-ICP-MS	[96]
Soil and plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V},	Shaking/mixing + sonication	(a) CH3OH/H2O 1 + 1 v/v; (b) 0.1 M HCl	HPLC, AAS and XANES	[97]
Plant	AS^{III}, AS^{V},	MW-heating	0.33 M sucrose, 50 mM MES, 5 mM EDTA, 5 mM Lascorbate	HPLC-ICP-MS	[98]
Plant	Total As, AS^{III}, AS^{V},	MW-heating	Methanol–water (1: 1) /HNO_3	HPLC-ICP-MS	[99]

Matrix	Arsenic species	Sample preparation/extraction	Extraction solution	Detection	References
Plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V},	MW-heating	1% (v/v) HNO_3	HPLC-ICP-MS	[100]
Plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V},	MW-heating	0.01 mol/L TMAH	ETAAS	[101]
Surface/drinking water	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}	Filtration	EDTA	HPLC-ICP-MS	[102]
Sea water	AsIII, AsV, MMA, DMA, AsB, TMAO	Shaking/mixing + ulta-sonication	1% (v/v) HNO_3	HPLC-ICP-MS	[26]

Table 2.
Several soil-water-plant sample preparation/extraction methods for determination of arsenic speciation.

3.2.2 Enzymetic hydrolysis

Biomolecular hydrolysis of complex matrix, enzymes are able to break down specific bonds of the substrate at neutral pH and room temperature, and they allow selective release of the analyte from the sample matrix without chemicalchanges. Enzymes can digest various matrix components, enzyme-assisted reactions usually require several hours of incubation. Microwave-assisted extraction (MAE) is used in combination with the enzyme extraction of pronase E and lipase to effectively extract AsB, As(III), DMA, MMA, and As(V) from seafood, rice, and plants [110, 111]. Viscozyme, was considered the most effective multi-enzyme mixture (consisted of a wide range of carbohydrases, including arabanase, cellulase, glucanase, hemicellulase, and xylanase) useful to extracted arsenic species from algae and terrestrial plant materials [112].

3.2.3 Microwave-assisted extraction

Microwave extraction is a common technique for extracting biological and environmental matrices, which is much faster than traditional Soxhlet extraction procedures. The extraction procedure using dilute acids or organic solvents at low temperatures can be easily achieved in a focused microwave oven. Generally microwave extraction is used to determine inorganic arsenic in food and provided good arsenic speciation extraction efficiencies (generally >90%) for samples of rice and wheat [113]. The method is based on extracting samples with trifluoroacetic acid/H_2O_2 and measuring arsenate by anion exchange HPLC-ICP-MS using aqueous malonic acid as the mobile phase. By using 2 M trifluoroacetic acid assisted with microwave heating for 6 h at 100°C to hydrolyze rice samples, the conversion between As^{III} and As^{V} was also observed and recovered 83, 88, 100, and 93% of fortified arsenite (100 ng As g^{-1}), arsenate (100 ng As g^{-1}), methylarsonic acid (MMA, 50 ng As g^{-1}), and dimethylarsinic acid (DMA, 200 ng As g^{-1}), respectively [114].

3.2.4 Solid phase extraction

Solid phase extraction (SPE) method is an efficient extraction technique for arsenic speciation from complex environmental and biological matrices. The principle mechanism of SPE is partitioning sorbent and sample matrix phase and may include simple adsorption, chelation, ion exchange or ion-pair solid phase extraction. In recent years, the techniques gaining popularity for As speciation because of its simple operation offers acceptable recovery and pre-concentration efficiency, lower reagent consumption and offer effective combination ability with different on-line and off-line As detection systems.

