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Review

Arsenic and its speciation in water samples by high performance liquid chromatography inductively coupled plasma mass spectrometry—Last decade review

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ABSTRACT

Arsenic composes a danger for human health all over the world as it is responsible for water resources contamination. The toxicity of arsenic depends on its chemical form. However, occurrence of particular arsenic species is dependent on processes occurring in water. Nowadays, more arsenic species is detected and analyzed in different kind of water (mineral, tap, waste), mainly owing to great possibilities resulting from coupling high performance liquid chromatography (HPLC) with inductively coupled plasma mass spectrometry (ICP-MS). This review mainly describes arsenic speciation analysis by HPLC–ICP-MS technique on the basis of articles that have been published since 2000. Arsenic chemistry, occurrence in different kind of water, total arsenic determination with interferences elimination and its validation and analytical performance are also reviewed.

Contents

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1. Introduction

1.1. Toxic effects of arsenic

Chemical species of elements in environmental samples are of importance to understand toxicity, metabolism and transport properties of elements. Therefore, speciation analysis becomes an increasing active-research field in recent years [1,2]. Arsenic is an essential element for human body, and is base of many chemical species in environmental samples. In addition, there are great differences in the toxicity of the single species. In general, organic arsenic compounds are significantly less toxic than inorganic arsenic compounds. Arsenite is reported to be more soluble, mobile and more toxic than arsenate compounds [3]. The toxicity is directly related to mobility in water and body fluids. The toxicity conforms to the following order (highest to lowest toxicity): arsines > inorganic arsenites > organic trivalent compounds (arsenooxides) > inorganic arsenates > organic pentavalent compounds > arsonium compounds > elemental arsenic [3,4,16]. Arsenobetaine and arsenocholine are considered as nontoxic. Additionally, arsenic is usually toxic to plants and soils biota at concentrations that do not affect animal or human health. Nevertheless arsenic, which is classified as genotoxic and carcinogenic by International Agency on Research Cancer (IARC), imposes significant risks to the health of people of many different countries. As many as 60–100 million people globally may be at risk of exposure to excessive levels of arsenic [5].

1.2. Analysis of arsenic species

The instrumentation necessary to perform speciation studies has often been utilized with complementary techniques. These involve the coupling a selective separation with sensitive and element-specific detection. Many different combinations (separation + element-selective detection) have been attempted but high-performance liquid chromatography (HPLC) in conjunction with inductively coupled plasma mass spectrometry (ICP-MS) has emerged as one of the best combinations. HPLC is a versatile technique, which due to the variety of separation mechanisms, can be applied to a great variety of environmentally important analytes. Also, ICP-MS is currently the most sensitive and robust commercially available elemental detector and coupling these techniques (HPLC and ICP-MS) is straightforward. ICP-MS offers several advantages in comparison to traditional detectors including: multielement and multisotope detection, and more importantly, high sensitivity along with a wide linear dynamic range detection [6]. The majority of the chemical elements have dynamic linear range of 4–11 orders of magnitude [7].

1.3. Law regulations

The current WHO provisional level of As in drinking water is 10 $\mu g\,L^{-1}$ [8], the target for the European Union is 10 $\mu g\,L^{-1}$ [9] and current level in the United States is also 10 $\mu g\,L^{-1}$, published by Environmental Protection Agency (EPA) [10]. Either in other European countries value of arsenic concentration in drinking water comes to 10 $\mu g\,L^{-1}$. In September 1993, EPA developed, with contractor support, a document entitled "Treatment and Occurrence-Arsenic in Potable Water Supplies" [11]. This document summarized the results of pilot-scale studies examining low-level arsenic removal, from 50 $\mu g\,L^{-1}$ down to 1 $\mu g\,L^{-1}$ or less. Nowadays, permissible value of arsenic concentration in drinking water is only temporary, what is caused by lack of routine, validated analytical methods enabling determination of low concentrations of arsenic.

Many review articles about arsenic were published in the space of several dozen years. They concern the following issues: origin and occurrence (sources, behaviour, distribution in water, biogeochemistry, transformations in water) [12–14,19,20,29]; arsenic biochemistry (biogeochemical cycle, bioavailability, microbial metabolism, mechanisms of biotransformations) [15,18]; threat (toxicity, risk assessment, health effects, human exposure to various arsenic species) [12–14,34]; sample handling (pre-treatment, preservation, storage, stability) [1,12,17,22]; neutralization of arsenic (biotreatment processes, remediation, chemical, catalytic and photocatalytic strategies) [14,18,29]; validation [22]; analytical techniques with different object analysis (different separation techniques connected with different detection techniques on-line and off-line methods) [1,12,13,17,22,23,34].

This manuscript addresses the comprehensive summary of publications that have been published since 2000. The objective of this work was to trace the following aspects: (1) the chemistry of arsenic in water samples, (2) concentration of arsenic species in different types of water, (3) interferences accompanying arsenic detection by ICP-MS water samples, (4) separation of arsenic species from water samples by HPLC with ICP-MS detection, (5) analytical validation and performance.

2. Arsenic chemistry

Arsenic occurs in the environment in four oxidation states (As^{-3}, As^{0}, As^{+3} and As^{+5}) in inorganic as well as in organic forms. In natural waters, arsenic appears most often in inorganic forms, to a lesser extent in organic forms, such as monomethylarsonic acid – MMA(V) and dimethylarsinic acid – DMA(V) [3,20,22]. Among inorganic forms mostly occurs in the form of oxyanions, such as: as trivalent arsenate (H_3AsO_3) in the reducing environment and as pentavalent arsenite ($H_2AsO_4^-$) under oxidizing conditions [21]. Organic arsenic compounds appear in natural waters rarely, because they are produced as a result of biological activity. Mainly surface waters are vulnerabled to presence of organic arsenic forms, what is mostly caused by inflow of industry contaminants [24]. About 25 different arsenic species are identified in waters (chosen compounds are given in Table 1). Besides arsenate, arsenite, monomethylarsonic acid and dimethylarsenic acid, which are the dominant forms in water environment, the rest of forms occur mainly in water organisms, which demonstrate capability to bind arsenic in their own tissues, what generates arsenosugars and arsenolipids [24].

Arsenic is unique element among elements which form metalloids and oxyanions, such as: selenium, antimony, vanadium or chromium, with regard to its mobility that demonstrates for pH values typical for underground waters (6.5–6.8) and in the wide range of redox conditions. Oxyanions of other elements are not as mobile as arsenic oxyanions. For example selenium has an oxyanion (SeO_4^{3-}) that is mobile under oxidizing conditions, however in the reducing environment is immobilized. Therefore, in case of arsenic speciation analysis, most of difficulties are connected with keeping the stability of arsenic species during preparation of sample and proper analysis [24].

Chemical compounds containing arsenic might undergo series of transformations and turn one into another under the influence of different processes. Most of these conversions are caused by change of pH. Most often disturbance of the chemical balance between particular species is caused by setting of different redox processes (also with the participation of microorganisms), but additionally can be caused by methylation, sorption or adsorption [25,26]. In the figure below (Fig. 1) arsenic compounds mainly occurring in the water environment are presented. In case of very high concentration of sulphides, dissolved arsenic species may be significant. Reducing, acid environment favours precipitation of orpiment and realgar, as

Table 1
Arsenic compounds found in water matrix.

