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Review

New procedures for arsenic speciation: A review

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ABSTRACT

Considerable analytical methods have been developed for arsenic speciation in the last 5 years, the details of these new arsenic speciation procedures are thus summarized in present mini review. The performances of various sample pretreatment techniques including solid phase extraction, liquid–liquid extraction, hydride generation, liquid chromatography and capillary electrophoresis, which offer effective preconcentration/separation and eventually contribute greatly to excellent sensitivity and selectivity in arsenic speciation when coupling with suitable detection mode, are discussed and compared thoroughly. High-performance liquid chromatography coupling with inductively coupled plasma mass spectrometry and hydride generation atomic spectrometry are proved to be the most powerful hyphenated methodologies for arsenic speciation in environmental and biological matrices.

Contents

1. Introduction

Exposure to arsenic (As) is a global public health concern due to the wide distribution in environment of As and its close association with numerous adverse effects [1]. It has been estimated that about hundred million people in India are at risk of drinking arsenic-contaminated water [2,3]. Total arsenic level of 22 in 23 total water samples from Hungary are confirmed to be higher than the health limit value of European Union (10 $\mu g\,L^{-1}$) [4], the highest total arsenic content is up to 210.3 $\mu g\,L^{-1}$. Serious arsenic pollutions in groundwater are also found in China [5], and arsenic concentration in some water samples are even higher than 500 $\mu g\,L^{-1}$. With the

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deterioration of environment pollutions, humans are at an increasing risk of As exposure. The survey on the water and diet contributions to As exposure in northwest of China reveals that As content in high percentages of water (77% of $n=131$ total samples), vegetables (92%, $n=120$), and cereals (32%, $n=25$) are higher than the acceptable levels [5].

It is well known that the simple knowledge of total arsenic content in real-world samples is far from enough, as the toxicity of As element is predestined by its chemical species presented [6]. For example, inorganic As is the number one toxin in the United States Evnironmental Protection Agency (USEPA) list of prioritized pollutants [2] and classified as Group I carcinogens based on human epidemiological data, while the methylated As species such as monomethylarsonic acid (MMA) and dimethyarsinic acid (DMA) are less toxic, arsenobetaine (AsB), arsenocholine (AsC) and other arsenosugars are even considered to be of non-toxicity [7].

In the past 5 years, various methodologies have been developed to figure out arsenic species in environmental and biological samples including water, plant, sea food, rice, blood, saliva [8], nail, hair and *Euglena gracilis* cells [9]. The construction of new analytical procedures for As speciation not only improve our knowledge on As biogeochemistry, toxicity and metabolism, but also provide abundant information relating to the biomarkers of exposure and As cycling in natural environment. At the same time, the acknowledgment of exact arsenic species in biological and environmental samples facilitates the more accurate assessments of environmental impact and health risks induced by As exposure.

During As speciation, suitable sample pretreatment techniques are usually adopted to eliminate the effect of matrices, to enrich the aimed species and/or to separate the As species for accurate identification. With suitable detection mode, excellent selectivity and sensitivity have been achieved for the newly developed As speciation protocols in last 5 years, which also gain practical demonstration in various environmental and biological assays. In this mini-review, the extraction/separation procedures including solid phase extraction, liquid–liquid extraction, hydride generation, liquid chromatography and capillary electrophoresis, are thus discussed and summarized. Also, the commonly used strategies for arsenic speciation and determination techniques in different samples are also reviewed.

2. Procedures for arsenic extraction/separation

2.1. Solid phase extraction

Solid phase extraction (SPE) is an effective sample pretreatment technique for the extraction/preconcentration of analyte from complex matrices, with the merits of satisfactory recovery and preconcentration efficiency, low cost and reduced reagent consumption as well as environmental friendliness. At the same time, the simple operation offers SPE approach great popularity in on-line or off-line analysis of As species combining with other analytical techniques. In recent years, various materials have been adopted for the extraction/preconcentration of As species from environmental and biological samples, along with improved and satisfied selectivity and preconcentration efficiencies.

2.1.1. Conventional sorbent

Quite a few novel procedures have been developed for arsenic speciation, based on conventional sorbent such as ion exchange resin, glass and modified mesoporous silica.

A simple field separation method is developed for inorganic As speciation, with anion exchange cartridges prior to the inductively coupled plasma sector field mass spectrometric (ICP-SF-MS) detection [4], with the aim to prevent interconversion of arsenic species in the samples. On-site arsenic separation is successfully achieved by SPE cartridges packed with anion exchange resin, in which As(V) is retained on the column, meanwhile As(III) passes through it. The detection limit of As using ICP-SF-MS is 0.06 $\mu g\ L^{-1}$. 23 water samples from public wells in 3 different counties, including a history site of high natural arsenic occurrence in Hungary, and a resort area close to the capital city, are applied for speciation analysis of As(III) and As(V). As(III) and As(V) also can be effectively separated by anion-exchange resin (AG 1-X8) due to the fact that AG 1-X8 shows selective adsorption ability to As(V) in acetate form, while no adsorption to As(V)/As(III) in chloride form [10]. The developed SPE method is suitable for on-site separation and speciation of inorganic arsenic in high arsenic-groundwater, and also could be used for arsenic speciation during arsenic removal by ferrihydrite in the absence of oxygen [10]. 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 [11]. Both SBAE and hydrate iron oxide particles integrated HY resin posses high adsorption capacities toward As species, i.e., more than 370 $\mu g\ g^{-1}$ of As(V) for SBAE resin, more than 4150 $\mu g\ g^{-1}$ of As(III) and 3500 $\mu g\ g^{-1}$ of As(V) for the HY resin. With detection by atomic absorption spectrometry-hydride generation technique, a detection limit of 0.24 $\mu g\ L^{-1}$ is achieved.