3.2.4.1 Conventional sorbent

Several conventional sorbent (i.e ion exchange resin, glass and modified mesoporous silica) based protocols have been developed for inorganic As speciation. To avoid inter-conversion of arsenic species, extraction with anion exchange cartridges prior to the inductively coupled plasma sector field mass spectrometric (ICP-SF-MS) becomes an efficient technique. During on- site separation and speciation of inorganic arsenic (As (III) and As (V)) from high arsenic- groundwater and ferrihydrite removal anaerobic arsenics species, anion-exchange resin (AG 1-X8) adsorbed As(V) in acetate form, while no adsorption to As(V)/As(III) in chloride form [115]. A dual-sorbent SPE protocol, in which the sorbent is composed of strong basic anion exchange (SBAE) resin and hydrate iron oxide particles

integrated HY resin, has been adopted successfully for the retention of inorganic arsenic species As (V) and As(III) simultaneously [116]. On-line continuous leaching extraction method is also effective for speciation of bio-accessible As species in plant [108].

3.2.4.2 Functional nanomaterials extractant

The modern technological invention of nanomaterials such as Nanofibers [117], magnetic nanoparticles [118], metal hydroxide precipitation [119], and nano-TiO_2 colloid [120] has offered selective and efficient extraction techniques for As speciation from different matrix. Like ammonium pyrroine- dithiocbonate (APDC) have excellent selectivity of As (III) from ground water samples [117]. Moreover, yttrium hydroxide precipitate layer coated cellulose fiber is used as extracting material, [119] of As (III) and As (V) at acidic condition. Multi-wall carbon nanotubes (MWCNTs) modified with branched cationic polyethyleneimine(BPEI)is also proved to be excellent adsorbent with favorable selectivity toward adsorption of As(V) [121] in combined with sequential injection technique. Nano particle TiO_2 colloid has effectively extracted ultra-trace As from environmental water sample without agglomeration [120]. Besides, As (III) and As(V)from aqueous solution can be effectively extracted by hematite-coated Fe_3O_4 particles. Moreover, due to the fact simple and rapid separation capacity of As species, magnetic extraction techniques also gaining much popularity day by day.

3.2.4.3 Multi-sorbent based SPE procedure

A combined SPE procedure for arsenic speciation developed by using three molecular recognition technology (MRT) gel resins, which includes strong base anion exchange (SBAE) and two hybrid (HY) resins, HY–Fe and HY–AgCl, This methods has constructed for simultaneously extraction of four water-soluble arsenic species: arsenite, arsenate, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) and retain in the SPE columns and separatedly eluted by using different elution [115].

3.2.5 Liquid–liquid extraction (LLE)

A liquid–liquid extraction generally used dodecane modified with 4% dodecanol containing Aliqua t336 as the extractant has been developed for the extraction of arsenic species in environmental matrices [122]. Here only As (V) is quantitatively transported to organic phase but no transport of As(III) takes place. A rapid in-situ liquid–liquid micro-extraction procedure has been developed for successfully determination of As (III) and As(V) in water samples, food salts, and total As in biological samples [123].

4. Derivitization of total arsenic

The vital challenge in element speciation is to determine each form independently without interference from other species. Because arsenic could complex with certain derivatizing agents, that hampered the detection. The derivitization process consists of two steps for example. i) reduction of AsV to AsIII and ii) convert to arsine (AsH_3) [124]. During measurement, the inert g N_2 is pushed by hydride

generation (HG) step, reaches the atomic absorption spectrophotometer or ICP-MS and finally produced arsines [125]. The main limitation of derivitization is that it only limits the formation of volatile arsines materials, but it is difficult to separate un-derivatized arsenic species (eg. AsB, AsC, or arsenosugars), using conventional reversed phase liquid chromatography and almost impossible by spectrophotometry or mass spectrometry [126]. In addition, the derivitization process requires control condition In addition, the derivitization process requires control condition. This technique largely depends on the type and concentration of the sample matrix. To overcome obstacle, sodium borohydride is now commonly used for the hydrides synthesis [18]. Arsenic speciation after derivatization can be overcome by combining couple technique with detection techniques such as LC–MS/MS retention in liquid chromatography and ionization in mass spectrometry. Under such circumstances, the hyphenated technique is the most reliable because it includes several facilities like high sensitivity, good reproducibility, short analysis time and reduced risk for species transformation [18].

5. Separation techniques of arsenic speciation

Usually, two main techniques, namely chromatography (gas and liquid) and capillary electrophoresis are used to separate arsenic from various complex matrices [65]. Based on the complexity of As compounds, sometimes two technologies are introduced simultaneously or cumulatively.

