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Review

Arsenic speciation in environmental samples by hydride generation and electrothermal atomic absorption spectrometry

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ABSTRACT

For the past few years many studies have been performed to determine arsenic (As) speciation in drinking water, food chain and other environmental samples due to its well-recognized carcinogenic and toxic effects relating to its chemical forms and oxidation states. This review provides an overview of analytical methods, preconcentration and separation techniques, developed up to now, using HGAAS and ETAAS for the determination of inorganic As and organoarsenic species in environmental samples. Specific advantages, disadvantages, selectivity, sensitivity, efficiency, rapidity, detection limit (DL), and some aspects of recent improvements and modifications for different analytical and separation techniques, that can define their application for a particular sample analysis, are highlighted. HG-AAS has high sensitivity, selectivity and low DL using suitable separation techniques; and it is a more suitable, affordable and much less expensive technique than other detectors. The concentrations of HCl and $NaBH_4$ have a critical effect on the HG response of As species. Use of L-cysteine as pre-reductant is advantageous over KI to obtain the same signal response for different As species under the same, optimum and mild acid concentration, and to reduce the interference of transition metals on the arsine generation. Use of different pretreatment, digestion, separation techniques and surfactants can determine As species with DL from ng L^{-1} to μg L^{-1}. Out of all the chromatographic techniques coupled with HGAAS/ETAAS, ion-pair reversed-phase chromatography (IP-RP) is the most popular due to its higher separation efficiency, resolution selectivity, simplicity, and ability to separate up to seven As species for both non-ionic and ionic compounds in a signal run using the same column and short time. However, a combination of anion- and cation-exchange chromatography seems the most promising for complete resolution up to eight As species. The ETAAS method using different separation techniques and chemical modifiers can determine As species in seawater with DL of 0.02 μg L^{-1}, eliminate interferences of transition metals, improve the selectivity of the measurement, and enhance the sensitivity.

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1. Introduction

1.1. Toxicity and species of As

Speciation and quantification of the different chemical forms of As in natural waters and food chain is important in assessing overall health risk, because of their various toxicological effects related to their speciation [1]. Out of about 25 different As species identified in waters, arsenate (As(V), arsenite (As(III), monomethylarsonic acid (MMAA) and dimethylarsenic acid (DMAA) are the dominant forms in water environment, and the rest of forms occur mainly in water organisms [2–5]. The most commonly analyzed species are As(III), As(V), MMAA, DMAA, arsenocholine (AsC), arsenobetaine (AsB) or TMAs+ (tetramethylarsonium ion—Me_4As+), TMAO (trimethylarsine oxide—Me_3AsO), arsenosugars, phenylarsonic acid (PAS) and metaloproteins [6,7]. In case of very high concentration of sulfides, dissolved As species may be significant. Reducing acid environment favors the precipitation of orpiment and realgar, as well as other minerals containing co-precipitated As. Therefore, in waters, where concentration of free sulfides is high, the most probable is that content of As is lower. On the other hand, species containing trivalent As most commonly appears in neutral and alkaline pH in the presence of sulfides [5]. The most important factors controlling As speciation analysis are redox potential and pH [8].

1.2. Analytical techniques for As speciation

Atomic absorption spectrometry (AAS) is a useful and, importantly, less expensive tool for studying the As speciation. In the beginning time, AAS was used for the speciation of As in the 1980s [9]. A number of techniques, as for example, the electrothermal vaporization inductively coupled plasma mass spectrometry (ET-ICPMS), electrothermal atomic absorption spectroscopy (ETAAS), hydride generation atomic absorption spectroscopy (HGAAS) and hydride generation atomic fluorescence spectrometry (HGAFS) as well as a number of hyphenated techniques, such as ion chromatography (IC) coupled with hydride generation inductively coupled plasma atomic emission spectrometry (HG-ICPAES), IC or high performance liquid chromatography (HPLC) coupled to inductively coupled plasma mass spectrometry (ICPMS) and electrospray mass spectrometry (ES-MS) have been reported for As speciation and determination of metal complexes with bioligands and the molecular structure of separating compounds. Hydride generation (HG), liquid chromatography (LC), gas chromatography (GC) and capillary electrophoresis (CE) are commonly being utilized for the separation of As species. However, the advantage of HG method is that it can easily be connected to various detection systems like AAS, ETAAS, ICPAES, AFS, and ICP-MS. The inherent advantages and disadvantages of each method can be used to select and develop the most appropriate and stabilizing method based on the type of sample matrix to be analyzed and the As species and concentration levels to be determined [10].

In case of As speciation analysis, most of the difficulties are connected with keeping the stability of As species during preparation of sample and proper analysis. Some studies recommend freezing aqueous samples at −20 °C [11]. Some authors used ascorbic acid and HCl addition for preservation [12]. Hydrochloric acid works well as preservative for As redox species for a wide range of natural water samples, and is preferred when HG-AAS is used for determination because the sample matrix is similar to the HCI carrier solution.

1.3. Separation/preconcentration

The lack of selectivity and insufficient sensitivity of some spectrometric detection techniques for As speciation made it necessary to develop analytical methods by combination of chromatographic separation and preconcentration techniques with the sensitive spectrometric detection [6,13]. The most effective method for the speciation of As(III) and As(V) is to combine simple and selective separation/preconcentration methods with sensitive detection techniques. Due to the different chemical and physical properties of As compounds, a reliable separation of the various species within one single run has been difficult. For this reason, a combination of various separation and detection procedures is commonly being employed. These techniques either separately or in combination are subject to significant errors due to interference arising from the presence of other chemicals, especially when the analyte is present at trace levels [14]. Various separation/preconcentration methods including liquid–liquid extraction (LLE), cloud point

extraction (CPE) [13], solid phase extraction (SPE) [15], hollow fiber liquid phase microextraction (HFLPME) [16] and liquid phase microextraction (LPME) [17] have been widely applied to the speciation of As(III) and As(V).

Hyphenated techniques that have highly efficient separation, sensitive and selective detection limits were developed and coupled with AAS because of the low concentrations (about 1–2 $\mu g\,L^{-1}$) [2,18] and complexity of matrices of samples like sea water [19,20] and microwave assisted digest. High performance liquid chromatography is a versatile technique, which due to the variety of separation mechanisms, can be applied to a great variety of environmentally important analytes [5,21]. The main problems of these hyphenated techniques are associated with chromatographic separation of species, and the different efficiency of hydride generation for various As species. Coupling a selective separation technique with sensitive and element-specific detector is necessary to perform speciation studies. Many different combinations (separation + element selective detection) have been attempted. The use of HPLC-HG-AAS enabled the elimination of interference and the highly sensitive determination of As(V), As(III), MMAA and DMAA at ng L^{-1} level [22,23].

1.4. Hydride generation AAS

Hydride generation is a well-known technique for the determination of As at trace levels, which consists of the reaction of As compounds with sodium tetrahydroborate in acidic medium to produce various arsines (AsH_3) [24]. As for example, As(III) and As(V) give AsH_3, MMAA gives monomethylarsine (MMA-CH_3AsH_2) and DMAA produces dimethylarsine (DMA-$(CH_3)_2AsH$). Their boiling points are different (−55, 2, 35.6 °C) what make possible to separate them [25,26]. Generated arsine gas is then transported by means of neutral inert carrier (argon, helium) to atomizer (AAS, AFS) or excitation source (ICP, MIP). The reaction forming hydride AsH_n at the oxidation state $+m$ may be described as follows [27]:

$$NaBH_4 + 3H_2O + HCl \rightarrow H_3BO_3 + NaCl + 8H$$

$$As^{+m} + 8H \rightarrow AsH_n + H_2\,(\text{excess})$$

The HG method can be easily connected to various detection systems (AAS, ETAAS, ICP-AES, AFS, and ICP-MS) for As speciation analyses of water samples. This improves the detection limits up to 100-fold over the commonly used liquid sample nebulization process [28]. It can eliminate spectral and chemical interferences encountered in the detection system as only gaseous hydrides are introduced into the detector. However, some drawbacks have been reported [29] for this method, including that: (i) the method is limited to the materials that form volatile gases and single element detection; (ii) reaction conditions have to be strictly controlled; (iii) the presence of certain interfering elements can reduce the efficiency of HG; and (iv) the method is laborious.