Name of species	Abbreviation	Structure of species
Most often determined		
Inorganic compounds		
Arsenous acid (arsenite)	As(III)	$As(OH)_3$
Arsenic acid (arsenate)	As(V)	$AsO(OH)_3$
Organic compounds		
Monomethylarsenic acid	MMA(V)	$CH_3AsO(OH)_2$
Dimethylarsenic acid	DMA(V)	$(CH_3)_2AsO(OH)$
Arsenobetaine	AsB	$(CH_3)_3As^+CH_2COOH$
Arsenocholine	AsC	$(CH_3)_3As^+CH_2CH_2OH$
Rarely determined		
Trimethyl arsine oxide	TMAO	$(CH_3)_3AsO$
p-Arsanilic acid	*p*-ASA	$C_6H_8AsNO_3$
Trimethylarsoniopropionate	TMAP	$(CH_3)_3As^+CH_2CH_2COO^-$
Dimethyldithioarsinic acid	DMDTA(V)	$(CH_3)_2As(S)(SH)$
Dimethylmonothioarsinic acid	DMMTA(V)	$(CH_3)_2As(S)(OH)$
Thio-arsenosugar glycerol	Thio-Gly	$C_7H_{14}AsO_3(S)OCH_2CH(OH)CH_2OH$
Thio-arsenosugar sulfate	Thio-SO_4	$C_{10}H_{16}AsO_5(S)OSO_3H$
Thio-arsenosugar phosphate	Thio-PO_4	$C_7H_{14}AsO_3(S)OCH_2CH(OH)CH_2OPO_2^-OCH_2CH(OH)CH_2OH$
Trimethylarsine sulfide	TMAS	$(CH_3)_3As(S)$
Thio-arsenosugar sulfonate	Thio-SO_3	$C_{10}H_{16}AsO_5(S)SO_3H$
Thio-dimethylarsenoacetate	Thio-DMAA	$(CH_3)_2As(S)CH_2COOH$
Thio-dimethylarsinate	Thio-DMA	$(CH_3)_2As(S)(OH)$
Thio-dimethylarsenoethanol	Thio-DMAE	$(CH_3)_2As(S)CH_2COOH$
Phenylarsonic acid	PhAs, PAA	$C_6H_5AsO(OH)_2$
4-Hydroxy-3-nitrobenzenearsonic acid	Roxarson, Roxarsone	$C_6H_5As(O)(OH)_2$
Phenylarsine oxide	PhAsO, PAO	C_6H_5AsO
Dimethylarsinous acid	DMA(III)	$(CH_3)_2As(OH)$
Monomethylarsonous acid	MMA(III)	$(CH_3)_3As(OH)_2$
Dimethylarsinyolacetic acid	DMAA	$(CH_3)_2As(O)CH_2COOH$
Dimethylarsinyolethanol	DMAE	$(CH_3)_2As(O)CH_2CH_2OH$
Tetramethylarsonium ion	TMAs, Tetra, TeMA, TMA	$(CH_3)_4As^+$
Diphenylarsinic acid	DPAA	$(C_6H_5)_2AsO(OH)$

well as other minerals containing co-precipitated arsenic. Therefore in waters, where concentration of free sulphides is high, the most probable is that content of arsenic is lower. On the other hand, species containing trivalent arsenic most commonly appear in neutral and alkaline pH in the presence of sulphides [27].

The most important factors controlling arsenic speciation analysis are: redox potential and pH [28]. Level of redox potential indicates strength of oxidation or reduction reaction set in the measured solution. Its negative value confirms that solution demonstrates reducing properties, however positive value indicates about oxidizing reaction in the solution [29]. Under oxidizing conditions, the dominant form at pH < 6.9 is $H_2AsO_4^-$, however in the higher pH $HAsO_4^{2-}$ dominates. In extremely acidic or alkaline conditions, $H_3AsO_4^0$ and AsO_4^{3-} occur in the highest amounts. At pH < 9.2 in reducing conditions dominates neutral arsenic form – $H_3AsO_3^0$ [21].

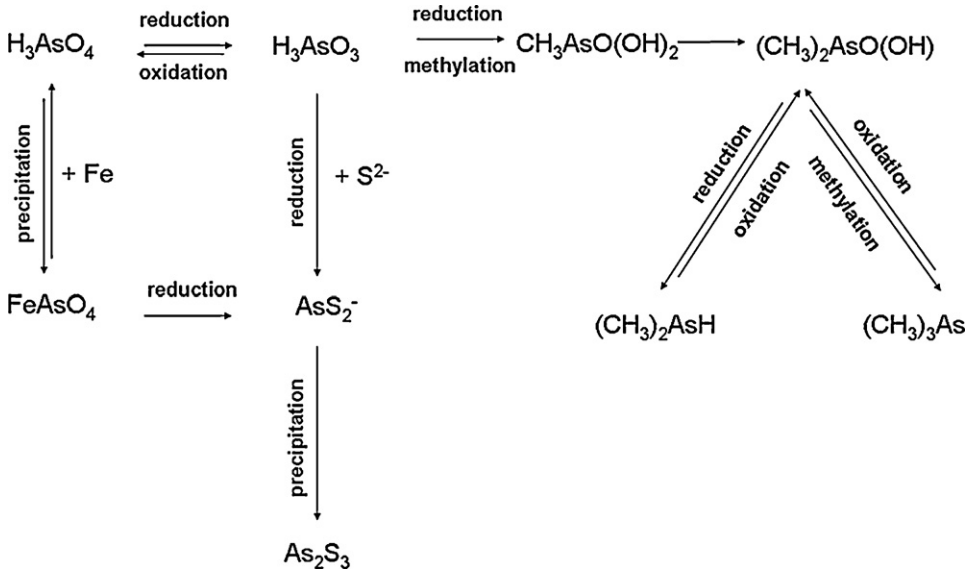

Fig. 1. Arsenic transformations in the environment (modified [3]).

3. Arsenic in water samples

Arsenic is widespread in the nature as it appears in more than 250 different minerals. As a result it may get through other environment compartments, such as: water, air or soil. Among these, water represents the greatest threat for human health as it can be directly introduced to the human body. Levels of arsenic present in water are typically in the low $\mu g\,L^{-1}$ (ppb) to several dozens of $mg\,L^{-1}$ (ppm) range, which mainly depends on bed-rock type. However, maximum permissible concentration of arsenic in liquid substances (juices, beer, soft drinks) which may be introduced to the human body is the same as for drinking water – $10\,\mu g\,L^{-1}$. This maximum permissible value is sometimes difficult to obtain, especially if underground water used for preparation of beverages or just used as drinking water originate from area rich in arsenic. Levels of arsenic in different water samples, which are directly analyzed using HPLC–ICP-MS are presented below in Table 2.