Escudero et al. propose a highly efficient separation and preconcentration method for arsenic species determination, based on ionic liquid (IL) dispersive microextraction technique implemented in a flow analysis system. After the selective chelation between As(III) and sodium diethyldithiocarbamate (DDTC), the obtained complex is dispersed IL 1-octyl-3-methylimidazolium hexafluorophosphate ([C(8)mim]PF_6) to form a homogeneous solution. The dispersed IL phase is thus on-line retained by a microbore glass column filled with Florisil® resin, followed by the eluting with acidified methanol [12]. As(III) is determined in eluent solution by electrothermal atomic absorption spectrometry (ETAAS), with a detection limit of 0.05 $\mu g\ L^{-1}$. Concentration of As(V) is then deduced by the difference between total inorganic arsenic and As(III).

As As(V) could be selectively adsorbed on the surface of 3-(2-aminoethylamino) propyltrimethoxysilane (AAPTS) modified ordered mesoporous silica [13], a sensitive quantitative method with inductively coupled plasma optical emission spectrometry (ICP-OES) for the speciation of inorganic arsenic has been developed, along with a detection limit of 0.05 $\mu g\ L^{-1}$. Total inorganic arsenic is determined after the oxidation of As(III) to As(V) with $KMnO_4$ and the As(III) content is obtained by the subtraction As(V) from total As. The adsorption capacity of AAPTS modified ordered mesoporous silica for As(V) is deduced to be 10.3 $mg\ g^{-1}$.

2.1.2. Functional nanomaterials

With the great progress in material science, quite a few functional materials have been emerged, providing excellent sorbent candidate in the field of sample pretreatment. The newly emerged materials, especially nanomaterials such as nanofibers [14], magnetite nanoparticles [15], metal hydroxide precipitate [16,17], and nano-TiO_2 colloid [18], usually offer improved separation/extraction efficiency, selectivity and adsorption capacity in As speciation, contributed by the specific functional groups on their surface and their huge surfaces/volume ratio.

Carbon nanofibers (CNFs) modified with ammonium pyrroine-dithiocarbarnate (APDC) is demonstrated to own excellent selectivity to As(III), thus a SPE procedure is constructed for arsenic speciation in groundwater samples using microcolumn packed

surface modified CNFs [14]. The As(III) retained on CNFs can be easily desorbed and no carryover is observed in the next analysis, 30 adsorption–elution cycles could be performed with the same column without obviously decrease in the recoveries for the analytes. As(III) retained by the microcolumn and As(V) collected from the effluents are determined by ICP-MS, with detection limits of 0.0045 μg L^{-1} and 0.24 μg L^{-1} for As(III) and As(V), respectively. Doker et al. demonstrate that hydrophobic poly (hydroxyethylmethacrylate) (PHEMA) microbeads is an effective adsorbent for the retention of As-APDC complex [19]. The retained arsenic could be quantitatively eluted by NH_3 solution. They also indicate that improved sensitivity and precision for As determination using graphite furnace atomic absorption spectrometry (GFAAS) could be achieved by injection of large-volume sample to graphite tube and use of $Mg(NO_3)_2$ as chemical modifier.

Favorable selectivity to As(V) in the presence of As(III) is achieved under pH condition of 11–12 when cellulose fiber coated with yttrium hydroxide precipitate layer is used as adsorbent [16]. The same material would takes up ca. 98% of As(III) and As(V) at acidic circumstance. After reduction of arsenate to arsenite, total inorganic arsenic is quantitatively measured with detection by atomic fluorescence spectrometry, and arsenic speciation is achieved by difference. A similar procedure is also reported using aluminum hydroxide precipitate as the sorbent [17]. Total arsenic measurement by hydride generation atomic absorption spectrometry (HG-AAS) was performed after oxidation of As(III) by using $KMnO_4$, giving rise to a detection limit of 0.012 μg L^{-1}.

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) [20]. Combined with sequential injection technique, an on-line SPE protocol incorporating with MWCNTs–BPEI packed column is developed. The retained As(V) is readily recovered by NH_4HCO_3. Under a sample volume of 2.0 mL, an enrichment factor of 16.3 is obtained, along with a detection limit of 14 ng L^{-1}. Speciation of As(V) and As(III) in snow water and rain water samples is achieved with above on-line mode.

Compared with nanometre-size TiO_2 powder, nanometer-size TiO_2 colloid is more advantageous as adsorbent with the merits of better dispersal without agglomeration. Separation and preconcentration of ultra-trace arsenic in environmental water samples has been achieved by nano-sized TiO_2 colloid. With slurry sampling technique, the precipitated TiO_2 is directly inverted to colloid after centrifugation and transferred to AFS detection without desorbing the concentrated arsenic, giving rise to a detection limit of 10.6 ng L^{-1} [18]. The slurry sampling technique has also combined successfully with a Fe_3O_4 nano-particle based SPE procedure in the preconcentration of arsenic species [21]. With 0.64 g L^{-1} Fe_3O_4 slurry, a detection limit of 13.5 ng L^{-1} is achieved for arsenic within a linear range of 0.05–3.5 μg L^{-1}.

Magnetic separation technique has attracted much attention in the field of sample pretreatment, due to the fact that simple and rapid separation manipulation could be accomplished with the assistance of external magnetic field. Huang et al. proposed a SPE procedure for the speciation of inorganic arsenic in environmental water by using amino-modified silica coated magnetic nanoparticles (MNPs) as the sorbent followed by ICP-MS detection [15]. As(V) could be selectively adsorbed on MNPs in pH range of 3–8, while As(III) is not be retained. The As(V)-loaded MNPs can be separated easily from the aqueous sample solution by simply applying an external magnetic field. Total inorganic arsenic is thus quantified after the permanganate oxidation of As(III) to As(V).

A single-step magnetic separation procedure that can remove arsenic from contaminated water is clearly a desirable goal. A kind of water dispersible magnetite nanoparticles is prepared by anchoring carboxymethyl-beta-cyclodextrin (CMCD) cavities to the surface of magnetic nanoparticles. The as-prepared CMCD capped Fe_3O_4 nanocrystals have the advantage of allowing for the simultaneous removal of both arsenic and organic contaminants. On dispersion of the nanocrystals in contaminated waters, organic pollutants can sequester within the anchored hydrophobic CD cavities while As ions can be adsorbed onto the surface of the iron oxide nanocrystals; both can then be removed by magnetic separation in a single-step process [22].