1.5. ETAAS/GFAAS

The ETAAS is an efficient technique for the determination of As(III) and As(V) in natural waters, particularly because, the organic matrix, consisting of the surfactant and residual organic substances from the digested material, can be eliminated at least in part during the gradual increase in temperature prior to the atomization of the analyte [13]. To reduce matrix interferences and to increase accuracy, the use of a chemical modifier has become indispensable for the stabilization of volatile elements during the pretreatment step. The main purpose of using a modifier or a modifier mixture in ETAAS is to stabilize relatively volatile elements so that higher permissible pyrolysis temperatures can be used to efficiently volatilize the matrix components in a sample prior to atomization of the analyte [30–32], and less interference effects on the analyte are encountered [30].

Although there have been developed a lot of analytical techniques for the separation and speciation of As in water samples, AAS hyphenated with HG and ETAAS are still in wide applications worldwide, because these instruments are fast, easily affordable and less expensive. For the last few decades, many articles including a few reviews on the separation and speciation of As in water samples have been published [3–6,21,33,34]. Most of these reviews described the speciation of As using many different instruments. A review on speciation of As using only HGAAS and ETAAS is not available. The different analytical techniques have been developed that have some advantages and disadvantages. Therefore, in the present review, we focused on As separation and speciation using the HG-AAS and ETAAS/GFAAS, advantages and disadvantages of these techniques, interferences accompanying As detection and their improvements and modifications. At last, we suggested a few selected appropriate methods that are accurate, fast and inexpensive for measurement of As species.

2. Hydride generation atomic absorption spectrometry

The AAS combined with HG is widely used for As speciation (Table 1), due to its high sensitivity, selectivity and low DL (decimal parts of $\mu g\,L^{-1}$), provided that, with appropriate different separation techniques (DL for As(III) and As(V) <1 $\mu g\,L^{-1}$) [26,35–40]. The HG-AAS is a more affordable and much less expensive technique than ICP-MS to detect trace concentrations of As speciation in environmental samples [38]. However, HG technique strongly depends on type and concentration of the sample matrix. Nevertheless, HG-AAS and LC-ICP-MS showed excellent and similar sensitivity in As speciation of groundwaters [14]. Absolute detection limits in this method (in element mass unit), using IP-RP, in groundwater samples, equal 0.07 for As(III), 0.10 for As(V), 0.10 for MMAA, 0.11 for DMAA, ngAs [21,41]. Akter et al. [14] determined As speciation with DL from 0.10 (AsIII, AsT) to 0.19 (DMA) $\mu g\,L^{-1}$, while Maity et al. [42] reached DL minimum up to 0.4 $\mu g\,L^{-1}$ for As(III) in groundwater samples using HG-AAS method. Shraim et al. [37] found DLs ($\mu g\,L^{-1}$) to be 1.1 for total As, 0.5 for DMA, 0.6 for As(III) and 1.8 for MMA, respectively. Therefore, given these low DLs and high sensitivity, HG is most widely used for As speciation. Pohl [27] lowered the DL of hydride-forming element to 0.1 $\mu g\,L^{-1}$, and they obtained the precision of measurements (relative standard deviation) better than 5% by adding the organized surfactant-based compounds such as micelles and vesicles to the sample solutions that changed the physical and chemical properties of the HG reaction. It was found that positively charged surfactants (i.e., didodecylmethylammonium bromide—DDAB) enhanced the generation of As hydrides by concentrating the reactants at the molecular level. This improved the transport and separation efficiency of the species, resulting in better sensitivity and selectivity of the reaction [27].

Macedo et al. [43] determined total As and As(III) in phosphate fertilizers by slurry preparation with HCl in an ultrasonic bath using a full two level factorial and a Box–Behnken design, and they found limits of detection and quantification to be 0.1 and 0.3 $\mu g\,L^{-1}$, respectively. The AsIII) and As(V) can be measured in wines by ethanol evaporation and total As by microwave digestion with DL of 0.1 $\mu g\,L^{-1}$ [44]. Some organoarsenicals such as AsB, AsC, Me_4As+ or arsenosugars are not hydride reactive that need to be converted to hydride reactive forms using microwave or UV irradiation [22,45]. Using this process Hasegawa et al. [46] determined the inorganic, methylated and ultraviolet-labile fractions of As species by combining cold trap-HGAAS with ultraviolet irradiation. Selection of the appropriate mineralization is important because HNO_3, strong

Table 1
Optimum operational conditions in the determination of As species by HG-AAS.

Atomizer/temperature	Background	Lamp, current (mA)	Absorbance	Slit	Detector	Species	Matrix	DL (unit)	Ref.
QTA, air-acetylene/1000 °C	Deuterium	HCL(12)	193.7	1.0	HGAAS	As(V), As(III), DMA	Groundwater	0.10; 0.19 ($\mu g L^{-1}$)	[14]
QTA, air-acetylene/950 °C	Deuterium	EDL(8)	193.7	0.7	HGAAS	As(III), As(V)	Water	0.1; 0.06 ($\mu g L^{-1}$)	[54]
Quarts cell, air-acetylene flame	Deuterium	HCL(5)	193.7	0.5	FI-HG-AAS	As(V), As(III), MMA, DMA	Water	20–60 ($ng L^{-1}$)	[65]
QTA, air-acetylene flame	Deuterium	EDL (380)	193.7	0.7	FI-HG-AAS	As(V), As(III), MMA, DMA	Water	Na	[26]
QTA, air-acetylene flame	Deuterium	HCL(10)	193.7	1.0	FI-HG-AAS	As(III), As(V)	Water	0.3; 0.5 ($\mu g L^{-1}$)	[52]
QTA, air-acetylene flame	Deuterium	HCL(10)	193.7	2.6	UV-CT–HGAAS	As(V), As(III), MMA, DMA	Lake water	13-17 ($ng L^{-1}$)	[124]
QTA, air-acetylene/900 °C	Deuterium	HCL(18)	193.7	0.7	FIAS-HGAAS	As(III), As(V)	Sea water	0.05; 2 ($\mu g L^{-1}$)	[125]
QTA, air-acetylene/900 °C	Deuterium	HCL (10)	193.7	0.5	HGAAS	As(V), As(III)	Phosphate rock	0.1 ($\mu g L^{-1}$)	[43]
QTA, air-acetylene flame	Deuterium	HCL(8)	193.7	1.0	HGAAS	As(III), As(V)	Groundwater	0.4 ($\mu g L^{-1}$)	[42]
QTA, air-acetylene flame	Deuterium	HCL(7)	193.7	0.6	FIHGAAS	As(V), As(III)	Water	0.03–-0.3 ($\mu g L^{-1}$)	[66]
QTA, air-acetylene/950 °C	Na	Na	193.7		CTFIEc-HGAAS	As(III), As(V)	Water	Na	[67]
QTA, air-acetylene flame	Deuterium	HCL(7)	193.7	0.5	HG-AAS	As(V), As(III), MMA, DMA	Acid media	1.1, 0.5, 0.6, 1.8 ($\mu g L^{-1}$)	[37]
QTA, air-acetylene flame	Deuterium	HCL(9)	193.7	0.7	FIHGAAS	As(V), As(III)	Groundwater	1.4 ($\mu g L^{-1}$)	[61]
QTA, air-acetylene flame	Deuterium	HCL(11)	193.7	0.7	FIHGAAS	As(III), total As	Groundwater	0.5, 0.6 ($\mu g L^{-1}$)	[62]
QTA, air acetylene/920 °C	Deuterium	HCL	193.7	0.5	HGAAS	As(III), As(V)	Wine	0.1 ($\mu g L^{-1}$)	[44]
QTA, air acetylene/920 °C	Deuterium	HCL(18)	193.7	0.7	HGAAS	As(III), As(V)	Water	12 ($ng L^{-1}$)	[63]
QTA, air acetylene/920 °C	Deuterium	HCL(18)	193.7	0.7	HGAAS	As(III), As(V)	Water, food	11 ($ng L^{-1}$)	[64]
QTA, air acetylene flame	Deuterium	HCL	193.7	Na	HGAAS	As(III)	Water	Na	[60]
QTA, air acetylene flame	Deuterium	HCL	193.7	0.5	HGAAS	As(III), As(V), DMA, MMA	Water	0.1 ($\mu g L^{-1}$)	[143]