5.1 Liquid chromatography

Liquid chromatography generally provides excellent possibilities for the separation of environmental and biological samples [18]. Various commonly used liquid chromatography techniques are high performance liquid chromatography (HPLC), ion chromatography and ion interaction chromatography [127]. Chromatographic separation can be performed by using ion exchange columns to separate metal ions directly or by adsorption (reverse phase or normal phase) liquid chromatography (if the metal species are complexed with organic ligands). Liquid chromatography is connected to many other detection systems, such as ICP-MS, HG-AFS, HG-AAS and GF-AAS [65]. Several liquid chromatography techniques can be used for the organic and inorganic As species, as follows:

5.1.1 Anion exchange liquid chromatography

Anion exchange chromatography is commonly used for speciation analysis of arsenic in environmental and biological samples. The anionic nature of arsenic species is different (at neutral pH, arsenic acid As(V), monomethylarsonic acid (MMA) and dimethylarsonic acid (DMA) are deprotonated, but As(III)) exists) to make anion exchange chromatography suitable for their separation. Anion exchange chromatography has been used to analyze many arsenic compounds, including As(III), As(V), MMA, DMA, arsenobetaine (AsB), arsenocholine (AsC), oxoarsenic sugar (oxoAsS), thiosulfate Arsenic sugar (thioAsS) and benzene arsenic [27, 28]. The most commonly used column for arsenic speciation analysis is a strong anion exchange column, such as PRP-X100. Generally, the As form of the matrix separated by anion exchange chromatography techniques is detected by inductively coupled plasma mass spectrometry (ICP-MS) and electrospray ionization tandem mass spectrometry (ESI-MS/MS).

5.1.2 Cation exchange liquid chromatography

Cation exchange chromatography works similarly to anion exchange, except that the stationary phase is negatively charged to interact with the cation analyte. However, in cation exchange liquid chromatography, the separation speed of As species is relatively fast. The retention of arsenicals is directly related to the strength of its cationic charge: positively charged analytes have stronger retention. Cation exchange chromatography is commonly used for speciation analysis of positively charged As compounds, such as AsB, AsC, trimethylarsenic oxide (TMAO) and tetramethylarsenic ion (TMA) [15].

5.1.3 Reverse phase liquid chromatography

Reversed-phase chromatography is the most common HPLC separation technique used to separate compounds that are less hydrophobic or polar. In particular, reversed-phase liquid chromatography is particularly suitable for the analysis of arsenic lipids, including arsenic-containing hydrocarbons, fatty acids, phospholipids, phosphatidylcholines, fatty alcohols, and phosphatidylethanolamines of biological samples [24].

5.1.4 Ion pair chromatography

Ion pair chromatography can separate ions and neutral analytes using popular reversed-phase chromatography. It has been widely used for arsenic speciation analysis of various substrates. The reagent of ion pair chromatography reagent comprises with two groups a charged group for interaction with the analyte and a hydrophobic region for interrelates with the stationary phase. Usually, tetraalkylammonium, tetrabutylammonium and tetraethylammonium are used as the ion pair reagents for the separation of anionic and neutral arsenic species, and alkyl sulfonates, such as hexanesulfonic acid and 1-pentane sulfonic acid, for cationic and neutral arsenic species. Two most commonly used organic modifiers, methanol and acetonitrile are added to the mobile phase to decrease retention time [15].

5.1.5 Hydrophilic interaction liquid chromatography

Hydrophilic Interaction Chromatography (HILIC) is an important substitute to RP-HPLC separations of polar compounds. Although the stationary phase is polar, HILIC can separate neutral, cationic and anionic species simultaneously. HILIC has great potential to separate more arsenic species in a single analysis. This separation technique is more useful for organoarsenicals. Xie et al. [128] successfully detected nine kinds of organoarsenicals (I,e MMA, DMA, AsB, AsC, TMAO, phenylarsonic acid (PAA), phenylarsine oxide (PAO), 4-hydroxy-3-nitrophenylarsonic acid (Roxarsone), and 4-aminophenylarsonic acid (p-arsanilic acid, ASA) using a zwitterionic HILIC column followed by ICP-MS/ ESI-MS detection.