Angelakeris et al. demonstrated that hematite-coated Fe_3O_4 particles are very effective in the removal of As(III) and As(V) from aqueous solution as the adsorption capacities to As(III) and As (V) high up to 1.0 μg mg^{-1} and 2.1 μg mg^{-1}, respectively [23]. The existence of magnetic core facilitates their application in a magnetic separation system, offering very easy and simple removal manipulations under an external magnetic field.

Arsenic removal is also be successfully performed by combining magnetic seeding flocculation and open/high gradient superconducting magnetic separation (OGMS or HGMS) [24]. Magnetite (Fe_3O_4) is used as magnetic seeding material and polymeric ferric sulfate (PFS) is added for combining the arsenic with the magnetite. In OGMS mode, arsenic removal efficiency increases with the magnetite dosages and the amount of polymeric ferric sulfate (PFS). In HGMS mode, the exploration of cationic polyacrylamide (CPA) would contribute to a 15% improvement on the arsenic removal capacity without any sacrifice on the arsenic removal efficiency.

2.1.3. Biological materials

Egg-shell membrane (ESM) is a biomaterial consists of calcareous layer and inner lamellar layer. Due to the abundant functional groups on its unique structure and high surface area, ESM has been used as an adsorbent for the sorption of organic molecules and metal ions. Though efforts have been taken to use ESM as sorbent for As removal [25], while the carboxylic groups on ESM surface are not favorable for arsenic adsorption, leading to a not-so-satisfied removal efficiency. Recent research show that the methyl esterified egg-shell membrane (MESM) possesses positive charge within pH 1–9, exhibiting a 200-fold improvement on sorption capacity of arsenate with respect to original ESM; at the same time, no adsorption of As(III) by MESM is observed under the tested conditions. An inorganic arsenic speciation procedure is thus developed based on the different adsorption ability to As(III) and As(V), and validated by the identification of inorganic arsenic content in Hijiki and water samples [26]. The LOD is 15 ng L^{-1} under a sample volume of 4.0 mL with hydride generation atomic fluorescence spectrometry detection.

The functional groups of amines amides, hydroxyls, carboxylates, ethers, thioles and phosphates on cell wall have make cells an attractive sorbent. The diversity of functional groups provides potential for selective binding of various metal species, which opens a promising avenue for metal speciation. A disposable cell microcolumn with the live Hela cells immobilized on Sephadex G-50 beads has been explored for the preconcentration and speciation of inorganic arsenic by Wang et al. [27], a micro-sequential injection LOV system is adopted for the renewal of cell column, as illustrated in Fig. 1. The sorption of arsenic species by live HeLa cells involves both surface uptake and bioaccumulation. At a sample pH of 3.0, the cells accumulate arsenate with high specificity over arsenite, the speciation of inorganic arsenic is thus achieved by direct determination of arsenate followed by quantifying total inorganic arsenic after conversion of arsenite to arsenate. Arsenic concentration is directly measured by GFAAS with a LOD of 0.05 μg L^{-1}.

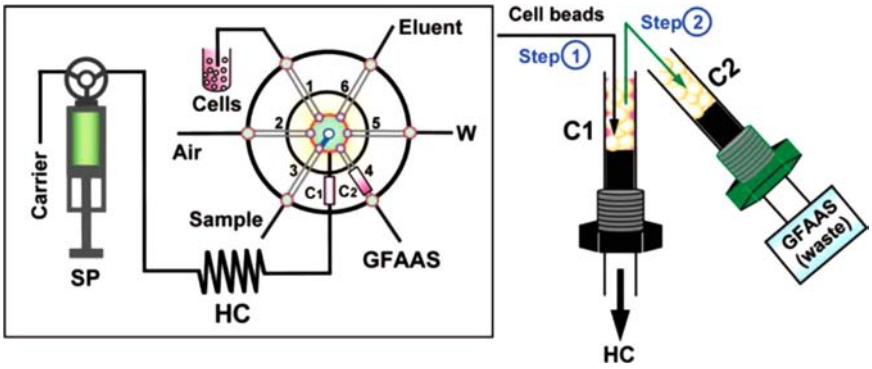

Fig. 1. Flow manifold of the microsequential injection LOV system for conducting renewable sorption of arsenate via metabolism-dependent and metabolism-independent bioaccumulation with detection by GFAAS. SP, syringe pump; HC, holding coil; W, waste; C1 and C2, microcolumn positions. Ref. [27], reprinted with permission from (Chen XW et al., Anal. Chem. 2009, 81, 1291–1296. Copyright (2009) American Chemical Society.

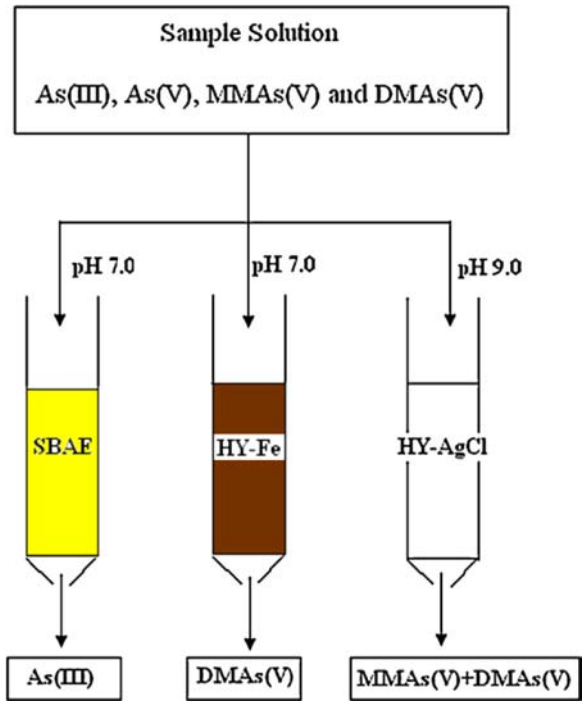

Fig. 2. Scheme for selective separation of the arsenic speices in water using SBAE, HY–Fe and HY–AgCl resins. Ref. [31], reprinted from Analytica Chimica Acta, 706, Ben Issa N, et al., Separation and determination of arsenic species in water by selective exchange and hybrid resins, 191–198, Copyright (2011), with permission from Elsevier.