Quartz tube atomizer: QTA; Hollow cathode lamp: HCL; Electrodeless discharge lamp: EDL; Detection limit: DL; Not available: Na; Reference: Ref.

oxidizing factor, may cause As(III) decomposition due to nitrogen oxides formation. Interferences with reduction to As(III) are also possible [10]. Li et al. [47] determined inorganic As species by electrochemical HGAAS, without pre-reduction of As(V) using glassy carbon as cathode material in the flow cell. The As(III) and As(V) can be determined by controlling the electrolytic currents to 0.6 and 1 A, respectively. The detection limits of the method were 0.2 and 0.5 $\mu g L^{-1}$ for As(III) and As(V) at 0.6 A, respectively.

A quantitative determination of methylated As-species (MMAA, DMAA) and arsenate (As(V)) with HG techniques is only possible using standard addition procedures for calibration and not with external calibration. These problems do not occur when a detection system (e.g. ICP-MS) is used. Here a pneumatic nebulizer is used, so that different hydride generation rates cannot influence the quantitative determination of As-species. Another possible source of error in As speciation analysis is changes in the chemical equilibrium after sampling. Attention should be given on the storage of As samples especially at trace levels. Often a variation of the As(III)/As(V) ratio is observed even if samples are stored under cool conditions. Possible reasons are contact to air, changes of sample pH or other changes in redox parameter. However, these problems may occur with any type of detection techniques like HGAAS/ETAAS/HG-AFS/ICP-MS. A simple method of sample stabilization is the separation of different As species immediately after sampling.

2.1. Relation of arsine formation with concentration of acid and reducing agent

In HG method, the formation of arsines is pH dependent. The pH requirements of the reduction reaction indicate that the As species must be fully protonated before they can be reduced to the corresponding arsine [29]. In strong acid environment (pH < 1), hydrides are generated from both inorganic and organic As including MMAA, and DMAA compounds. However, they are not generated from other arseno-organic compounds. In weak organic acid environment (citric, acetic, tartaric etc.), hydrides can form only from the trivalent As species, but not from the pentavalent As species [10,48]. The sensitivity of As(III) remains constant in the sample pH range of 2.3–10.6. However, there are still considerable differences between the sensitivities obtained from inorganic and organic As species for the HG. The type and concentration of the acid used have a critical effect on the HG response of arsenite, arsenate, MMAA and DMAA [26,49]. Therefore, it is very difficult (if not impossible) to find a compromise acid concentration under which the same response can be obtained for all As species. The consistence of the sample solution especially the acid concentration (but also the presence of metals, sulfides etc.) has a dominant influence on the yield of As-hydrides (AsH_3) generated from different arsenic compounds. Great differences between MMAA and DMAA in acid water samples are observed.

In HG, the signal response obtained from As(V) is about 40% lower than that obtained from As(III). Thus, an on-line pre-reduction of As(V) to As(III) or off-line steps before the formation of the arsine, is necessary[50–52]. Usually, two procedures are demanded for the discrimination of the As(III) content from the total As, one; a selective procedure for As(III) and another one, including a pre-reduction step for As(V) and total As (by means of reduction reagents like HCl, ascorbic acid, potassium iodide (KI), L-cysteine, thiourea or their mixture) and next hydride generation from As(III) [10,35,53,54]. Although, KI has been widely used in pre-reduction step, it creates various problems [55]. As for example, KI demands relatively strong acidic conditions for both the sample and the reduction medium; and high concentrations applied can lead to generation of considerable levels of iodine, which is especially disadvantageous if the quantification of the

analyte is effected via HG and AAS. By contrast, use of L-cysteine as pre-reductant is advantageous to obtain the same response for all the four As species under the same and optimum acid concentration, and it allows the reduction to occur under mild acidic conditions [26,52,56]. In addition, the presence of L-cysteine in the reaction medium results in the reduction of interference from transition metals on the arsine generation [26]. The absorbance signals for As speciation such as As(III), As(V), MMA, and DMA in environmental samples were found to be greatly enhanced in low acid concentration in both the absence (0.03–0.60 M HCl) and the presence of L-cysteine (0.001–0.03 M HCl). However, when L-cysteine was present, higher signals were obtained [37,57].

However, complete volatilization of arsenate in the absence of pre-reducing step could be achieved by using higher HCl and $NaBH_4$ concentrations [54]. The effect of the arsenic oxidation state on the analytical signal can be decreased or eliminated by applying (i) longer reaction time [58], (ii) higher $NaBH_4$ concentrations [59] and/or (iii) integrated absorbance measurements. Carrero et al. [26] suggested two mechanisms for the arsine generation: (i) at low acid concentration, the thiolate complexes of As(III) are rapidly converted into the respective arsines by BH^{4-} and (ii) at high acid concentration, the arsines are generated by the action of nascent hydrogen produced by the decomposition of BH^{4-}.

2.2. Hydride generation and matrix interference

Hydride generation technique makes possible almost 100% efficiency of introducing the determined analyte to atomizer or spectroscopic excitation source, because only gaseous hydrides are introduced to the detector. Thus, spectral and chemical interferences in the detection system are eliminated. In this technique, large sample volume and appropriate separation technique of analyte from matrix are applied that improve the detection limit. However, there are possibly some problems in the transportation of generated hydrides to excitation source or matrix influence on the reaction of hydride generation [10]. Chemical interferences from the matrix of transition and noble metals, and other metals such as Ag, Au, Co, Cu, Ni, Fe and Pb have the most serious interferences in HG reactions that result in the drastic suppression of analytical signals of hydride-forming elements. L-cysteine, L-histydine, *o*-phenanthroline, EDTA with tartaric acid, a mixture of tartaric acid and ascorbic acid, KI and KCN were the complexing agents used to mask the interfering metals ions [26,27]. The precipitation of hydroxides of the interfering metals or the extraction of their complexes was another method of avoiding chemical interferences coming from transition-metal ions.

Pohl [27] pointed out that the increase in acid concentration or to decrease the $NaBH_4$ successfully diminished the interferences caused by transition metals. In addition, use of positively charged surfactants (e.g., DDAB) enhanced the generation of As hydrides by increasing tolerance of transition-metals ions [27]. The separation method utilizing synthetic zeolite (mordenite) can eliminate the gas phase interference of Sb(III) on As(III), and also reduce the suppression effects of transition-metal ions on As(III) signal [60]. Sigrist and Beldomenico [61] found 6% interferences of As(V) in the case of water samples with 6 $\mu g\,L^{-1}$ As(III) in the presence of 54 $\mu g\,L^{-1}$ As(V). However, another study reported that concomitant mineral matrix of the contaminated groundwater samples did not interfere with As determination by HGAAS [42].