4. Interferences accompanying arsenic detection by ICP-MS

There exist a lot of methods which may be applied for determination of total arsenic, but undeniably inductively coupled plasma mass spectrometry (ICP-MS) is recently predominantly used. Certainly ICP-MS technique as all of techniques which could be applied for arsenic determination, suffers from spectral and non-spectral interferences. Spectral interferences appear mainly due to polyatomic species. Normally, spectral interferences may be eliminated by determination of other element's isotope, but in case of arsenic it is impossible as it is monoisotopic element. The most often appearing ion, which interferes during total arsenic determination is a polyatomic connection of argon and chloride – $^{40}Ar^{35}Cl$. These polyatomic ions are created by interaction between components of gaseous plasma, reagents and sample matrix [64]. Additionally, a lot of problems during arsenic determination is caused by complex matrix, especially by macroelements. However, nowadays exist a lot of solutions to effectively solve that problem, mainly by application of: mathematical equation, reaction cells, dynamic reaction cells or using high resolution ICP-MS. The last option seems to be the best as using high-resolution ICP-MS, a resolving power of about 8000 m d_m^{-1} is required to separate $^{75}As^+$ (m = 74.92160 amu) and $^{75}ArCl^+$ (m = 74.93124), but unfortunately it is compromised by a significant decrease in sensitivity [69].

5. Mathematical equation (correction)

Isobaric interferences brought about isotopes of different elements with the same proportion m/z^+, which cannot be separated because of insufficient resolution of mass spectrometer, may be evaluated with use of mathematical correction [64]. For total arsenic determination in standard mode (without any cell) United States Environmental Protection Agency (US EPA) introduced a mathematical equation which relies on deducting of some values responding for interferences from the counts value of total arsenic $^{75}As - {}^{75}As = 1.000(^{75}As) - (3.127)[(^{77}Se) - 0.815(^{82}Kr)]$ [65].

However, International Organization for Standardization recommends using the following corrections: $^{75}As = -3.127(^{77}Se - 0.815^{82}Se)$ or $^{75}As = -3.127(^{77}Se + 0.322^{78}Se)$ [64]. In this equation counts on m/z^+ 75, 77 and 82 are measured. Different authors apply different versions of this correction, introducing to equation additional isotopes, which are counted. Below a modification of the abovementioned equation with additional counts from krypton 83 and further with participation of chloride 35 provided by some authors are presented.

$$^{75}As = 1.000(^{75}As) - (3.127)[(^{77}Se) - 0.815(^{82}Kr) + 0.883(^{83}Kr)] \quad [66]$$

$$I_{75,corr} = I_{75,meas} - \frac{x_{35Cl}}{x_{37Cl}}\left[I_{77,meas} - \left(\frac{x_{77Se}}{x_{82Se}}\right)[I_{82,meas} - \left(\frac{x_{82Kr}}{x_{83Kr}}\right)I_{83,meas}\right]\right] \quad [67]$$

Most often for checking usefulness of given equations, model samples are followed. Authors prepare standard blank with addition of HNO_3, distilled water solution spiked with proper amount of HCl (checking the signal derived from chloride), distilled water solution spiked with proper amount of $NaNO_3$ (checking the signal derived from sodium), distilled water solution spiked with proper amount of $NaNO_3$ and HCl together or NaCl (checking the signal derived from both of ions) [66]. Subsequently, ion of the elements contained in the equation are monitored. Authors [65] observed extremely high signal for m/z^+ 83 for the solution where both of ion were added, however in the presence of only one element's ions there was no significant difference. They explained it could be provided by formation of $^{23}Na^{23}Na^{37}Cl$ ion. As a result of it, authors are not recommending the correction factor of m/z^+ 83 in the mathematical equation. Others authors who also applied mathematical correction concluded that it removes $[^{40}Ar^{35}Cl]^+$ interferences from the calibration standard spiked with additional chloride. However, the results of the CRMs analysis reported that the interferences present during analysis are not removed by mathematical correction as the recoveries are high. For that reason authors inferred that critical interferences appearing during analysis are rather not caused by $[^{40}Ar^{35}Cl]^+$ or $[^{40}Ca^{35}Cl]^+$ [67].

6. Dynamic reaction cells

Nowadays, dynamic reaction cells are one of the best solutions used to overcome problems caused by forming interferences.

The dynamic reaction cell (DRC) is a RF/DC quadrupole, which acts as an interface between the single lens ion optics chamber and the mass analyzer high vacuum chamber [68]. DRC may be pressurized with a reactive gas in order to promote ion–molecule reactions intended to suppress plasma-based polyatomic interferences. The bandpass of the DRC is tuned to control the formation of new in-cell interfering species, improving the selectivity of the system [69–72]. Reduction or elimination of polyatomic interferences has been achieved by molecular gas addition to modify the argon plasma. Since the reaction gas flows through the pressurized cell, reaction products are swept from the cell with a continuous flow of fresh reaction gas [73]. The mechanism of their activity is based on neutralization or exchange reaction between interfering ions and reaction gas, which cause that as a result we obtain product with different m/z^+. Possible gases or its combinations used for this purpose are: NH_3, CH_4, H_2, O_2, He. Reactions, which occur in the argon plasma during usage of abovementioned gases are presented below.

The dominant plasma ion (argon) is known to react with gases according to the following, exemplary reactions [68]:

(1) ammonia

$$Ar^+ + NH_3 \rightarrow NH_3^+ + Ar$$

$$ArH^+ + NH_3 \rightarrow NH_4^+ + Ar$$

$$Ar^+ + NH_3 \rightarrow ArH^+ + NH_2$$

Table 2
Arsenic concentration in chosen water matrix samples.