The same research group also demonstrates that *Bacillus subtilis* (*B. subtilis*) might be a safer alternative with respect to the HeLa cell when referring As speciation. Native *B. subtilis* can remove very low concentrations of inorganic arsenic of either oxidation states, while incubating the bacteria with iron(III) would enhance significantly the selectivity to As(V) at acid condition and in the meantime achieve recorded sorption capacity for arsenic at a higher pH [28].

Bioremediation based on the genetically engineered bacteria has been demonstrated to be a green and effective approach in the removal of various metals, especially arsenic. Yang's work reveal that the expression of ArsR, a metalloregulatory protein with high selectivity and affinity toward arsenic, in *Escherichia coli* by cell engineering can significantly enhance the adsorption/accumulation capacity of methylated arsenic species [29]. Compared to native *E. coli* cells, the ArsR-expressed *E. coli* cells provide 5.6-fold and 3.4-fold improvements on the adsorption/accumulation capacity for monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). At the same time, the accumulation of MMA and DMA on ArsR-expressed *E. coli* cells is less sensitive to the variation of pH value respect to the black control cells, suggesting that the expression of special regulatory protein in cell by cell engineering paves new way to develop arsenic species methodologies with high selectivity.

2.1.4. Multi-sorbent based SPE procedure

Specific interaction between sorbent and aimed analyte is usually highly demanded to ensure an excellent selectivity, which has been the principle to design and develop new materials using surface modifications/functionalization. Selective adsorbent and selective elution process will facilitate the separation of different arsenic species. A combined SPE procedure has been constructed for simultaneously extraction of four water-soluble arsenic species: arsenite, arsenate, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Three molecular recognition technology (MRT) gel SPE columns are combined to design a multi-step extraction procedure. The aimed four arsenic species are all retained on the SPE columns with the flow-through of sample, then the adsorbed As species is separately eluted by using different elution. With detection of arsenic species by GF-AAS technique, the method limits are 0.06 μg L^{-1} for As(III) and As(V), and 0.05 μg L^{-1} for MMA and DMA [30].

The performance of three resins, including strong base anion exchange (SBAE) and two hybrid (HY) resins, HY–Fe and HY–AgCl, are investigated in arsenic speciation [31]. The scheme for selective separation of arsenic species is illustrated in Fig. 2, the quantitative separation of molecular and ionic forms of iAs and oAs are achieved by SBAE under suitable pH condition. The molecular form of As(III) at pH < 8.0 is separated from As(V) and oAs species because it only exists in the effluent, while DMAs(V) could be measured in the effluent of HY–Fe resin which retain all other arsenic species. All iAs species are retained by HY–AgCl resin, facilitating the direct determination of oAs species in the effluent. ICP-MS is applied for the determination of arsenic in all arsenic species in water, the limit of quantification is 0.03 μg L^{-1}.

A sequential injection system incorporating two mini-columns followed by detection with HG-AFS is applied to facilitate the separation and speciation of inorganic As(III) and As(V) [32]. Octadecyl immobilized silica is used for selective retention of the As(III)–APDC complex, while the sorption of As(V) is accomplished by 717 anion exchange resin. The detection limits are 0.02 μg L^{-1} and 0.03 μg L^{-1} for As(III) and As(V), respectively. The practical applicability of the procedure has been demonstrated by analyzing a certified reference material water and lake water sample.

2.2. Liquid–liquid extraction (LLE)

A liquid–liquid extraction using dodecane modified with 4% dodecanol containing Aliquat 336 as the extractant has been developed for the separation of arsenic species in environmental matrices [33]. As(V) is quantitatively transported to organic phase whereas no transport of As(III) takes place. A supported liquid membrane (SLM) system is used to enable the separation of As (V) and As(III) species based on their different kinetic behavior. The extracted As(V) could be stripped using 0.1 M HCl.

Ionic liquids (ILs) are kinds of organic salts which are showing great promises as potential alternatives to conventional volatile toxic organic solvents due to their unique and attractive properties including negligible vapor pressure, nonflammability, high chemical/thermal stability, low toxicity and favorable conductivity. These attractive features of ILs make them as popular candidates in the field of sample pretreatment, including As species separation. An IL-based LLE procedure coupling with HG–AAS detection has been proposed for the speciation assay of inorganic As(III). As(III)–APDC complex is first selectively extracted into IL phase at pH=4, then it is back-extracted from the IL phase by HCl [34]. A 5 ng L^{-1} LOD is achieved and this LLE method is applied successfully to the speciation of As (III) and As (V) in biological samples of multiple sclerosis patients.

A similar liquid–liquid microextraction procedure has been developed for As(III) separation by using hydrophobic IL 1-hexyl-3-methylimidazolium hexafluorophosphate as extraction media. With the assistance of ultrasound during the extraction process, an enhancement factor high up to 208 is achieved [35].

Farzaneh et al. reported a rapid in-situ solvent formation microextraction procedure for the extraction and preconcentration of inorganic As from sample solutions containing high concentration of salt. As-contained samples are first mixed with hydrophilic IL $HmimBF_4$, then ion-exchange reagent $NaPF_6$ is added to produce the hydrophobic IL $HmimPF_6$, which acts as the analyte extractant to form the cloudy homogeneous solution. With ETAAS detection, a detection limit and enrichment factor of 6 ng L^{-1} and 198 are achieved. The proposed method is successfully applied for the determination of As(III) and As(V) in water samples, food salts, and total As in biological samples [36].

Solvent bar microextraction (SBME) is normally performed by using a short length of hollow fiber membrane (sealed at both ends), which is filled with organic extractant solvent and placed in a stirred aqueous sample solution [37]. SBME procedure combined with electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) for the speciation of As(III) and As (V) in water samples has been developed [38]. The method is accomplished on the chelation of As(III) and APDC under optimal conditions, and the extraction of As(III)–APDC complex into organic phase. The post-extraction organic phase is directly injected into ETV-ICP-MS for determination of As(III) with iridium as permanent chemical modifier. As(V) is reduced to As(III) by L-cysteine and then subjected to SBME prior to total As determination. The LOD for As(III) is 0.32 μg L^{-1}.