2.3. Flow injection preconcentration and selective As speciation

Anthemidis et al. [54] developed an on-line sequential insertion system coupled with HG-AAS for selective As(III) and total inorganic As determination without pre-reduction step using an integrated reaction chamber/gas–liquid separator. Arsine is able to be selectively generated either from inorganic As(III) or from total As, using different concentrations of HCl and $NaBH_4$ solutions. Sigrist and Beldomenico [61] reported DL of 1.4 $\mu g\,L^{-1}$ for As(III) in presence of As(V) by FI-HGAAS using sufficiently low concentration of $NaBH_4$ (0.035%, w/v) as reductant in highly acidic condition (pH < 0). Sigrist et al. [62] determined As(III) in groundwater with Cl^-, SO_4^{2-}, NO_3^-, HPO_4^{2-}, and HCO_3 without any kind of sample pretreatment, but selective retention of As(V) in a cartridge containing a chloride form strong anion exchanger, using an online sequential injection system coupled to a FI-HGAAS. Detection limits were 0.5 $\mu g\,L^{-1}$ and 0.6 $\mu g\,L^{-1}$ for As(III) and inorganic total As, respectively. The As(III) and As(V) species in water samples can be determined by selective adsorption of As(V) on aluminum hydroxide precipitate [63] after oxidation of As(III) using dilute $KMnO_4$ [63], while As(III) ion can be selectively adsorbed on Alternaria solani coated Diaion HP-2MG resin [64] after pre-reduction of As(V) using KI and L(+) ascorbic acid [64]. Tuzen et al. [64] found DL of 11 $ng\,L^{-1}$ for As(III).

The preconcentration and selective determination of As(III) and As(V) and its methylated species can be determined by FI-HGAAS using the different separation techniques as follows: automated pH-selective arsines generation using $NaBH_4$ as reductant [65,66]; selective generation of arsine from As(III) using 0.1% $NaBH_4$ concentration and from total As concentration with 3.0% $NaBH_4$ [52]; electrochemical HG cryogenic trapping AAS using flow-through cell with fibrous carbon as cathodic material [67]. Cabon and Cabon [23] determined As species in seawater by FI-HG-ETAAS with a preconcentration factor of about 1000 lowering the detection limit of As to about 1.5 $ng\,L^{-1}$. Total As was determined by using high $NaBH_4$ and HCl concentrations after a thermal or a UV irradiation treatment, and As(III) by performing hydride generation at a pH of about 7–8. Based on the different boiling points, the arsine species were selectively liberated by using a heating cycle of microwave radiation, followed by AA detection [65].

2.4. Coupling chromatographic techniques with HGAAS/ETAAS

For element-specific detection and speciation of As compounds, ion-pair chromatography can be coupled with HGAAS and other detectors [68]. The separation of different As forms in water samples using chromatographic techniques (Table 2) makes an important advancement in As speciation [4,21,69]. The most common separation techniques used in As speciation are gas and liquid chromatography (GC and LC). Due to some difficulties involved with GC, LC is preferred. Hyphenating HPLC with HGAAS and other detectors is frequently used in speciating As species in water samples [5,21,70]. Tseng et al. [71] used microdialysis sampling and HPLC-HGAAS for the continuous in vivo monitoring of As species in the blood of living rabbits. The most commonly used methods are ion-pair chromatography (IP-HPLC), reversed-phase chromatography (RP-HPLC), ion-pair reversed-phase chromatography (IP-RP-HPLC), and ion-exchange (IE) or ion-exclusion chromatography (IE-HPLC). However, vesicular chromatography has also been used. In determination of large biological particles, capillary electrophoresis is preferred [72].

2.4.1. Ion-pair chromatographic separation of As species

Ion-pair high performance liquid chromatography has been developed for routine analyses of neutral and ionic As species. The choices of IP-HPLC separation conditions and resolution of these As species depend on the selection and optimization of ion-pair reagent concentration, flow rate, buffer concentration, methanol concentration, ionic strength and pH of the mobile phase [73,74]. The optimum pH range for separating the As(III), As(V), MMAA and DMAA is between 5.0 and 7.0 In this range, As(III) ($pK_a = 9.2$) is a neutral species, which is eluted in the void volume. When the pH of

Table 2
Arsenic species separation by ion-pairing reversed-phase and ion-exchange chromatography coupled to HGAAS and GFAAS.

ST	Column	Mobile phase	Flow	Matrix	Species (Rt (min))	Detector	DL (ng As)	Ref.
IP-RP	C_{18} ChromSpher 5 μm 2 × (100 mm × 3 mm)	10 mM TBA + 20 mM NaH_2PO_4, pH 6	1	Urine	As(III) (1.0); DMA (1.5); MMA (2.0); As(V) (2.7)	HGAAS	0.05; 0.08; 0.06; 0.24	[128]
IP-RP	[PB]Dionex NS-1 (ns)	5 mM TBAP + 5% MeOH, pH 7.3	1	Groundwater	As(III) (2.1); DMA (3.2); MMA (4.0); As(V) (6.3)	HG-AAS	0.07; 0.15; 0.10; 0.10	[129]
IP-RP	[PB]Dionex NS-1 5 mm (250 mm × 4.6 mm)	0.15 mM TBAP pH 5.8	1	Water, NIST	As(III) (2.7); DMA (5.3); MMA (8.4); As(V) (18.5)	HG-AAS	0.07; 0.11; 0.12; 0.30	[130]
IP-RP	[PB]Hamilton PRP-1 10 mm (150 mm × 4.1 mm)	10 mM TBAOH/TBAP, pH 6.15	1	Tuna; fish	As(III) (2.4); DMA (4.2); MMA (6.0); As(V) (13.1)	HG-AAS	0.15; 0.43; 0.33; 0.84	[131]
IP-RP	C_{18} Phenomenex Bond-clone 10 μm (300 mm × 3.9 mm)	10 mM hexanesulfonate, pH 3.5	1	Standard	DMA (6.0); As(III) (4.9); MMA (8.7); As(V) (4.0); AsB (12.6)	MD-HG-AAS	0.2; 0.2; 0.3; 0.4	[56]
IP-RP	C_{18} Phenomenex ODS(3) 5 μm (250 mm × 4.6 mm), 70 °C	10 mM hexanesulfonate + 0.5% MeOH + 1 mM tetraethylammonium hydroxide, pH 4.0	1	Standard	As(V) (4.0); As(III) (5.1); MMA (6.8); DMA (9.0); AsB (11.8); AsC (24); TMAs (30)	MD-HG-AAS	Na	[68]
IP-RP	C_{18} Phenomenex ODS(3) 5 μm (30 mm × 4.6 mm), 30 °C	10 mM TBAH + 1 mM malonic acid + 5% MeOH, pH 6.0	1	Standard	As(III) (0.3); DMA (0.7); MMA (1.0); As(V) (1.5)	MD-HG-AAS	Na	[75]
IP-RP	Supelcosil LC CN 5 μm (150 mm × 4.6 mm)	0.01% Acetic acid (v/v)	0.6	Dogfish muscle	As(V) (2.0); MMA (3.0); DMA (4.0); As(III) (6.9)	THG-AAS	0.7; 1.0; 1.0; 0.8	[132]
IP-RP	Phenomenex Spherisorb ODS 15 μm (150 mm × 4.6 mm)	12 mM phosphate buffer, pH 10.7	2	Water, sediment	As(III) (2.8); AsB/AsC (3.7); DMA (6.5); MMA (7.2); As(V) (8.0)	MO-HG-AAS	9.7; 10.0; 12.2; 12.8; 14.3	[133]
IP-RP	C_{18} Altex Lichrosorb RP-1 10 μm (250 mm × 4.6 mm)	Gradient: 1 mM HTAB, pH 9.5, then H_2O/MeOH/ACN (6:4:1)	0.4/0.5	River water	As(III) (3.0); DMA (11); MMA (28); As(V) (45)	GFAAS (on line)	15; 15; 15; 15	[134]
IP-RP	C_{18} Machery-Nagel 5 μm (250 mm × 4.6 mm)	4.0 mM Na_2HPO_4 + 3.0–4.0 mM TBA, pH 5.5–6.5	Na	Mammal	As(III) (4); DMA (6); MMA (7); As(V) (9)	GFAAS (off-line)	0.025–0.2 (μg L^{-1})	[73]
IP-RP	[PB]Dionex NS-15 μm (250 mm × 4.6 mm)	5 mM TBAP + 5% MeOH, pH 7.3	1.0	Groundwater	As(III), DMAA, MMAA, As(V)	HG-AAS	0.07, 0.15, 0.10, 0.10	[41]
AEx	Spherisorb ODS/NH_2 mixed column 5 μm (250 mm × 4.6 mm), 25 °C	5 mM NaH_2PO_4/Na_2HPO_4, pH 5.0	1.5	Mineral water	AsC, As(III), AsB, DMAA, MMAA, As(V)	MO-HG-AAS	2.4, 1.4, 1.7, 1.9, 2.2, 2.1	[135]