Sample		As(III) ($\mu g\,L^{-1}$)	As(V) ($\mu g\,L^{-1}$)	MMA(V) ($\mu g\,L^{-1}$)	DMA(V) ($\mu g\,L^{-1}$)	AsB ($\mu g\,L^{-1}$)	AsC ($\mu g\,L^{-1}$)	Literature
Water	Well water	0.19 ± 0.03	0.64 ± 0.03	–	–	–	–	[36]
		0.22 ± 0.03	1.40 ± 0.15	<LOD	<LOD	<LOD	–	[43]
		0.44 ± 0.06	1.86 ± 0.19					
		0.87 ± 0.11	1.03 ± 0.12					
		0.0068–0.501	0.0068–0.501	0.001–0.005	0.001–0.007	–	–	[52]
	Tap water	<0.08	0.17 ± 0.03	–	–	–	–	[36]
	Water	0.117 ± 0.038 to 0.240 ± 0.027	0.662 ± 0.182 to 3.98 ± 0.735	–	0.140 ± 0.019 to 0.98 ± 0.0002	–	–	[41]
		0.07–0.15						[47]
	Surface water	0.23 ± 0.03	1.79 ± 0.21	<LOD	0.12 ± 0.01 <LOQ	<LOQ	–	[43]
		0.11 ± 0.01	0.24 ± 0.03					
		0.1 to 1	1.1 to 5	0.02 to 0.3	–	–	–	[53]
		–	–	6	0.2	–	–	[58]
	Ground water	–	–	–	10–100	–	–	[58]
	Hot spring water	0.0004 ± 0.0001	0.0016 ± 0.0003	–	–	–	–	[50]
	Natural mineral water	0.07 ± 0.01 or <LOQ	0.09 ± 0.01 to 26.20 ± 0.76	<LOQ	<LOQ	<LOD	–	[43]
	River water	0.13 ± 0.03	0.17 ± 0.03	–	–	–	–	[36]
	Well water	5782.4 ± 23.1 or <LOD	–	–	–	–	–	[83]
	NASS-5 seawater	<LOD	1.2 ± 0.1	<LOD 0.03 ± 0.01	–	–	–	[77]
			1.23 ± 0.04					
Water	Water from industrial treatment of shale	3.72 ± 0.51	1363 ± 10	130 ± 2	13.2 ± 0.4	–	–	[39]
		6.41 ± 0.68	1031 ± 33	100 ± 2	8.01 ± 0.08			
		4.54 ± 0.29	808 ± 22	142 ± 3	6.93 ± 0.26			
	Landfill samples	0.2 ± 0.1 to 4.4 ± 0.4	0.9 ± 0.7 to 20.9 ± 0.1	0.2 ± 0.1 to 23.2 ± 0.7	0.6 ± 0.1 to 8.6 ± 0.5	– nd	0.8 ± 0.1 to 10.5 ± 0.7	[40]
	Municipal landfill leachate	<0.3 to 4.0	<0.7 to 30	<0.3 to 19	2–70	–	–	[76]
Beverages	Soft drink	1.19 ± 0.1	1.95 ± 0.2	–	–	–	–	[42]
	Lemon juice	1.27 ± 0.1	0.43 ± 0.1	–	–	–	–	[42]
	Beer	1.19 ± 0.1	1.37 ± 0.1	–	–	–	–	[42]
	Wine	$(4.2–9.3) \pm 1$	–	–	5.5 ± 1 or <LOD	–	–	[81]
Urine	Urine	nd*	5.3–8.8	7.5–55	22.8–171	4–451	–	[37]
	Urine	$<(0.1–2.3) \pm 0.15$	$<(0.1–0.6) \pm 0.11$	$<(0.1–2.7) \pm 0.33$	$(0.2–0.9) \pm 2.6$	$<(0.123) \pm 1.4$	–	[44]
	Urine after administration of DMPS	$(0.1–13.4) \pm 1.1$	$< (0.1–11.3) \pm 0.46$	$(0.4–25.6) \pm 3.3$	$(0.6–18) \pm 2.2$	$<(0.1–28) \pm 1.2$	–	[44]
	Human urine	2.27 ± 0.34 to 6.71 ± 0.69	1.56 ± 0.24 to 4.69 ± 0.61	2.56 ± 0.29 to 16.23 ± 1.97	7.35 ± 0.41 to 20.45 ± 1.66	0.64 ± 0.06 to 7.99 ± 0.26	–	[45]
	Urine	nd*	0.3 ± 0.1	nd*	1.5 ± 0.2	1.7 ± 0.2	–	[46]

* nd – not detected.

Table 3
Spectral interferences appearing while measurement of arsenic ion at m/z 75 [64].

Theoretical interferences		Interferences with practical significance
Izobaric	Poliatomic ions	
$^{150}Sm^{2+}$	$^{40}Ar^{35}Cl^{+}$	$^{40}Ar^{35}Cl^{+}$
$^{150}Eu^{2+}$	$^{59}Co^{16}O^{+}$	
$^{150}Nd^{2+}$	$^{36}Ar^{38}Ar^{1}H^{+}$	
	$^{36}Ar^{39}K$	
	$^{43}Ca^{16}O_2$	
	$^{23}Na^{12}C^{40}Ar$	
	$^{12}C^{31}P^{16}O^{2+}$	
	$^{40}Ca^{35}Cl^{+}$	
	$^{38}Ar^{37}Cl^{+}$	

(2) methane

$$Ar_2^+ + 2CH_4 \rightarrow 2CH_2^+ + 2Ar + H_2$$

$$Ar_2^+ + 2CH_4 \rightarrow 2CH_3^+ + 2Ar + H_2$$

$$Ar^+ + CH_4 \rightarrow CH_4^+ + Ar$$

In the case of helium, removing interferences is not caused by chemical reaction between interfering ion and gas, but it is caused by collision of particles. To separate particular ions, the energy of gas particles must be higher then energy of interfering ions. Spectral interferences that could appear during determination of arsenic ions are presented in Table 3.

Grotti and Frache [69] in their research focused on the selection of proper gas for dynamic reaction cell in order to analyze arsenic. They tested the following gases: ammonia, hydrogen, methane, oxygen and nitrogen protoxide through optimization of DRC parameters, such as: QRO, CRO, a and q, for each gas individually. As a result the best gas for sea-water samples turned out to be oxygen, its use for DRC under the optimized conditions proved to efficiently resolve the polyatomic spectral interferences appearing from the direct analysis of 15-fold diluted sea-water samples [69]. However, another authors state that the preferable gas for DRC for determination of total arsenic in the presence of chloride is hydrogen as the relative reactions rates of $[^{40}Ar^{35}Cl]^+$ and As^+ with H_2 are sufficiently different to allow the interference-free determination of trace amounts of As even in the presence of 1 g L^{-1} NaCl [72]. Nixon et al. tested the influence of chloride and calcium on arsenic signal measured at *m*/*z* 75. They concluded that addition of chlorides increases arsenic signal, which is observed without DRC mode. However, using DRC enabled to obtain the same counts at *m*/*z* 75 even in samples with increasing concentration of chlorides. In case of calcium, authors obtain only little effect on arsenic counts per second with standard mode, with DRC application, they observed no changes [73]. In this research authors applied a mixture of 5% H_2–95% Ar. McShane et al. used an argon as cell gas for attenuating $[^{40}Ar^{35}Cl]^+$ [74]. However, Verdon et al. for eliminating the problem of argon chloride interference utilized a mixture of 10% H_2–90% Ar as the reaction gas and obtained satisfying results [38].

7. Arsenic speciation by HPLC–ICP-MS

Liquid chromatography inductively coupled plasma mass spectrometry (LC–ICP-MS) [30,31,46] has become an established technique for arsenic speciation analysis [32]. One of the most important advantages of LC is extended range of separation mechanisms available using different mobile and stationary phases, which provide nearly all conditions necessary for separation of element species [33]. Currently, inductively coupled plasma mass spectrometry (ICP-MS) is the most widely used detector for elemental speciation analysis because it provides high sensitivity, wide linear dynamic range and it can be easily combined with many separation techniques [32,34,35]. The separation system is coupled with the detection system; in consequence separation, identification and quantification of As are carried out in a one –step analytical process. The on-line techniques are preferable because they are relatively fast and require minimal sample pre-treatment. More detailed information about the on line method (HPLC–ICP-MS) applied for arsenic speciation is given in Table 4. Analytical procedures were grouped according to the same species determined by different authors.

8. Analytical validation and performance

Validation study is indispensable for proper characterization of the method. In the case of speciation analysis, the main problem with determination of some parameters is a lack of certified reference materials, which have certified values of different chemical forms of analyzed element. The only thing, which authors may do is comparison of obtained total arsenic value with its certified value. Unfortunately, it enables only checking the correctness of the analytical procedure for total arsenic determination. However, checking the analytical procedure for separation and determination of particular chemical species in this way is not possible. Above-mentioned difficulties cause that determination of some parameters characterizing analytical method is impossible.