2.3. Hydride generation technique

Speciation of inorganic arsenic is achieved by hydride generation atomic fluorescence spectrometry under proportional equations corresponding to two different measurement conditions [39]. As(III) is measured by directly feeding sample diluted with HCl, while total arsenic concentration is detected after reduction with KI and ascorbic acid for 30 min. The detection limits are 6.3 and 5.0 ng g^{-1} for As(III) and As(V), respectively. The proposed method is applied to arsenic species in cultivated and wild mushroom samples from different origins. Liu et al. demonstrated that arsine could be selectively generated from As(III) in suitable medium [40]. Arsine is first trapped on resistively heated tungsten coil, then released at higher temperature and subsequently delivered to atomic fluorescence spectrometer by a mixture of Ar and H_2 for measurement. Total inorganic arsenic is determined after pre-reduction of As(V) to As(III) in thiourea–ascorbic acid solution. The limit of detection is 10 ng L^{-1} for As(III) and 9 ng L^{-1} for total As.

An ultra-sensitive method for arsenic speciation based on selective hydride generation and ICP-MS detection is recently proposed by Dedina et al. [41]. Tri- and pentavalent As species are distinguished on the basis of selective HG after L-cysteine pre-reduction. Methylated species are resolved on the basis of thermal desorption of the formed methyl substituted arsines after collection at −196 °C. Hydride generation based inorganic arsenic separation is also successfully coupled with metal furnace atomic absorption spectrometry [42]. Under mild conditions for hydride formation, such as slightly acid pH media and low tetrahydridoborate concentration, As(III) is selectively separated and determined, then total arsenic concentration is obtained after pre-reduction by L-cysteine.

2.4. Liquid chromatography

Two independent liquid chromatography inductively coupled plasma-mass spectrometry (LC/ICP-MS) methods for the separation of arsenic species in urine have been developed with standard addition methodology [43]. Detection limits of various As species range from 0.2 to 0.8 μg L^{-1}. Seven arsenic species, i.e., As(III), As (V), MMA, DMA, arsenobetaine (AB), arsenocholine (AC) and trimethylarsine oxide (TMAO), are found and quantified in a new NIST frozen human urine Standard Reference Material (SRM) 2669.

Speciation of arsenic is accomplished by anion/cation exchange chromatography with inductively coupled plasma mass spectrometry (HPLC-AEC/CEC-ICP-MS) [44]. Speciation results indicate that the dominant As species in raw and cooked anemone are DMA, followed by AB, As(V), monomethylarsonic acid (MA), tetramethylarsonium ion (TETRA) and trimethylarsine oxide (TMAO). Arsenocholine (AsC), glyceryl phosphorylarsenocholine (GPAsC) and dimethylarsinothioic acid (DMAS) are identified by liquid chromatography coupled to triple quadrupole mass spectrometry (HPLC-MS), it is the first time to report the identification of DMAS in marine food.

Gradient hydride generation procedure (GHG) is found to be able to converse arsenic species into corresponding hydrides effectively. Arsenic speciation is thus accomplished by liquid chromatographic separation followed by GHG and quartz atomizer atomic absorption spectrometric detection [45]. The hydrides are separated by a specially-designed gas–liquid separator, which not only ensures a complete separation but minimizes the dispersion of hydrides when the hydrides are delivered into the atomizer. The separation process is finished within 800 s by injecting 100 μL sample solution, achieving detection limits of 0.9, 1.4, 1.4, 1.6, 1.5 μg L^{-1} for As(V), As(III), MMA, DMA and TMAO, respectively. Three arsenic species As(V), DMA and TMAO are identified in Hijiki samples by this proposed procedure.

A HPLC separation coupling with gas phase chemiluminescence (CL) detection system has been proposed for speciation of As(III), As(V), MMA and DMA [46]. MMA and DMA are converted into As (V) in several seconds after post-column derivatization by high-efficiency photooxidation, then the reaction of ozone and arsine upon hydride generation produce a CL signal for detection. Detection limits are 3.7, 10.3, 10.2, 10.0 μg L^{-1} for As(III), As(V), MMA and DMA, respectively. The recoveries of the four arsenic species in human urine sample range from 87% to 94%.

Arsenic speciation in typha latifolia (cattail) is achieved using strong anion exchange, ion pairing and strong cation exchange chromatography with MS detection [47]. The results well reveal the presence of inorganic arsenite, arsenate, DMA, and MMA in the material widely used in traditional food and medicine. At the same time, it also indicates that the level of exposure to arsenic can be substantially reduced by removing the skin of cattail.

HPLC coupled to hydride generation atomic fluorescence spectrometry (HPLC–HG-AFS) also demonstrate their practical application in inorganic arsenic speciation in coal samples [48]. Microwave-assisted extraction is adopted for sample pretreatment, and the LODs are 0.01 $\mu g\,L^{-1}$ and 0.02 $\mu g\,L^{-1}$ for As(III) and As(V), respectively.

After investigating the performance of different extraction solvent on arsenic speciation in terrestrial plants using ion-exchange HPLC [49]. Zheng et al. recommend that water alone should be used for the extraction of inorganic arsenic species, while for organic arsenic species, high content of methanol, i.e., methanol–water mixture with a volume ratio of 9:1, should provide most effective extraction. Wang et al. proposed a novel method for arsenic speciation by interfacing solid phase preconcentration-liquid chromatography (LC) separation-gradient hydride generation (GHG)-quartz flame atomic absorption spectrometry (QFAAS) [50]. MnO_2 mini-column is used to concentrate the arsenic species of As(III), As(V), MMA and DMA, in which As (III) is converted to As(V) via oxidation by MnO_2, while other species remain unchanged. The recovery of As(V), MMA and DMA from the MnO_2 mini-column is facilitated by tetramethylammonium hydroxide (TMAH). After LC separation, arsenic species in the eluate are subject to gradient hydride generation with detection by QFAAS. Cellulose fiber is adopted for the selective adsorption As(III)–APDC complex. After elution with HNO_3, As(III) in the original sample is quantified by graphite furnace atomic absorption spectrometry (GFAAS), and the amount of As(V) is obtained by subtraction. Detection limits of 0.019, 0.33, 0.39, 0.62 $\mu g\,L^{-1}$ are obtained for As(III), As(V), MMA and DMA.