Table 2 (*Continued*)

ST	Column	Mobile phase	Flow	Matrix	Species (Rt (min))	Detector	DL (ng As)	Ref.
AEx	BAX-10 polystyrene (200 mm × 5 mm)	10^{-4}% (v/v) H_2SO_4/0.1 M $(NH_4)_2CO_3$	4	Water	As(III), As(V), MAA, DMAA	HPLC-HGAAS	2; 2; 2; 1	[85]
AEx	Supelco LC-SAX1 5 μm (250 mm × 4.6 mm)	5 mM Na_2HPO_4, 50 mM KH_2PO_4, pH 5.4	3	Groundwater	As(III) (1.3); As(V) (2.2)	HPLC-HGAAS	7.8; 12 (μg L^{-1})	[84]
AEx	Hamilton PRP-X100 DBB + TMA (250 mm × 4.1 mm, 10 μm)	Gradient: 50 mM tetraborate/30 mM NaCl, pH 9	1.4	Urine	As(III) (2.4), As(V) (10.3), MMA (8.5), DMA (3.3), TMAO (1.9)	HPLC-HGAAS	1.1–2.6 (μg L^{-1})	[83]
AEx	Hamilton PRP-X100, polymer-based (250 mm × 4.1 mm)	17 mM phosphate (pH 6.0), ultrapure water (pH 6.0)	2	Fish	As(III), As(V), MMA, DMA, AsB, AsC	HPLC–MW–HGAAS	0.3–1.1	[82]
AEx, CEx, RP	C_{18} Altex LiChrosorb SAX 10 μm (250 mm × 3.2 mm)	aqueous acetate/ammonium acetate-acetic acid	1.0	Water, soil	As(III), MAA, DMAA, As(V)	GFAAS	5 (μg L^{-1})	[91]
AEx, CEx	Resin-based SCX (Alltech)/Silica-based SAX (Supelco)	0.5 M HCl/1.0 M HCl/0.1 M acetic acid	1–2	Urine	As(III), MAA, DMAA, As(V)	HPLC-HGAAS	1.0–2.0 (μg L^{-1})	[136]
AEx, CEx	AG 50W-X8 resin	Na	Na	Urine	As(III), MAA, DMAA, As(V)	HPLC-HGAAS	2.0 (μg L^{-1})	[137]
CEx					AsB, AsC, TMAs	HG-AAS		[138]
AEx	Hamilton PRP-X-100, Supelcosil SAX 1	Phosphate buffer containing KH_2PO_4–K_2HPO_4	1.0	Urine	As(III), MMA, DMA, AsB, AsC, TMAO	HPLC-HGAAS	2–6 (μg L^{-1})	[139]
CEx	Dionex Ionpac CS 10, 4 mm × 250 mm	100 mM HCl + 50 mM NaH_2PO_4 solution	1.0	Human serum	MMA, DMA, AsB, AsC	HG-AAS	1.0, 1.3, 1.5, 1.4 (μg L^{-1})	[140]
AEx	Ficklin columns (10 cm × 1 cm)	0.12 M HCl	Na	Water	As(III), As(V)	GFAAS	Na	[141]
CEx	Dionex Ionpac CS 10 (250 mm × 4 mm)	100 mM HCl + 50 mM NaH_2PO_4	0.5	Urine	DMA, AsB	HG-AAS		[142]
AEx	Supelco LC-SAX1 (250 mm × 4.6 mm)	50 mmol/L Na_2HPO_4 + KH_2PO_4, pH 5.8–6.2 at 80 °C	Na	Sediment	As(III) (1.3); As(V) (2.35)	HG-AAS	0.5–0.7 (μg L^{-1})	[145]

Ion-pairing reversed-phase: IPRP; Retention time: Rt; Detection limit: DL; Flow in mL min^{-1}: Flow; Not available: Na.

the mobile phase increases above 9.2, As(III) becomes a negatively charged species. Using a resin-based column and a mobile phase at pH 9.0, As(III) is retained and can be separated from AsB, which like the zwitter ion is not retained under these conditions [12]. The separation of As(III), As(V), MMAA and DMAA usually requires 8–10 min when conventional 30 cm column is used. Using a 15-cm column or two guard columns reduce the time of resolution to 4 min [75]. The elution order is constant: (1) As(III), (2) DMAA, (3) MMAA and (4) As(V)and independent of the various columns used.

2.4.2. Reversed-phase or vesicle-mediated separation of As species

Reverse-phase liquid chromatography is the most popular LC separation mode due to its high separation efficiency, good sample loading tolerance, and ability to separate a broad range of different polarity samples. In reversed-phase chromatography, most authors used C_{18} or PRP-1 columns and isocratic conditions to separate methylated as well as inorganic As species. An advantage of using RP is the simplicity of the technique [76]. The elution order of the various species is different, and may even vary drastically for the same authors with slight differences in eluent composition [56,68,75,77]. The lowest DLs are obtained through post column hydride generation (approximately 1 $\mu g L^{-1}$). Hyphenating optical ICP to HPLC, on the contrary, leads to DL in the range of 50–100 $\mu g L^{-1}$, i.e. far too high to allow direct application to tap water analysis. The recent vesicular chromatography has been essentially used for analysis of synthetic samples or standards. It has often been coupled to atomic fluorescence detector, but the detection limits obtained are not better than those obtained for reversed-phase chromatography. However, interfacing hydride generation improves, once more, the DL by a factor of 6–14 [78,79].

2.4.3. Ion-pair reversed-phase chromatography

Selection of applied techniques depends on the size, shape and charge of separate species. However, due to the difference in structure and charge of the As compounds, sometimes combination of two or more separation methods must be used (for example, IP-RP-HPLC). Ion pairing in reverse mode and ion exchange are the favorite chromatographic processes used by most authors. Ion-pair reverse phase chromatography has been developed to routinely separate both non-ionic and ionic compounds in a signal run using the same column [74]. Le and Ma [68] determined As(III), As(V), MMA, DMAA, AsB, AsC, and TMAA by coupling IP-RP-HPLC (reversed-phase C_{18} column) with HG-AAS using mixed ion-pair reagents containing 10 mM hexanesulfonate and 1 mM tetraethylammonium hydroxide, as mobile phase. An off-line IP-RP coupled with GFAAS can determine different As species (As(III), As(V), MMA, DMA) [73]. The advantage of RP-IP is its versatility that permits the analysis of organic As compounds (metaloproteins and arsenosugars), charged and uncharged compounds in a single chromatographic run with great reproducibility, high resolution selectivity and short time [10]. The change in resolution can be achieved by varying the ion-pairing reagents and maintaining the MeOH:water ratio. However, some authors [21] point out that reversed-phase chromatography is prone to severe matrix interferences and pH effects. They suggest that the ion exchange mode, although producing a poorer selectivity, is much less sensitive to these unfavorable effects because of the higher buffering capacity of the mobile phase.

2.4.4. Ion exchange separation of As species

Since the As species are anionic, cationic and/or neutral depending on pH, complete separation of all eight As species (As(III), As(V), MMAA, DMAA, AsB, AsC, TETRA and TMAO) on a single column is difficult to achieve [80]. The IP-RP-HPLC has been applied with some success for the separation of up to seven As species [77,81]. However, a combination of anion- and cation-exchange materials seems the most promising for complete resolution of all eight As compounds. For cationic As compounds, a polymer-based cation-exchange column using an ion-pairing reagent (3-carboxy-4-hydroxybenzenesulfonic acid) in the mobile phase and for anionic As, an anion-exchange separation can be used [80]. In ion-exchange chromatography, anion-exchange chromatography is most commonly used to analyze As(III), As(V), MMAA and DMAA, whereas cation exchange is used to separate AsB, AsC, TMAO and TMAs+ species [12,82–84].