The validity of methods and procedures used for arsenic speciation in different kind of water, urine or beverages was tested by different authors through determination of the following parameters: linear equation, correlation coefficient, linearity, limit of detection (LOD), limit of quantification (LOQ), precision, recovery, repeatability, reproducibility and traceability. Authors, who developed procedures for arsenic speciation analysis put emphasis on parameters, which are presented below:

(a) *Linear equation and correlation coefficient, linearity*. Sathrugan and Hirata [36] analyzed an As(III) and As(V) in river water, well water and tap water. An eight-point calibration was performed in the concentration range of 1–100 μg L^{-1}. Linear equations were calculated and good correlation coefficients for As(III) and As(V) were obtained. Samanta et al. [37] analyzed arsenic compounds (As(III), As(V), DMA(V), MMA(V), AsB) in human urine. The calibration curves were constructed in the concentration range of 1–20 μg L^{-1}. Authors obtained high correlation coefficients from 0.996 to 1.000. Also Verdon et al. [38] analyzed seven arsenic compounds (As(III), As(V), MMA(V), DMA(V), AsB, AsC, TMAO) in human urine. Authors constructed calibration curves for all arsenic species, then marked out linear equation and correlation coefficients. Values of correlation coefficients were very close to unity (from 0.99984 to 0.99999). Successive authors, Duarte et al. in their work focused on arsenic speciation analysis of the following compounds: As(III), As(V), MMA(V), DMA(V), in aqueous effluent from the shale industrial plant. Calibration curves within the range of 0.1–100 μg L^{-1}. As were obtained with good correlation coefficients for all arsenic species (≥0.999). Ronkart et al. in the research developed a method for speciation analysis of five arsenic compounds – AsB, DMA(V), As(III), MMA(V) and As(V) in surface, well and natural mineral water samples. Calibration curves were performed in the range of 0.1–50 μg L^{-1}, obtained correlation coefficients were in all cases better then 0.9999. Further, Morita et al. [50] developed a method of speciation analysis of eight arsenic compounds: As(III), As(V), MMA(V), DMA(V), AB, TMAO, TeMA and AsC and applied this method to analysis of drinking water samples. Calibration curves constructed for each chemical form were linear in concentration range 0.2–400 μg L^{-1}. Xie et al.

Table 4
Important aspects of analytical procedures according to arsenic species determination by HPLC–ICP-MS technique on the basis of articles that have been published since 2000.

No	Species	Matrix	Column	Eluent	Optimization	Retention time [min]	Time OF analysis (min)	Literature
1.	As(III) As(V)	Water (tap, well, river)	Reserved phase: Capcell C18 Pak (250 mm × 4.6 mm)	Isocratic elution: 5 mM butanesulfonic acid, 2 mM malonic acid, 0.3 mM hexanesulfonic acid, 0.5% methanol	pH 2.5 Flow rate = 1.0 mL min^{-1}	2.4 for As(V) 3.0 for As(III)	4	[36]
2.	As(III) As(V)	Natural water	Anion exchange: LC-SAX (4 mm × 50 mm)	Isocratic elution: 12.5 mM malonate and 17.5 mM acetate	pH = 4.8 Flow rate = 1.0 mL min^{-1} Column temperature = 33 °C	0.9 for As(III) 1.5 for As(V)	3	[57]
3.	As(III) As(V) MMA(V)	Seawater samples	Ion-exclusion: SCR-102H (300 mm × 8.0 mm, 7 μm)	Nitric acid	pH = 2.0 Flow rate = 1.5 mL min^{-1} Column temperature = 30°C	4.5 for As(V) 6.2 for As(III) 13.6 for MMA(V	15	[77]
4.	As(III) As(V) MMA(V) DMA(V)	Drinking water	Anion exchange: Hamilton PRP-X100 (250 mm × 4.1, 10 μm)	Isocratic elution: 14 mM phosphate buffer	pH = 6 Flow rate = 1.5 mL min^{-1}	2 for As(III) 4.7 for DMA(V) 6.5 for MMA(V) 11.5 for As(V)	10	[41]
				Gradient elution: 30 mM to 100 mM TRIS acetate buffer	pH = 7	2 for As(III) 4.7 for DMA(V) 6.5 for MMA(V) 11.5 for As(V)	13	
5.	As(III) As(V) MMA(V) DMA(V	Beverages (soft drink, lemon juice, beer)	Anion exchange: Hamilton PRX-100 (250 mm × 4.1, 10 μm)	5 mM potassium monohydrogen phosphate, posassium dihydrogen phosphate	pH = 8.5 Flow rate = 1.0 mL min^{-1}	2.75 for As(III) 3.33 for DMA(V) 5.17 for MMA(V) 12.5 for As(V)	14	[42]
6.	As(III) As(V) MMA(V) DMA(V)	Environmental waters	Anion exchange: Dionex AS7	Gradient elution: 1-50 mM nitric acid	pH mobile phase	1.6 for As(III) 2.7 for MMA(V) 4.4 for DMA(V) 5.6 for As(V)	6	[47]
7.	As(III) As(V) MMA(V) DMA(V)	Water	Anion exchange: Hamilton PRP-X100 (150 mm × 1 mm; 3 μm)	Gradient elution: A: 5 mM ammonium nitrate, 1 mM ammonium dihydrogen phosphate B: 80 mM ammonium nitrate	pH = 8.3 for A and B Flow rate = 100 μL min^{-}	1.5 for As(III) 2.6 for DMA(V) 3.2 for MMA(V) 4.1 for As(V)	5	[49]
8.	As(III) As(V) DMA(V) MMA(V)	Well water	Reserved phase: ODS-3 (150 mm × 4.6, 3 μm)	5 mM TBAH, 3 mM malonic acid, 5% methanol	Flow rate = 1.5 mL min^{-1} Column temperature = 50 °C	1.5 for As(III) 2.4 for DMA(V) 3.2 for MMA(V) 4.7 for As(V)	6	[52]
9.	As(III) As(V) MMA(V) DMA(V)	Surface water	Anion exchange: ION 120 (120 mm × 4.6 mm, 10 μm)	Gradient elution: 4 mM–0.3 M ammonium hydrogen carbonate/2%methanol	pH = 10.3	2.5 for DMA(V) 3.5 for As(III) 7 for MMA(V) 8.5 for As(V)	13	[53]
			Hamilton PRP-X100 (250 mm × 4.1 mm, 10 μm)	10 mM–100 mM ammonium dihydrogen phosphate/2%methanol	pH = 6	2.5 for As(III) 3.7 for DMA(V) 4.7 for MMA(V) 5.8 for As(V)	7 without re-equlibration	
			Hamilton PRP-X100 (250 mm × 4.1 mm, 10 μm	4 mM-0.3 M ammonium hydrogen carbonate/2%methanol	pH = 8	2.5 for As(III) 4.25 for DMA(V) 5.5 for MMA(V) 7 for As(V)	8	
10.	As(III) As(V) MMA(V) DMA(V)	Model samples	Anion exchange: Dionex Ion Pak AS 14 (250 mm × 4 mm)	Gradient elution: A: 2 mM ammonium hydrogen carbonate, 2.2 mM tartaric acid B: 2 mM ammonium hydrogen carbonate, 45 mM tartaric acid	pH = 8.2 for A and B Flow rate = 1.0 mL min^{-1}	2.6 for As(III) 3.3 for DMA(V) 4.5 for MMA(V) 9.8 for As(V)	11	[54]
11.	As(III) As(V) MMA(V) DMA(V)	Surface water	Anion exchange: Hamilton PRP-X100 (250 mm × 4.1 mm, 10 μm)	Isocratic elution: 20 mmol L^{-1} $NH_4H_2PO_4$	pH = 5.6 Flow rate= 1 .5 mL min^{-1}	1.7 for As(III) 2.5 for DMA(V) 5.0 for MMA(V) 9.7 for As(V)	11	[56]