5.1.6 Size exclusion chromatography

Size-exclusion chromatography (SEC), also known as molecular sieve chromatography, is a chromatographic method in which molecules in solution are separated by their size, and in some cases molecular weight. SEC is very effective for analysis of arsenic interactions with large molecules or macromolecular complexes such as arsenic-protein binding, humic acid-arsenic complexesand industrial polymers.

SEC commonly used to separate protein-bound arsenic from free arsenic [129]. This separation method is expensive and useful for biological samples.

5.1.7 Multidimensional chromatography

Combining a variety of chromatographic columns and separation modes, try to separate a series of arsenic substances. Multidimensional separation has been performed offline or online. These usually involve a cation exchange column and an anion exchange column connected by a switching valve. This combination allows separation of cationic and anionic arsenic species. Applications were demonstrated for the determination of water-soluble arsenic species [20].

5.2 Capillary electrophoresis

Capillary electrophoresis separates As species according to the electrophoretic mobility related to the charge, viscosity, and atomic radius of the molecule, which is controlled by the composition, concentration, and pH of the buffer. This method is applicable for all type of soil–plant-water samples. Capillary electrophoresis can be used in many different detection systems but the most common is ICP-MS [15]. Although, Although capillary electrophoresis separation is simple, cost-effective, fast analysis and a certain degree of matrix independence, the additional complexity of coupling with the detection system makes CE a less common As speciation analysis method.

6. Detection systems of arsenic species

Several sensitive and element techniques can be used for the detection of arsenic species. Various detection techniques are: atomic mass spectrometry, molecular mass spectrometry, optical spectrometry, X-ray methods and others (voltammetry, potentiometry, conductometry and spectrophotometry), which provide different level of specificity, cost effectiveness and detection limits [21]. Detection methods applied for the arsenic speciation analysis of soil–plant-water samples are assembled in **Table 3**.

ICP-MS is the most commonly used technique for the detection of multiple arsenic species because of its high sensitivity, high selectivity and wide dynamic range. The coupling of chromatography to ICP-MS has several benefits due to the compatibility of the mobile phase with the behavior of the plasma torch and the carefully determined quality inspection interference. Various techniques have been developed to eliminate or reduce isobaric interference in the detection of arsenic by mass-to-charge ratio. Recently, compared with the traditional single quadrupole ICP-MS, the combination of ICP and triple quadrupole tandem mass spectrometry (ICP-QQQ) helps to eliminate isobaric interference, reduce background, and improve selectivity [156]. Quantification is performed by preparing standard solutions of commercially available substances, such as iAs(III), iAs(V), MA, DMA, and AB. It is generally believed that arsenate is used to calibrate anionic substances, and arsenobetaine is used to calibrate cationic substances [157]. DMA is considered to be the most suitable calibration standard for arsenic lipid quantification [158]. The sensitivity of ICPMS to detect arsenic is limited by its relatively high ionization potential. In order to compensate for this effect, various methods have been used, including adding supplemental methanol or ethanol solution to the spray chamber [159] or after the column via the T-piece [91], and the use of correction response