In order to minimize spectral interferences caused by polyatomic species such as $^{40}Ar^{35}Cl^{+}$ in HPLC–ICP-MS procedure, the interference standard (IFS) [51] method using $^{83}Kr^{+}$ as the IFS probe is employed for the speciation of As(III), As(V), DMA and MMA in plant samples and chicken feed samples. The IFS method contributes to improve precision and sensitivity.

The liquid chromatography procedures for arsenic speciation are summarized in Table 1.

2.5. Capillary electrophoresis separation

Capillary electrophoresis is very powerful separation technique widely adopted in same pretreatment. Compared with LC, CE offers some unique merits that make it particularly attractive for elemental speciation analysis, such as high separation efficiency, small volume of sample requirement and fast analysis.

A capillary zone electrophoresis is developed for the speciation of five arsenic species including As(III), DMA, p-As, MMA and As(V) in sea foods [52]. The interested As species are successfully base-line separated within 11 min. With an ultraviolet detection mode, the detection limits are among 0.004–0.30 mg L^{-1}. For the speciation of arsenic, ICP-MS offers excellent sensitivity, wide linear dynamic range, high-speed analysis and isotope-specific detection capabilities, which facilitate accurate and fast detection. In the coupling of CE and ICP-MS, the interface is very important and it should be able to provide a stable electrical circuit from CE to nebulizer, to introduce CE effluent into ICP-MS efficient and keep a low dead volume. An improved sheath-flow interface is designed to facilitate the coupling of CE separation and ICP-MS detection [53], the schematic diagram of the sheath-flow interface is shown in Fig. 3. The improved sheath-flow interface completely avoids laminar flow in CE capillary caused by the suction from ICP-MS, makes electric supply more stable in CE, and transports analyte solution to ICP-MS easily and more efficiently. With the help of this improved sheath-flow interface, four arsenic species, As(III), As(V), MMA and DMA in dried Mya arenaria Linnaeus and shrimp samples are identified within 10 min with a recovery of 96–105%.

Jiang et al. has adapted a commercial sprayer kit as the nebulizer and fixed the outlet of CE capillary on an exact position at the sprayer tip. The effluent from the capillary is directly nebulized at the sprayer tip, ensuring no dead volume before nebulization. The as-designed sprayer kit is used as an interface in CE-ICP-MS for the speciation and quantification of ten arsenic com-pounds: As (III), As (V), DMA, MMA, AsB, AsC, 3-NHPAA, 4-NPAA, o-ASA (o-arsanilic acid) and p-UPAA. The ten arsenic species are baseline separated under the optimized conditions and the proposed method is applied for arsenic speciation in several environmental samples such as ground water samples, herbal plants and chicken meat [7]. As an alternative to ICP, AAS offers some advantages in terms of simple structure, easy operation, lower equipment and operation cost, good selectivity and good precision. A novel interface of capillary electrophoresis coupling hydride generation with electrothermal atomic absorption has been proposed by Deng et al. for the quantitative assay of As(III) and As(V) [54]. This novel interface presents the advantages of good stability, good gas–liquid separation efficiency, less dead volume, good reproducibility and easy operation. Electrophoretic separation of the two arsenic species is obtained within 8 min with detection limits less than 160 ng g^{-1} for each species.

Table 1
Arsenic speciation using liquid chromatography.

Arsenic species	Sample source	Chromatography column	Detection mode	Detection limit	References
As(III), MMA, DMA, AB, AC, TMAO, As(V)	Frozen human urine	Dionex IonPac AS7 Nucleosil 100-5 SA PRP X-100 PEEK	ICP-MS	0.2–0.8 $\mu g\,L^{-1}$	[43]
AB, DMA, MA, AsV, AsIII, TMAO, TETRA	Marine food	Hamilton PRP X-100 Supelcosil LC-SCX	ICP-MS	1.0–5.9 ng g^{-1}	[44]
As(V), As(III), MMA, DMA, TMAO	Hijiki	Wakopak Navi C30-5	HG-AAS	0.9–1.5 $\mu g\,L^{-1}$	[45]
As(III), DMA, MMA, As(V)	Human urine	Hamilton PRP X-100	Gas phase CL	3.7–10.3 $\mu g\,L^{-1}$	[46]
As(III), As(V)	Coal	Hamilton PRP-X100	HG-AFS	0.01 $\mu g\,L^{-1}$ (As(III)) 0.02 $\mu g\,L^{-1}$ (As(V))	[48]
As(III), DMA, MMA, As(V), Cationic As	Terrestrial plants	Hamilton PRPX-100 Zorbax 300-SCX	ICP-MS/ICP-TOF-MS	–	[49]
As(III), DMA, MMA, As(V)	Plant and chicken feed	IonoSpherA	Quadrupole-based ICP-MS	–	[51]