Table 4 (*Continued*)

No	Species	Matrix	Column	Eluent	Optimization	Retention time [min]	Time OF analysis (min)	Literature
12.	As(III) As(V) MMA(V) DMA(V)	Natural water	Anion exchange: Hamilton PRP-X100 (250 mm × 4.1 mm)	Gradient elution: 38–75 mM phosphate buffer	pH = 5.7 Flow rate = 1.0 mL min^{-1}	3.1 for As(III) 3.6 for DMA(V) 4.7 for MMA(V) 6.1 for As(V)	7	[57]
13.	As(III) As(V) MMA(V) DMA(V)	Human urine	Anion exchange: IonPak AS11 analytical column (4 mm × 250 mm	Gradient elution: A: 50 mM NaOH B: water	pH = 11.3–12.7 Flow rate = 1.0 mL min^{-1}	3.3 for DMA(V) 4.0 for As(III) 5.8 for MMA(V) 7.2 for As(V)	8	[59]
14.	As(III) As(V) MMA(V) DMA(V)	Drinking water	Agilent (250 mm × 4.6 mm, 5 μm)	Isocratic elution: 2.0 mM NaH_2PO_4 + 0.2 mM EDTA, pH = 6.0	Flow rate = 1.0 mL min^{-1} Column temperature = 23 °C	2.1 for As(III) 3.2 for DMA(V) 4.2 for MMA(V) 8.7 for As(V)	10	[60]
15.	As(III) As(V) MMA(V) DMA(V)	Human urine CRM and control material	Anion exchange: ICSep ION-120 (4.6 mm × 120 mm, 10 μm) Hamilton PRX-100 (150 mm × 4.1 mm, 3 μm)	Gradient elution: 5–50 mM ammonium carbonate	Mobile phase pH = 10.3	3.5 for DMA(V) 5.5 for As(III) 10.5 for MMA(V) 13.5 for As(V)	15	[48]
16.	As(III) As(V) MMA(V) DMA(V)	Municipal landfil leachates	Anion exchange: Hamilton PRP-X100 (4.6 mm × 250 mm, 1 μm)	Isocratic elution: 20 mM ammonium dihydrogen phosphate	pH = 5.6 Flow rate = 1.5 mL min^{-1} Column temperature = 30 °C	1.2 for As(III) 2.2 for DMA(V) 4.7 for MMA(V)	7	[76]
17.	As(III) As(V) MMA(V) DMA(V) AsB	Human urine	Anion exchange: Gel Pack GL- IC-A15 (150 mm × 4.6 mm)	0.38 g L^{-1} phosphate buffer	pH = 10.75	1.8 for AsB 2.7 for DMA(V) 3.1 for As(III) 6.4 for MMA(V) 9.3 for As(V)	10	[37]
18.	As(III) As(V) MMA(V) DMA(V) AsB	Water (surface, well)	Anion exchange: Dionex As7 (250 mm × 4 mm, 10 μm)	Gradient elution: A: 2.5 mM ammonium dihydrogen phosphate B: 50 mM ammonium dihydrogen phosphate	pH = 10	1.35 for AsB 2.0 for DMA(V) 3.0 for As(III) 8.7 for MMA(V) 14.8 for As(V)	16	[43]
19.	As(III) As(V) MMA(V) DMA(V) AsB	Human urine	Anion exchange: Agilent (150 mm × 4.6 mm)	1.6 mM sodium dihydrogen phosphate, 0.6 mM disodium EDTA, 8 mM sodium acetate, 2.4 mM sodium nitrate in 1% (v/v) methanol	pH = 11 Flow rate = 1.0 mL min^{-1}	1.8 for AsB 2.4 for DMA(V) 3.6 for As(III) 5.5 for MMA(V) 7.7 for As(V)	9	[44]
20.	As(III) As(V) MMA(V) DMA(V) AsB	Urine	Anion exchange: Altina (150 mm × 4.6 mm, 5 μm)	5 mM hexanesulfonic acid, 5 mM citric acid	pH = 4.5 Flow rate = 0.9 mL min^{-1}	1.4 for As(V) 1.65 for MMA(V) 2.2 for As(III) 2.8 for DMA(V) 3.5 for AsB	4	[46]
21.	As(III) As(V) MMA(V) DMA(V) AsB	Aqueous sample	Cation exchange: (17 5mm × 0.05 mm)	Isocratic elution: 10 mM ammonium nitrate	Flow rate = 0.4 mL min^{-1}	7.1 for As(V) 8.1 for MMA(V) 9.2 for DMA(V) 10.6 for As(III) 12.8 for AsB	15	[51]
22.	As(III) As(V) MMA(V) DMA(V) AsB	Human urine	Anion exchange: Hamilton PRP-X100 (4.1 mm × 250 mm, 10 μm)	Gradient elution: A: 20 mM ammonium bicarbonate B: 20 mM ammonium sulfate	pH = 8.5 for A pH = 7 for B Flow rate = 1.5 mL min^{-1} Column temperature = ambient	1.9 for AsB 2.5 for As(III) 4.3 for DMA(V) 9.7 for MMA(V) 13.6 for As(V)	33	[62]
23.	As(III) As(V) MMA(V) DMA(V) AsB	Model samples	Anion exchange: Hamilton PRP-X100 (4.1 mm × 250 mm)	Gradient elution: A: 0.25 mM ammonium dihydrogen phosphate, 2% (v/v) methanol B: 20 mM ammonium dihydrogen phosphate, 2% (v/v) methanol	pH = 9.0 for A pH = 8.8 for B Flow rate = 1.0 mL min^{-1} Column temperature = 25°C	2.83 for AsB 4.33 for As(III) 8.17 for DMA(V) 10.33 for MMA(V) 13.5 As(V)	15	[82]
24.	As(III) As(V) MMA(V) DMA(V) AsB	Model samples	Ion-120 (125 mm × 4.6 mm	Gradient elution: A: 5 mM ammonium hydrogen carbonate, 2% (v/v) methanol B: 50 mM ammonium hydrogen carbonate, 2% (v/v) methanol	pH = 10.3 for A and B Flow rate = 1.0 mL min^{-1} Column temperature = 25 °C	1.5 for AsB 2.5 for DMA(V) 3.5 for As(III) 4.0 for MMA(V) 7.9 for As(V)	9	[82]