Matrix	Arsenic species	Detection techniques	Coupled with	References
Atomic mass spectrometry				
Soil	AS^{III}, AS^{V}	ICP = MS	—	[130]
Water	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}			[131]
Soil-water-plant	Total As, AS^{III}, AS^{V},			[132]
Water	AS^{III}, AS^{V}	ICP-SFMS	—	[133]
Water	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}, AsB AsC	ICP = MS	HPLC	[134]
Plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}, AsB			[135]
Soil	AS^{III}, AS^{V}			[136]
Soil	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}	ICP-SFMS	HPLC	[137]
Plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}			[138]
Water	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}			[139]
Soil	MMA^{V}, DMA^{V}	ICP = MS	GC	[140]
Soil	AS^{III}, AS^{V}, MMA^{V}, $DMA^{V,}$	ICP = MS	CE	[137]
Molecular mass spectrometry				
Soil	PA and AA	ESI-qMS	HPLC	[141]
Soil -water	PA and AA	ESI-TOF-MS	=	[142]
Soil–plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}, MMMTA, DMMTA, DMDTA	ESI-qTOF-MS	=	[143]
Soil–plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}, MMMTA, DMMTA, DMDTA	ESI-qTOF-MS	HPLC	[143]
Soil	AS^{III}, AS^{V}, N-AHPAA, 3-AHPAA	ESI-triple quad-MS	=	[144]
Plant	Arsenolipids	ESI-triple quad-MS	HPLC	[145]
Water	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}, TMAO	ESI-Orbitrap-MS	=	[146]
Plant	Arsenic peptides	ESI-IT-MS	HPLC	[147]
Plant	PA and AA	EI-MS	GC	[141]
Optical spectroscopy				
Plant	AS total, AS^{III}, AS^{V}	GF-AAS	=	[148]
Soil	AS total, AS^{III}, AS^{V}	HG-AAS	=	[85]
Water	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}	HG-AAS	HPLC	[127]
Soil–plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}			[69]
Soil	AS total, AS^{III}, AS^{V}	HG-AFS	=	[87]
Soil	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}	HG-AFS	HPLC	[88]
Plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}			[149]

Matrix	Arsenic species	Detection techniques	Coupled with	References
X-ray methods				
Soil and Plant	AS^{III}, AS^{V}, MMA^{V}, DMA^{V}	XANES		[150]
Soil	AS^{III}, AS^{V}	EXAFS		[151]
Soil	AS^{III}, AS^{V}	STXM		[152]
Soil	AS^{V}	XPS		[153]
Others				
Water	AS^{III}, AS^{V},	Voltammetry	=	[154]
Water	AS^{V}	Potentiometry	=	[155]
Water	AS^{III}, AS^{V}	Spectrophotometry	HPLC	[126]

Aqueous phenylarsonic acid (PA); o-arsanilic acid (AA); N-acetyl-4-hydroxy-m-arsanilic acid (N-AHPAA), 3-amino-4-hydroxyphenylarsonic acid (3-AHPAA).

Table 3.
Examples of detection systems for arsenic speciation analysis of soil-water-plant samples.

factors. Finally, internal standardization was used to overcome the non-spectral matrix effects and instrumental drift [160].

Recently, molecular mass spectrometry is considered as a forward-looking technique for arsenic speciation analysis, especially for the detection of new organic arsenic species, such as thioarsenosugar [21, 161] and arsenolipids [21, 60, 162]. In this detection technique, the purified part of the extractable sample is introduced by electrospray ionization (ESI), and then mass spectrometry is combined with liquid chromatography. Generally, for the As forms, a simple single quadrupole mass analyzer is used, while tandem mass spectrometry is used for precise structure determination, whether it is a "spatial" triple quadrupole or a quadrupole time combination, or a "time" and Orbitrap system [21]. However, it has been recognized that ESI-MS analysis lacks selectivity for complex matrices, and quantification is more difficult than ICP-MS [163]. Therefore, the most powerful setting for arsenic speciation analysis that combines atomic and mass spectrometers is used as the detector of the same chromatographic system [21, 60, 145].

The optical spectroscopy technique such as atomic absorption spectroscopy (AAS) and atomic fluorescence spectroscopy (AFS) is popular to researcher as an attractive alternative to mass spectrometry. Due to the low purchase and operation cost, high speed, low consumption of organic solvents, high enrichment coefficient, combined with hydride generation provides high sensitivity and reduced matrix effect, this technology has been applied to the determination of arsenic species in environmental samples. Moreover, hydride generation systems (HG-AAS and HG-AFS) facilitate a direct measurement of the more As. Graphite furnace atomic absorption spectroscopy can be an independent facility and does not require AsH3 because of the low level of interference [18]. In fact, the optical spectroscopy is an effective technique, when combined with different separation techniques and chemical modifiers, iAs(III), iAs(V), MA, DMA and TMAO, can be identified, and significant hydride generation of arsenosugars [164] and thioarsenates can be observed [21]. Nevertheless, HGAAS and HG-AFS are mainly used for water samples [150], sediment extracts and soil, [165] and plants [97] mainly contain inorganic arsenic. These techniques are also applicable to biological substrates and more stubborn arsenic Analysis [166].