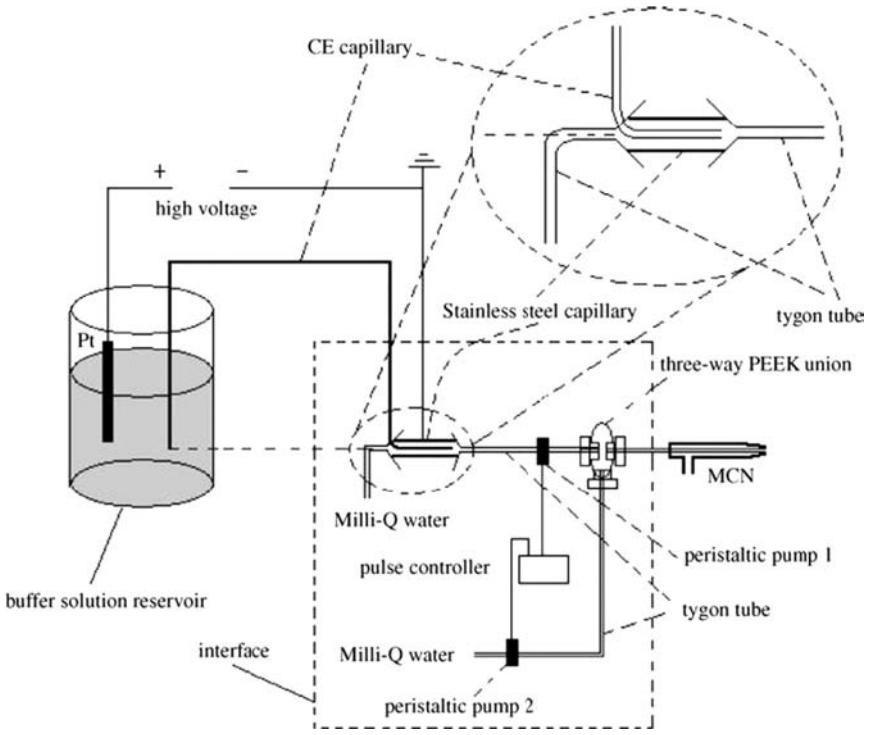

Fig. 3. Schematic diagram of the improved sheath-flow interface. Ref.[53], reprinted from Talanta, 78, Yang GD, et al., Speciation analysis of arsenic inMya arenariaLinnaeus and shrimp with capillary electrophoresis-inductively coupled plasma mass spectrometry, 471–476, Copyright (2009), with permission from Elsevier.

3. Strategies for arsenic speciation

Generally, As speciation strategies are classified into two categories, based on the diverse behavior of arsenic species or their complex in relation to the sorbent/solvent. The first strategy is the collection of specific arsenic species using an extraction/detection system of high selectivity. The other one involves in the retention of several interested arsenic species together, and then separated them with chromatography/electrophoresis techniques before detection.

3.1. Selective collection of specific arsenic species

This selective extraction/separation mode is usually applied in the speciation assay of inorganic As(III) or As(V). As(III)/As(V) is firstly selective discriminated through specific extraction process or hydride generation process. Subsequently, total inorganic arsenic concentration in sample is quantified after suitable pre-oxidation/pre-reduce. Normally, the speciation process is accomplished through difference.

In most cases, the selective retention of inorganic As(V) is more easily to be achieved due to the fact that As(V) has successive acid dissociation constants (pK_a) of 2.3, 7.0 and 11.5, and it exist mainly as anionic species at wide range of pH, while As(III), having pK_a of 9.2, 12.1 and 13.4 [31], is present as a neutral species – H_3AsO_3, when pH values is less than 8. Anion-exchange resin AG 1-X8 [4,10], styrenedivinylbenzene copolymer-based resin [11], 3-(2-aminoethylamino) propyltrimethoxysilane (AAPTS) modified ordered mesoporous silica [13], yttrium hydroxide modified cellulose fiber [16], aluminum hydroxide precipitate [17], amino-modified magnetic nanoparticles [15], live HeLa cell [27] and hydrous ferric oxide (HFO) membrane [28] have been proved to be powerful sorbent in the selectively adsorption of As(V).

As far as As(III) is concerned, APDC and DDTC are typically employed as the chalexation regent for their specific reaction with arsenite, then the formed complex are separated by suitable adsorbent or liquid phase. Apart from the above complex reaction, determination of As(III) could be also achieved by selectively generating arsine from arsenite in suitable condition [39–42], then quantified by hydride generation atomic spectrometry. Different procedures for selectively determination of specific arsenic species are summarized in Table 2.

3.2. Retention/separation of multi-arsenic species

Chromatography/capillary electrophoresis is very powerful separation technique for variable organic or inorganic analytes. Normally, the interested arsenic species in real-world samples could be retained directly on a commercial chromatography column and then separated for identification by adjusting the chromatography elution. The performance of different commercial chromatography column in the identifying arsenic species in a proposed liquid chromatography inductively coupled plasma-mass spectrometry (LC/ICP-MS) methods has been compared [43]. The results indicate that the commercial Dionex IonPac AS7 column facilitates the separation of seven arsenic species, i.e., As(III), As(V), MMA, DMA, arsenobetaine (AB), arsenocholine (AC), and trimethylarsine oxide (TMAO). Xue et al. reported a chromatography separation process for arsenic species with a Hamilton PRP X-100 column [46]. The identification of As(III), As(V), MMA and DMA in human urine samples are successfully achieved. The performance of the same anion-exchange column are also demonstrated by the direct separation of As(III), As(V), MMA, p-ASA, AsB and DMA in bivalve mollusks [55]. Tian et al. show that Wakopak Navi C30-5 columns is very effective in the separation of five arsenic species, i.e., As(V), As(III), MMA, DMA and TMAO [45]. Considering that both anionic arsenic compounds such as As(III), As(V), MMA and DMA, and cationic arsenic compounds AB, AC, TMAO and Tetra, may exist in the terrestrial plants, the exploitation of dual-column, i.e., anion-exchange HPLC column (Hamilton PRP X-100) and cation-exchange column (Zorbax 300-SCX), has been demonstrated to be an useful strategy for the simultaneous

Table 2
Different procedures for selective collection of specific arsenic species.

Arsenic species	Collection technique	Detection mode/LOD	Sample source	References
As(V)	SPE with resin	ICP-MS/0.06 μg L^{-1}	Public well water	[4]
	SPE with resin	ICP-MS/0.24 μg L^{-1}	Natural water	[11]
	SPE with silica	ICP-OES/0.05 μg L^{-1}	Natural water	[13]
	SPE with silica	ICP-MS/0.21 ng L^{-1}	Environmental water	[15]
	SPE with yttrium hydroxide layer	AFS/17 ng L^{-1}	Natural water	[16]
	SPE with aluminum hydroxide precipitate	AAS/0.012 μg L^{-1}	Montana soil, water	[17]
	SPE with MWCNTs	AFS/14 ng L^{-1}	Human hair, snow, water	[20]
	SPE with egg-shell membrane	AFS/15 ng L^{-1}	Hijiki and water	[25]
	SPE with HeLa cell	GF-AAS/0.05 μg L^{-1}	River water	[27]
	SPE with hydrous ferric oxide modified *Bacillus subtilis*	GF-AAS/0.08 μg L^{-1}	Human hair, spring water	[28]
As(III)–DDTC	SPE with microbore glass	ET-AAS/5 ng L^{-1}	Wines	[12]
As(III)–APDC	SPE with carbon nanofibers	ICP-MS/0.0045 μg L^{-1}	Environmental water	[14]
	SPE with poly(hydroxyl ethylmethacrylate) beads	GF-AAS/10 ng L^{-1}	Water, snow	[19]
	Liquid–liquid extraction	AAS/5 ng L^{-1}	Biological samples	[34]
	Liquid–liquid extraction	ET-AAS/ 0.01 μg L^{-1}	Water	[35]
As(III)	Hydride generation	HG-AFS/6.3 ng g^{-1}	Mushroom	[39]
	Hydride generation	ET-AFS/10 ng L^{-1}	Human hair, tea leaf and natural water	[40]
	Hydride generation	HG-AAS/2.0 μg L^{-1}	Water and plankton samples	[42]