Table 4 (*Continued*)

No	Species	Matrix	Column	Eluent	Optimization	Retention time [min]	Time OF analysis (min)	Literature
				Isocratic elution: 30 mM ammonium hydrogen carbonate, 2% (v/v) methanol	pH = 10.0 Flow rate = 1.0 mL min^{-} Column temperature = 25 °C	1.33 for AsB 2.0 for DMA(V) 2.5 for As(III) 6.5 for MMA(V) 11.0 for As(V)	12.5	
25.	MMA(III) DMA(III) AsB	Human urine	Cation exchange: PCX-500 (4 mm × 250 mm)	Isocratic elution: 70 mM HNO_3	pH = 1–3 Flow rate = 1.0 mL min^{-1}	3.4 for DMA(III) 5.3 for MMA(III) 8.4 for AsB	10	[59]
26.	As(III) As(V) DMA(V) MMA(V) p-ASA	Model samples	Reserved phase: Water NanoEase C18 (50 m × 0.3 mm; 3.5 μm)	Isocratic elution: 0.5 mM tetra-*n*-butylammonium phosphate (TBAP)	pH = 5.9 Flow rate = 0.9 mL min^{-}	4.49 for As(III) 5.63 for DMA(V) 6.74 for MMA(V) 7.72 for As(V) 10.3 for p-ASA	12	[55]
27.	As(III) As(V) MMA(V) DMA(V) p-ASA	Wine	Reversed phase narrow bore Discovery C18 (150 mm × 2.1 mm)	Isocratic elution: 5 mM tetrabutylammonium hydroxide	pH = 6.2 Flow rate = 0.7 mL min^{-1}	0.56 for As(III) 0.83 for DMA(V) 1.06 for MMA(V) 1.26 for p-ASA 1.43 for As(V)	2	[81]
28.	As(III) As(V) MMA(V) DMA(V) roxarsone	Natural water	Anion exchange: Dionex As7 (4 mm × 250 mm)	Gradient elution: 2.5–50 mM nitric acid in 0.5% methanol	Flow rate = 1.0 mL min^{-1} Column temperature = 33 °C	1.7 for As(III) 2.3 for MMA(V) 4.4 for DMA(V) 5.6 for As(V) 6.7 for Roxarsone	8	[57]
29.	As(III) As(V) MMA(V) DMA(V) AsB p-ASA	Water from industrial shale processing	IonPac As14 (250 mm × 4 mm, 9 μm)	Gradient elution: 1.5–20 mM ammonium carbonate	pH = 8.7 Flow rate = 1.5 mL min^{-1}	1.5 for AsB 3.5 for As(III) 6.5 for DMA(V) 16.5 for MMA(V) 18 for p-ASA 22 for As(V)	25	[39]
30.	As(III) As(V) MMA(V) DMA(V) AsB AsC	Human urine	Anion exchange: Hamilton PRP-X100 (4.1 mm × 250 mm, 10 μm)	Gradient elution: A: 10 mM ammonium carbonate/6 (v/v)% methanol B: 50 mM ammonium carbonate/6 (v/v)% methanol	pH = 9.0 Flow rate = 1.0 mL min^{-1} Column temperature = 25°C	5.0 for AsB 7.0 for As(III) 8.8 for DMA (V) 11.7 for AsC 14.8 for MMA(V) 17 for As(V)	30	[79]
31.	As(III) As(V) MMA(V) DMA(V) AsB TMAO	Landfill lachate	Cation exchange: Hamilton PRP-X200 (25 m × 4.1 mm)	Gradient elution: A: 4 mM nitric acid B: 4 mM nitric acid, 20 mM ammonium nitrate	pH = 2.5 for A and B	2.5 for As(III) 2.9 for MMA(V) 4.1 for As(V) 6.5 for DMA(V) 9.5 for AsB 13.7 for TMAs+ 15.2 AsC	25	[40]
32.	As(III) As(V) MMA(V) DMA(V) AsB AsC TMAO	Urine	Anion exchange: Hamilton PRX-100 (150 mm × 4.6 mm, 5 μm)	Gradient elution: A: 10 mM ammonium carbonate, 10 mM TRIS B: 10 mM ammonium carbonate, 10 mM TRIS, 15 Mm ammonium sulfate	pH = 8.7 for A pH = 8 for B	1.5 for AC 1.8 for AsB 2 for TMAO 2.5 for As(III) 4.5 for DMA(V) 8.5 for MMA(V) 10.2 for As(V)	11	[38]
33.	As(III) As(V) MMA(V) DMA(V) AsB AsC TMAO TeMA	Hot spring water	Reversed phase: Develosil C30-UG-5 (250 mm × 4.6 mm, 5 μm)	10 mM sodium butanesulfonate, 4 mM malonic acid, 4 mM tetramethylammonium hydroxide, 0.1 (v/v)% methanol, 20 mM ammonium tartrate (pH 2.0) mixed solution	pH = 2.0	5.2 for As(V) 5.5 for As(III) 5.75 for MMA(V) 7.0 for DMA(V) 8.5 for AsB 9.7 for TMAO 10.4 forTeMA 10.8 for AsC	12	[50]
34.	As(III) As(V) MMA(V) DMA(V) AsB AsC TMAO TMAs	Human urine	Ion-exclusion: TSKgel OApak-A	Isocratic elution: 0.35 mM sodium sulfate	pH = 3.8 Flow rate = 1.0 mL min^{-1} Column temperature = 40 °C	7 for As(V) 10 for MMA(V) 12 for DMA(V) 13 for As(III) 15 for AsB 25 for TMAs and AsC 72 for TMAO	80	[80]

Table 4 (*Continued*)