X-ray method is an important technique for morphological analysis of environmental samples, which can record raw data about the chemical environment of arsenic atoms in situ without sample preparation. X-ray atomic absorption spectroscopy (XAS) is generally divided into two regions: X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). These technologies are mainly used to directly detect solid samples, including sediments, [167] soil [97, 168] and plants [96, 97, 169]. Both XANES and EXAFS have studied abiotic matrices to measure arsenic redox status and geochemical correlation.

7. Accuracy evaluation of speciation methods

In order to obtain precise analytical information about the bioavailability and toxicity of arsenic in the environmental process, it is necessary to carefully consider any possible sources of error during analysis and validate the data. To avoid or minimize the impact of species changes and ensure the reliability and quality of speciation data, mass balance ratio, extraction efficiency, column recovery of arsenic species during separation and standard reference materials quality need to be tracked. The main difficulty of specific analysis of arsenic may occur in the sample preparation stage and species stability. Mass balance data provides information about the distribution of elements in each analysis step (extraction, separation, and species detection) and quantitatively determine the fate of arsenic during speciation [170]. The extraction efficiency can provide some important information about the extraction procedure, the polarity of the extracted species, and help to select the best extraction solvent and separation system. It helps to establish a nontoxic, effective and simple extraction procedure for arsenic speciation analysis. Column recovery is an important aspect of any separation technique. It is critical to eliminate loss and to ensure there is no cross-contamination between analyses. The column recovery compares the total arsenic concentration with the sum of the detected substances, which can provide information about the elution and retention of the analyte. In fact, depending on the type of sample and the concentration of the arsenic species, the column recovery rate of the arsenic species has great variability [171]. The column recovery also affected by the extraction solvent of the column. It is difficult to evaluate the mutual transformation of arsenic species in the actual sample in the column, which is related to the individual arsenic standard. However, the lack of available standards for new arsenic species is the main challenge in studying the inter-conversion of arsenic compounds during separation [15]. For accurate method validation of arsenic speciation, the use of standard reference materials (SRM) and certified reference materials (CRM) is essential. With reference or certified values available, SRM and CRM can be used to test and verify the accuracy of the method. In order to verify the arsenic speciation analysis methods of environmental samples, different types of soil and sediments, natural waters, marine and terrestrial plants and other biological samples are used as reference samples. It should be noted that a single SRM or CRM could not be used to verify method calibration and results [15]. SRM 1640 (NIST) is commonly used to check calibration curves for trace elements in water. The type of CRM used depends on the sample matrix and the type of arsenic studied [1].

8. Conclusion

Arsenic pollution is a universal problem. The form of arsenic in soil, water, and plants play an important role in understanding arsenic exposure, metabolism and

environmental arsenic cycle, and food chain. A crucial requirement for obtaining reliable speciation information is to maintain the concentration of the original chemical species in the sample prior to analysis. In order to determine the total element concentration, the main considerations for sample collection and storage are to prevent contamination and minimize the loss of trace analytes. Research on simple and efficient extraction procedures that use less or non-toxic solvents is very urgent for better arsenic speciation In the case of speciation analysis, the concentration of individual species of the element must be constant through sample handling and processing. Therefore, the time between the extraction procedure and the analysis must be as short as possible to avoid inter-conversion between species. The selection of extraction and sample preparation methods must be complementary and compatible with the separation method in order to perform qualitative and quantitative analysis of arsenic species and its concentration. It may require a combination of multiple extraction methods and multiple separation techniques to achieve a comprehensive arsenic speciation analysis. Several techniques have been used to study arsenic speciation, each with its advantages and disadvantages. However, research efforts are still needed to develop cheap, fast, sensitive, and reproducible methods for arsenic species that can work at low detection limits. However, research efforts are still needed to develop cheap, fast, sensitive, and reproducible methods for arsenic species that can work at low detection limits. In addition, in order to find a unified analysis protocol i.e. at least for the more common matrices, for the prevalent and unidentified arsenic species, advanced investigations and routine measurements are necessary.

Conflict of interests

The authors declare that they have no conflicting interests.

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