Many publications appeared especially during the last few years dealing with ion exchange separation of As species coupled to various specific detectors. Many different columns have been tested. Among them, Hamilton PRP-X100 is most commonly used with phosphate eluents in isocratic or gradient modes, gradients being often associated with post column hydride generation [82]. In addition to coupling this column with microwave digestion—HGAAS, Villa-Lojo et al. [82] used 17 mM phosphate buffer (pH 6.0) as mobile phase for As(III), As(V), MMA and DMA separation, and ultrapure water (pH 6.0) for AsB and AsC separation. The use of anion-exchange Supelco LC-SAX1 column and phosphate buffer at pH 5.40 as a mobile phase as well as the use of the HPLC–HGAAS allowed determination of As(III) and As(V) in fast sequential mode [84] with DLs of 7.8 $\mu g L^{-1}$ for As(III) and 12.0 $\mu g L^{-1}$ for As(V). Sur and Dunemann [83] determined As(III)), As(V), MMA, DMA and TMAO in human urine using HPLC/HG-AAS by anion-exchange chromatographic separation. Detection limits ranged from 1.1 (TMAO) to 2.6 $\mu g L^{-1}$ (As(V)).

HPLC-HGAAS can speciate As(III), As(V), MAA and DMAA with DLs of 2 ng (as As) for As(III), As(V)and MMA, and 1 ng for DMA using a silica-based Zipax anion-exchange column and polystyrene-based BAX-10 strong anion-exchange column [85] for the removal of matrix interferences. At pH lower than 10, the order of elution is usually As(III), DMA, MMA, As(V) and at higher pH, DMA appears first [56,86] or after MMA [87–90]. These apparently surprising differences of behaviour may probably be explained by rather strong hydrophobic interactions of organoarsenical species with some stationary phases.

GFAAS detector in conjunction with strong anion-exchange column (using aqueous acetate buffer as mobile phase) and cation-exchange column (using ammonium acetate as mobile phase) can determine As(III), MAA and DMAA, and As(III), DMAA and As(V), respectively, at $\mu g L^{-1}$ level[91]. All four As compounds can be separated on a C_{18} reversed-phase column with methanol–water mixtures saturated with tetraheptyl ammonium nitrate. The limitation is the possible degradation of silica-based (SB) columns; and after a few tens of analysis, the separation performance, efficiency and reproducibility may be seriously affected [76,92]. The lower pH range is used with SB columns than with polymer-based stationary phases, and cannot exceed pH 8.5 [93]. However, Chana and Smith [88] and Rauret et al. [89] noted similar – although slower – degradation phenomena. On the other hand, Heitkemper et al. [94] indicated a fast degradation of performances of their polymer-based column after only 50 urine analysis; and Zhang et al. [90] preferred a silica-based column giving a higher resolution and found it stable. Too fast degradation may be overcome by lowering the mobile phase concentration, with the following side effects: longer analysis and some loss of resolution for the most retained species.

2.4.5. Capillary electrophoresis separation of As species

The popularity of capillary electrophoresis has to a large extent been sustained by the success of the technique in speciation analysis [95]. Capillary electrophoresis, a technique ensuring high separation efficiency [96], has been tested for As(III), As(V), DMAA, MMAA, AsB and AsC speciation [97,98]. Buffer constituent,

concentration and pH affect the separation of As species, and this technique has been limited to simple matrix systems.

3. Electrothermal atomic absorption spectrometry

Recently many studies are published that have used ETAAS to determine the speciation of As(III), As(V), MMA, DMA and AsB (Table 3) in fish-based foods [99–101], water [7,16,17,102–105], human hair and nail [16,106], and environmental samples [107–109]. Zhang et al. [106] determined the multi-element inorganic speciation of As(III,V), Se(IV,VI) and Sb(III,V) in river water and seawater with GF-AAS using solid phase extraction of As(III), Se(IV) and Sb(III) by titanium dioxide (TiO_2) and lead-pyrrolidine dithiocarbamate (Pb-PDC), and dissolving in dilute nitric acid. For the determination of As(III), Se(IV) and Sb(III), palladium (Pd) was chosen as a modifier. Rivas et al. [104] determined As(III,V) and Sb(III,V) in water samples by dispersive liquid–liquid micro extraction separation using ammonium pyrrolidine dithiocarbamate (APDC), carbon tetrachloride, and methanol at pH 1, and then centrifugation and determination in the organic phase by ETAAS.

3.1. Chemical modifier

To reduce matrix interferences and to increase accuracy, the use of a chemical modifier has become indispensable for the stabilization of volatile elements during the pretreatment step (Table 4). The main purpose of using a modifier or a modifier mixture in ETAAS is to stabilize the relatively volatile elements so that higher permissible pyrolysis temperatures can be used to efficiently volatilize the matrix components in a sample prior to atomization of the analyte [30–32,110,111]. By using higher permissible pyrolysis temperature, less interference effects on the analyte are encountered in the atomization step [30]. The nitrate forms of nickel (Ni), copper (Cu), Pd, magnesium (Mg) etc. are appropriate modifiers, whereas the chloride forms of the same metals cause interferences. Nickel nitrate provides a pyrolysis temperature of 1300 °C for As. The most widely used universal modifier such as Mg–Pd nitrate [112] increased the maximum pyrolysis temperatures for As up to 1400 °C in the presence of NaCl and K_2SO_4. The chemical modifiers like thorium (Th), vanadium (V) and zirconium (Zr) caused the stabilization of As signal in the presence of nitric acid mainly for the aerosol introduction mode. However, the highest sensitivity and the best stabilization of As were obtained using Zr and Th as a chemical modifier, because pyrolysis temperatures as high as 1500 °C could be used. The mechanistic action of the chemical modifiers resulted in the formation of a mixture of oxides stabilized at high temperatures [113]. Reboucas et al. [114] found the worse performance of Pd + Mg, Pd, rhodium (Rh), tungsten (W) and silver (Ag) modifier for direct determination of As in complex organic matrices by ETAAS. But they found no severe tube corrosion from lanthanum (La) application and suggested the La as the best chemical modifier with minimum DL.

Although $Pd(NO_3)_2$ is highly recommended and widely used modifier for As determination using ETAAS [16,17,104], Volynsky et al. [115] reported that colloidal Pd is a more effective modifier than $Pd(NO_3)_2$ because Pd^{2+} in $Pd(NO_3)_2$ may react with some matrix constituents (e.g., Cl) which cause further interferences. However, it is not possible for colloidal Pd, since it is in elemental form (zero valent state); and it may form solid solutions or intermetallic compounds with analyte elements. Gunduz et al. [116] used silver nanoparticles and Gunduz et al. [117] used gold nanoparticles as a new chemical modifier for the elimination of interferences (almost interference-free) in determining As in aqueous NaCl or Na_2SO_4 solutions and in sea-water by ETAAS. In the presence of these modifiers the pyrolysis temperature of at least

Table 3
Optimum operational conditions in the determination of As species by GFAAS, ETAAS, HG-GFAAS/ETAAS.