separation of interested ionic As species [49]. Speciation of DMA, AB, As(V), MMA, tetramethylarsonium ion (TETRA) and trimethylarsine oxide (TMAO) in tissue extracts is also achieved by the combination of anion-exchange column Hamilton PRP X-100 and cation exchange column Supelcosil LC-SCX [44]. For some As species of trace level, a SPE column is usually adopted before chromatography separation for preconcentration of interested As species. A MnO_2 mini-column has been used to preconcentrate the arsenic species of As(III), As(V), MMA and DMA in snow water and Hijiki samples, followed by the successful chromatography separation with a C30 columns [50]. Sol–gel based amine-functionalized SPME fibers (PDMS-weak anion exchanger) has been prepared and used for direct mode extraction of DMA, MMA and As(V) from aqueous solutions followed by HPLC–ICPMS determination [56].

Capillary electrophoresis has been proved a useful tool in multi-arsenic species separation. As(III), DMA, p-As, MMA and As (V) in shrimp are successfully separated with capillary zone electrophoresis [52]. With the ultraviolet detection method, the detection limits locate in the range of 0.004–0.30 mg L^{-1}. After microwave-assisted extraction, arsenic species As(III), DMA, MMA and As(V) in Mya arenaria Linnaeus and shrimp samples are base line separated within 11 min using capillary electrophoresis [53]. With the help of a improved sheath flow interface, the separated As species are transported to ICP-MS detection smoothly, along with a recovery of 96–105%. By using a novel and high efficient interface as the nebulizer, a capillary electrophoresis coupled with inductively coupled plasma mass spectrometer (ICP-MS) system is developed for the simultaneous determination of ten arsenic compounds including As (III), As (V), DMA, MMA, AsB, AsC, 3-NHPAA, 4-NPAA, o-ASA (o-arsanilic acid) and p-UPAA. The separation is achieved on a 100 cm length × 50 μm ID fused-silica capillary [7].

4. Detection techniques for arsenic speciation

High sensitivity is always indispensable in As speciation as some As species are of very low concentration in real-world samples. Atomic adsorption spectrometry (AAS), atomic fluorescence spectrometry (AFS) and inductively coupled mass spectrometry (ICP-MS) are the most employed detection techniques in arsenic species because they are able to offer satisfactory sensitivity. Beside these, gas phase chemiluminescence detection is first employed for inorganic arsenic species [57] in 2006, based on the AsH_3–O_3 reaction to produce chemiluminescence signal. Coupled with high-efficiency photooxidation [46], gas phase chemiluminescence detection offer an improved sensitivity for both inorganic and organic arsenic assay. Electrochemical detection is also employed for arsenic species determination, anodic stripping voltammetry [62,63] and cathodic stripping voltammetry [64] based on different modifications of electrode systems are developed separately for inorganic arsenite detection. For fast and selective determination of specific arsenic species in simple environmental water samples, favorable sample pretreatment procedures with detection of ICP-MS, ICP-OES, HG-AFS, HG-AAS, GF/ET-AAS and ET-AFS have gain their successful applications. The lowest of detection of 4.5 ng L^{-1} for As(III) is obtained by ICP-MS with an enrichment factor of 33 [14]. As for ETAAS detection, a 5 ng L^{-1} LOD for As(III) is obtained with an enhancement factor of 46 [12]. For As(V) determination, a comparable LOD of 12 ng L^{-1} and 14 ng L^{-1} with detection by HG-AAS [17] and HG-AFS [20] have been achieved.

As referring to the samples of complex matrices, i.e., blood [58], urine [43,46,59], rice [60,61], marine food [44], saliva [8] and cells [9], in which more arsenic species are included, especially organic arsenic species, liquid chromatography provides an favorable strategy for efficient separation. In this case, AFS, gas phase chemiluminescence and ICP-MS are the most adopted detection techniques for multi-arsenic species analysis as their detection procedures could be performed under flow-through mode. Among above detection techniques, AFS and gas phase chemiluminescence are both based on the hydride generation chemical derivatization process to produce volatile hydrides, which limits their applications in the speciation of organoarsenic compounds as they do not form volatile hydrides after borohydride treating [6,46], while ICP-MS offers advantages of the extremely high sensitivity and the universality to all arsenic species.

5. Conclusion and perspective

In the last 5 years, different procedures are explored for arsenic speciation. With the assistance of suitable sample pretreatments, favorable selectivity and sensitivity have been achieved in acknowledging information on As species in environmental and biological samples. SPE/LLE coupling with element-specific spectrometry detection techniques is proven to be very effective for specific arsenic speciation. For multi As species analysis, the combination of chromatography with ICP-MS/hydride generation atomic spectrometry

should be more powerful to achieve efficient separation of all As species and subsequent simultaneous detection.

While it should be mentioned that most speciation protocols recently developed are specially designed for the assay of As content in aqueous phases, suitable sample treatments such as acid digestion are necessary for non-aqueous samples, i.e., biological tissue, minerals and sullage, etc. The external introduced reagents in the treating processes might induce the transform of As speciation/valence state, leading to inaccurate evaluations of As species for original sample sources. Therefore, it is an urgent task to develop direct analytical methodologies to obtain original species information of non-aqueous samples.

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