Atomizer	Background	Lamp, current (mA)	Pyrolysis, atomization, cleaning	Absorbance/slit	Detector	Species	Matrix	DL (unit)	Ref.
THGA	Na	EDL (400)	1200, 2100, 2500	193.7/2	FI-HG/GFAAS	As(III), As(V), MMA, DMA	Seawater	1.5 ($ng L^{-1}$)	[23]
THGA	Deuterium	HCL (8)	1000, 2200, 2600	193.7/1.0	ETAAS	As(III), As(V)	Water	9.2 ($ng L^{-1}$)	[17]
GTA	Off	HCL (15)	700, 2000, 2200	193.7/2.6	ETAAS	As(III), As(V)	Water, hair	0.12 ($\mu g L^{-1}$)	[16]
THGA	Zeeman	Na	1400, 2300, 2350	Na	ETAAS	As(III), As(V), MMA, DMA	Plant oils	4.4–4.7 ($\mu g kg^{-1}$)	[126]
PCGT	Off	HCL	Variable, 2800		GFAAS	As(V), As(III), DMAA, PAS	Water	0.04–0.13 ($\mu g L^{-1}$)	[7]
GTA	Deuterium	HCL(6)	800, 2000, 2200	193.8/0.4	GFAAS	As(III), As(V)	Water	24 ($ng L^{-1}$)	[103]
THGA	Deuterium/Zeeman	EDL(300)	800, 2400, 2600	193.7/0.5	ETAAS	As(III,V), MMA, DMA, AsB	Fish	15–50 ($\mu g kg^{-1}$)	[101]
End-capped THGA	Zeeman	EDL(380)	500, 2100, 2150	193.7/0.7	FIHG-ETAAS	As(III,V), MMA, DMA	Urine	0.4–1	[127]
THGA	Zeeman	EDL (380)	200, 1200, 2400	193.7/0.7	ETAAS	As(III,V)	Water	0.01 ($\mu g L^{-1}$)	[104]
THGA	Zeeman	EDL (380)	1400, 2000, 2300	193.7/0.7	HG-ETAAS	As(III,V), MMA, DMA	Fish	3.5–5.1 ($\mu g kg^{-1}$)	[99]
PCGT-IP	Deuterium	HCL (7.5)	300/600, 2000/2100, 2100/2400	193.7/0.7	ETAAS	As(III,V)	Fish	4–5 ($\mu g kg^{-1}$)	[100]
PCGT	Deuterium	HCL(12)	1400, 2400, 2600	193.7/2.0	ETAAS	As(III,V)	Water	0.01 ($\mu g L^{-1}$)	[13]
GT-IP	Zeeman	EDL	1200, 2000, 2400	Na	GFAAS	As(III,V), MMA, DMA	Water	Na	[105]
Cup-type GT	Zeeman	EDL (5)	1200, 2800, 2900	193.7/1.3	ETAAS	As(III,V)	Sea water	0.02 ($\mu g L^{-1}$)	[102]
THGA	Zeeman	EDL(380)	800, 2300, 2450	193.7	GFAAS	As(III,V)	Water	Na	[106]
GTA	Deuterium		1200, 2400, 2600	193.7/0.7	GFAAS	As(III,V)	Water	0.05 ($\mu g L^{-1}$)	[144]

Transversely heated graphite tube: THGA; Pyrolytic graphite coated graphite tube: PCGT; Integrated platform: IP; Electrodeless discharge lamp: EDL; Hollow Cathode Lamp: HCL; Not available: Na.

Table 4
Chemical modifiers and separation methods for As speciation in environmental samples.

Modifier	Separation methods of As species	Detector	As species	Matrix	DL (unit)	Ref.
H_2IrCl_6	Total As after a thermal or UV irradiation, total hydride-reactive species (As(III), As(V), MMA, DMA) for high $NaBH_4$ and HCl concentration, and As(III) at pH 7–8	FI-HG-GFAAS	As(III,V), MMA, DMA	Seawater	1.5 ($ng\,L^{-1}$)	[23]
$Pd(NO_3)_2$	As(III) was separated by As(III)-PDC complex; Total As after reduction of As(V)	ETAAS	As(III,V)	Water	9.2 ($ng\,L^{-1}$)	[17]
Pd permanent modifier	As(III) by APDC; As(V) by reducing to As(III) by L-cysteine	ETAAS	As(III,V)	Water, hair	0.12 ($\mu g\,L^{-1}$)	[16]
L-cysteine, Pd, citric acid/Zr–Ir	Oil samples are diluted with ethanol or *i*-propanol for lavender and rose oil, respectively	ETAAS	As(III,V), MMA, DMA	Essential oils	4.4–4.7 ($\mu g\,kg^{-1}$)	[126]
Ni, Pd, Pd–Mg	Phenylarsonic acid was separated by adsorption onto CeC; As(V) onto LaC; As(III) by APDC co-precipitation; DMAA onto ZrC	GFAAS	As(III,V), DMAA, PAS	Aqueous solution	0.04–0.13 ($\mu g\,L^{-1}$)	[7]
Pd salt, Ce(IV), Zr	For Pd salt modifier, the signal corresponds to total As; for Ce(IV), the signal to As(III + V) + MA; for Zr, the signal to DMA, and AB is obtained by difference with total As	ETAAS	As(III,V), MMA, DMA, AsB	Fish baby foods	50, 25, 15 ($\mu g\,kg^{-1}$)	[101]
Pd, Ni, Ir, W, Mo	At pH 1, As(III) are separated by APDC complex; Total As after reduction of As(V) with sodium thiosulfate	ETAAS	As (III,V)	Water	0.01 ($\mu g\,L^{-1}$)	[104]
Pd	Microwave assisted extraction in TMAH (0.075% *m*/*v*) or in water–methanol mixture (80 + 20 v/v) for leaching of As species	FIHG-ETAAS/AAS	As(III,V), MMA, DMA	Fish tissue	3.1–450 ($\mu g\,kg^{-1}$)	[99]
$Mg(NO_3)_2$, Pd	Added 10 mL of chloroform and placed in ultrasonic bath, and As^{3+} was extracted with 1 M HCl; Reduction of As^{5+} to As^{3+} by HBr and hydrazine sulfate	ETAAS	As(III,V)	Fish	4–5 ($mg\,g^{-1}$)	[100]
$Pd(NO_3)_2$	Reaction of As(V) with molybdate in H_2SO_4 at 55 °C and centrifugation for extracting analytes to surfactant phase. Total As after oxidation of As(III) to As(V) with $KMnO_4$	ETAAS	As(III,V)	Water, hair, nail	0.01 ($\mu g\,L^{-1}$)	[13]
$PdCl_2$, HCl, $(NH_4)_{10}(W_{12}O_{41})$, citric acid	Selective retention of As species on specific ion-exchange chromatography cartridges followed by selective elution	GFAAS	As(III,V), MMA, DMA	Water	Na	[105]
$Pd(NO_3)_2$	Total As(III,V) by adsorption on TiO_2; As(III) by coprecipitation with Pb-PDC; As(V) by difference	GF-AAS	As(III,V)	River, sea water	Na	[106]
Ni	As(III) by coprecipitation with Ni–APDC complex at pH 2–3; total As by pre-reduction of As(V) to As(III)	ETAAS	As(III,V)	Sea water	0.02 ($\mu g\,L^{-1}$)	[102]

Detection limit: DL; Not available: Na.

1100 °C for As could be applied without loss of analytes. The mixture of Zr and iridium (Ir) served as a permanent chemical modifier in As analysis using FI-HG–ETAAS [118]. The mixed W plus noble metals (W-Rh, W-ruthenium (Ru), W-Ir) permanent modifiers can be used for As determination in sludges, soils, sediments, coals, ashes and waters by ETAAS [119] with recoveries of certified values within 95–105%.

3.2. Differential determination of arsenic

The differential determination method has been applied to determine trace amounts of As(III), As(V), MMA, DMA and AsB in seawater with Ni–APDC complex separation [102] and in fish-based foods with 0.01 mol L^{-1} tetramethylammonium hydroxide (TMAH) separation [101] and chloroform extraction [100]. In order to determine total As, sodium thiosulfate and potassium iodide were used to reduce As(V) to the trivalent state in the sample solution before co-precipitation. The limits of detection were 0.004 and 0.005 μg g^{-1} for As^{3+} and As^{5+}, respectively, in fish [100], 0.02 μg L^{-1} in seawater [102], and 15, 25 and 50 μg kg^{-1} for AsB, DMA and inorganic As + MMA, respectively, in fish-based foods [101].

3.3. Microextraction for preconcentration and speciation of As

Microextraction technique based on a ternary solvent system has recently been popular. In dispersive liquid–liquid microextraction [120], an appropriate mixture of an extraction solvent and a disperser solvent is rapidly injected into an aqueous sample so that a cloudy solution is formed. The analyte in the sample is then transferred to the fine droplets of the extraction solvent and phase separation is performed by centrifugation. The advantages of this method include its simplicity of operation, rapidity, low cost, low consumption of organic solvents and high enrichment factors. The technique has been applied to the determination and miniaturized preconcentration of trace metal ions in environmental samples [107–109].

Various separation/preconcentration methods including LLE, CPE [13] and SPE [15] have been proposed for this purpose. Although these methods have been widely applied to the speciation of As(III) and As(V), there are still some limitations associated with them. Therefore, for preconcentration and speciation of trace amounts of As(III,V) in water, liquid phase microextraction has been used by As(III)–APDC complex separation[17], hollow fiber liquid phase microextraction [16] and dispersive liquid–liquid microextraction using APDC complex [104]. The detection limit was 9.2 ng L^{-1} in water [17], 0.12 μg L^{-1} [16] and 0.01 for As(III) [104].

3.4. Solid phase extraction

Solid phase extraction can eliminate transition-metal interferences, improve the selectivity of measurement, enhance sensitivity, and separate different As species effectively. Numerous substances have been used as solid phase extraction sorbent for the separation and preconcentration of As species, such as anion-exchange resin, C_{18} silica, PTFE turnings, mesoporous TiO_2 and immobilized yeast etc. [103]. A few recent studies have used nano-size adsorbents for the separation and preconcentration of As (III,V) species in water. As for example, immobilized nanometer TiO_2 can be used for total As at pH 6.0 and for As(III) at pH 10 [103], and specific ion-exchange chromatography cartridges for selective retention of As (III,V), MMA and DMA followed by selective elution [105]. The detection limits for As(III) were 24 ng L^{-1} with an enrichment factor of 50 [103]. Latva et al. [7] selectively separated phenylarsonic acid by adsorption onto cerium metal carbide (CeC), As(V) onto lanthanum carbide (LaC), As(III) by APDC co-precipitation and binding onto activated charcoal and DMAA by adsorption onto zirconium carbide (ZrC). The As(V,III) and DMAA species were removed from adsorbents with 12.8% HNO_3 and PAS with 7.0% NH_4OH and then finally measured by ETAAS with DLs in the range of 0.04–0.13 μg L^{-1}. Ni-modifier proved to be the most suitable out of several chemical matrix modifiers.

3.5. Cloud point extraction

Cloud point extraction technique is based on the property of most non-ionic surfactants in aqueous solutions to form micelles and become turbid when heated to the cloud point temperature [121]. The small volume of the surfactant-rich phase permits the design of extraction schemes that are simple, cheap, highly efficient, speedy and of lower toxicity to the environment than those extractions that use organic solvents [13]. The CPE technique is also very recently used to perform metal speciation [122,123]. As for example, CPE technique using molybdate as a complexing agent and the non-ionic surfactant Triton X-114 has been successfully applied for determination of As(V) species in water and total As in biological samples by ETAAS in the presence of $Pd(NO_3)_2$ modifier [13]. Total inorganic As(III,V) was extracted similarly after oxidation of As(III) to As(V) with $KMnO_4$ and As(III) was calculated by difference.

4. Conclusion and recommendation

4.1. Relation of HG with acid and reducing agent

The HG-AAS is a more suitable, affordable and much less expensive technique, widely used for As speciation, due to its high sensitivity, selectivity and low detection limit with different separation techniques like IP-RP-HPLC (DL for As(III) and As(V) <1 μg L^{-1}). The type and concentration of the acid used have a critical effect on the HG response of As species. As for example, in strong acid environment (pH < 1), hydrides are generated from As(III), As(V), MMAA, and DMAA, but in weak organic acid environment, hydrides can form only from the trivalent As species. Without pre-reduction step, As(III) and total As can be determined selectively using different concentrations of HCl and $NaBH_4$ solutions. The use of L-cysteine as pre-reductant is advantageous over KI to obtain the same signal response for all the four As species under the same, optimum and mild acid concentrations, and to reduce the transition-metals interference on the arsine generation. The effect of the arsenic oxidation states on the analytical signal can be decreased or eliminated by applying: (i) longer reaction time; (ii) higher $NaBH_4$ concentrations and/or (iii) integrated absorbance measurements.

4.2. Pretreatment, digestion and separation techniques

Using different pretreatment, digestion and separation techniques, some studies determined As speciation in phosphate fertilizers, wines, and environmental samples with DL of 0.1 μg L^{-1}. Organoarsenicals such as AsB, AsC, Me_4As+ or arsenosugars can be converted to hydride reactive forms using microwave or UV irradiation. After preconcentration and selective adsorption of As species on different adsorbents, FI-HGAAS can determine inorganic and their methylated As species in water samples.

4.3. Hydride generation and matrix interference

Although introduction of gaseous hydrides to the detector can significantly eliminate the spectral and chemical interferences in the detection system of HGAAS, there are still some possible

problems in the transportation of generated hydrides to excitation source and matrix influence of transition, noble and other metals on hydride generation reaction. L-cysteine, L-histydine, *o*-phenanthroline, EDTA with tartaric acid, a mixture of tartaric acid and ascorbic acid, KI and KCN are the complexing agents used to mask interfering metal ions. The increase in acid concentration or to decrease the $NaBH_4$ concentration can successfully diminish interferences caused by transition metals. In addition, use of positively charged surfactants (e.g., DDAB) enhances the generation of As hydrides by increasing the tolerance of transition-metal ions.

4.4. Coupling chromatographic techniques with HGAAS/ETAAS

The IP-RP-HPLC is the most useful separation technique due to its versatility, increased selectivity in resolution, high separation efficiency, simplicity, and ability to speciate both non-ionic and ionic compounds up to seven As species in a signal run using the same column and short time. Although it is not sure, some possible limitations such as the degradation of the silica-based columns, matrix interferences and pH effects are expected. The choices of IP-RP-HPLC separation conditions and resolution of the As species depend on the selection and optimization of ion-pair reagent concentration, flow rate, buffer concentration, methanol concentration, ionic strength and pH of the mobile phase. However, a combination of anion- and cation-exchange chromatography seems the most promising for complete resolution of all eight As species, and is much less sensitive to matrix interferences and pH effects because of the higher buffering capacity of the mobile phase. Above all, ion pairing in reverse mode and ion exchange are the favorite chromatographic processes used by most authors.

4.5. Electrothermal atomic absorption spectrometry

Using different separation techniques and chemical modifiers, ETAAS, an efficient technique, can determine trace amounts of As(III), As(V), MMA, DMA and AsB with DL of 4–5 $\mu g\,kg^{-1}$ in fish and 0.02 $\mu g\,L^{-1}$ in seawater. Less matrix interference on the analyte and increase in accuracy are encountered in the atomization step when use of modifiers increases the higher permissible pyrolysis temperatures. The commonly used chemical modifiers are the nitrate forms of Ni, Pd, and Mg, Mg–Pd universal modifier, Zr and Th, La, colloidal Pd, silver nanoparticles, gold nanoparticles, Zr-Ir, W-Rh, W-Ru and W-Ir permanent modifiers.

Due to simplicity of operation, rapidity, low cost, low consumption of organic solvents and high enrichment factors, dispersive liquid–liquid microextraction technique has been applied to the preconcentration and determination of As speciation in environmental samples with DL of 9.2 $ng\,L^{-1}$ and 0.01–0.12 $\mu g\,L^{-1}$ in water. Cloud point extraction, using surfactants has been successfully applied for preconcentration and separation of As(III,V) species in water and total As in biological samples (hair and nail) by ETAAS. Numerous substances have been used as solid phase extraction sorbent for the separation and preconcentration of As species, such as anion-exchange resin, C18 silica, PTFE turnings, mesoporous and immobilized nanometer TiO_2, immobilized yeast, specific ion-exchange chromatography cartridges and metal-loaded activated charcoals. Solid phase extraction can eliminate transition-metal interferences, improve the selectivity of the measurement, enhance sensitivity and separate the different As species successfully.

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