No	Species	Matrix	Column	Eluent	Optimization	Retention time [min]	Time OF analysis (min)	Literature
35.	AsB AsC TMAO Tetra	Lake water	Cation exchange: Zorbax 300-SCX (150 mm × 4.1 mm, 5 μm)	Isocratic elution: 20 mM pyridine	pH = 2.31 Flow rate; = 1.5 mL min^{-1}	1.7 for AsB 2.4 for TMAO 3.3 for AsC 3.8 for Tetra	5	[56]
36.	AsB AsC TMAO Tetra	Fish sauce	Cation exchange: Zorbax 300 SCX (4.6 mm × 250 mm)	10 mM pyridine, pH = 2.3	pH = 2.3 Column temperature = 30 °C	3.8 for AsB 4.3 for TMAO 5.9 for AsC 7.0 for Tetra	8	[61]
37.	As(V) DMA(V) AsB AsC TMAO Tetra	Model samples	Cation exchange: Nucleosil 5SA (250 mm × 4.0 mm)	Isocraic elution: 30 mM pyridine, 2% (v/v) methanol	pH = 3.0 Flow rate = 1.0 mL min^{-1} Column temperature = 25°C	2.5 for As(V) 3.33 for DMA(V) 4.5 for AsB 6.33 for TMAO 9.2 for AsC 11.3 for Tetra	13	[82]
38.	DMA(V) TMAO AsB DMAA TMAP DMAE	Human urine CRM and control material	Cation exchange: ChromPack Ionospher 5C (3.0 mm × 100 mm, 5 μm)	Gradient elution: 0–20 mM pyridinium ion	pH = 2.7	2.0 for DMA(V) 2.8 for DMAA 6.5 for AsB 10.0 for DMAE 10.5 for TMAO 11.5 for TMAP	13	[47,75]
39.	As(III) As(V) MMA(III) MMA(V) DMA(III) DMA(V) AsB	Human urine	Reserved phase: Prodigy ODS-3 (150 mm × 4.6 mm, 3 μm) Cation exchange: Supelcosil™ LC-SCX (250 mm × 4.6 mm, 5 μm)	Isocratic elution: 4.7 mM tetrabutylammonium hydroxide, 2 mM malonic acid, 4% methanol Isocratic elution: 20 mM pyridine	pH = 5.95 for ODS Column temperature = 30 °C Flow rate = 1.5 mL min^{-1} pH = 3 for Supelcosil Column temperature = 30 °C Flow rate = 1.5 mL min^{-1}	1.25 for As(III) 1.7 for MMA(III) 2.25 for DMA(V) 2.8 for MMA(V) 4.0 for DMA(III) 5.4 for As(V)	6	[45]
40.	As(III) As(V) MMA(V) DMA(V) MMA(III) DMA(III) AsB AsC	Human urine	Anion exchange: ES-502N 7C (7.6 mm × 100 mm)	Isocratic elution: 15 mM citric acid	pH = 2.0 Flow rate = 1.0 mL min^{-1}	2.3 for AsC 2.7 for AsB 3.0 for DMA(V) 3.6 for MMA(V) 4.0 for As(V) 4.9 for DMA(III) 6.0 for MMA(III) 8.1 for As(III)	10	[78]
]]7941.	As(III) As(V) MMA(V) PhAs Roxarson PhAsO TMAO	Groundwater	Sodex Rspak NN-614 column (150 mm × 6 mm)	Gradient elution: A: 5 mM nitric acid B: 5 mM nitric acid, 50 mM ammonium nitrate	Flow rate = 1.0 mL min^{-1}	3.0 for As(V) 3.3 for MMA(V) 4.2 for As(III) 4.7 for PhAs 7.0 for Roxarson 12.2 for PhAsO 16.5 for TMAO	18	[58]
42.	Thio-Gly Thio-SO_4 TMAS Thio-PO_4 Thio-DMAE Thio-SO_3 Thio-DMAA Thio-DMA	Urine	Reversed phase: Atlantis dC18, (4.6 mm × 150 mm)	Isocratic elution: 20 mM ammonium phosphate or 20 mM ammonium formate	pH = 3.0 Flow rate = 1.0 mL min^{-1} Column temperature = 30°C	6.3 for thio-DMA 7.0 for thio-DMAA 7.4 for thio-SO_3 8.1 for thio-DMAE 8.4 for thio-PO_4 9.2 for TMAS 10.4 for thio-SO_4 13.3 for thio-Gly	15	[63]
43.	DMDTA(V) DMMTA(V)	Municipal landfil leachates	Thermo HyPURITY C18 (4.6 mm × 250 mm, 5 μm)	Isocratic elution: 5 mM formic acid	pH = 2.9 Flow rate = 1.3 mL min^{-1} Column temperature = 25°C	2.7 for DMDTA(V) 4.7 for DMMTA(V)	7	[76]
44	As(III) PAA PAO DPAA	Well water	Inertsil C4 (150 mm × 2.1 mm, 10 μm)	Isocratic elution: acetonitrile:water = 30:70	pH = 2.0 Flow rate = 0.2 mL min^{-1} Column temperature = 40 °C	1.81 for As(III) 2.25 for PAA 2.98 for PAO 3.36 for DPAA	4	[83]
45.	As(III) As(V) PAO PAA DPAA	Groundwater	Sodex Rspak NN-614 column (150 mm × 6 mm)	Gradient elution: A: 5 mM nitric acid B: 5 mM nitric acid, 50 mM ammonium nitrate		3.1 for As(V) 4.2 for As(III) 4.9 for PAA 12.5 for PAO	16	[58,84]

Table 5
The most important analytical performance parameters in arsenic speciation analysis.

Species	LOD [μg L^{-1}]	Precision [%]	Recovery [%]	Injection volume [μL]	Literature
As(III)	0.046	2.8	97 for 5 μg L^{-1}		[53]
	0.03	4.89	90 for 2 μg L^{-1}	100	[37]
	1.2	4.9		20	[38]
	0.02			200	[39]
	0.09	3			[41]
	0.2	1.2	104.8 for 5 μg L^{-1}	100	[42]
	0.017	5.9		20	[43]
		2.4		20	[46]
	0.08	3.5		25	
	0.36	1.9 (RT)*		50	[54]
		3.3 (PA)*			
		4.9 (PH)*			
	108	3.5 (PA)*		0.05	[55]
		4.4 (PH)*			
	0.11	1.9		100	[59]
	0.067	0.36	96	100	[60]
	0.08	3.7		25	[36]
	0.07		112	50	[52]
	0.04	3.2	95 for 2 μg L^{-1}	15	[49]
	0.06	4.5	97 for 20 μg L^{-1}	20	[51]
	0.015 for pure water	1.2 for pure water	87	200	[77]
	0.057 for 2% Cl-solution	2.6 for 2% Cl-solution			
	0.025 for pure water	5.9 for pure water	104	200	[77]
	0.022 for 2% Cl-solution	4.3 for 2% Cl-solution			
	0.2	2–8 (ST)*		200	[79]
		4 (LT)*			
	0.089	2.1		50	[79]
	0.3	0.8			[81]
		1.7–3.0			[83]
As(V)	0.03	1.9	107 for 5 μg L^{-1}		[53]
	0.04	5.29	99 for 2 μg L^{-1}	100	[37]
	1	5.8		20	[38]
	0.1			200	[39]
	0.027			100	[40]
	0.3	8			[41]
	0.5	3	90.8 for 5 μg L^{-1}	100	[42]
	0.026	1.7		20	[43]
		2		20	[46]
	0.2	2		25	[48]
	0.34	0.4 (RT)*		50	[54]
		6.4 (PA)*			
		6.7 (PH)*			
	7.8	4.2 (PA)*		0.05	[55]
		3.4 (PH)*			
	0.25	2.7		100	[59]
	0.089	1.15	96	100	[60]
	0.07	2.7		25	[36]
	0.09		97	50	[52]
	0.03	0.1	95 for 2 μg L^{-1}	15	[49]
	0.05	2.1	95 for 20 μg L^{-1}	20	[51]
	0.012 for pure water	1.6 for pure water	104	200	[77]
	0.116 for 2% Cl-solution	11.0 for 2% Cl-solution			
	0.020 for pure water	4.1 for pure water	105	200	[77]
	0.021 for 2% Cl-solution	6.7 for 2% Cl-solution			
	2	8–45 (ST)*		200	[79]
		15 (LT)*			
	0.34	2.1		50	[80]
	1.3	3.9			[81]
MMA	0.025	1.8	98 for 5 μg L^{-1}		[53]
	0.02	7.19	101 for 2 μg L^{-1}	100	[37]
	0.9	3.5		20	[38]
	0.04			200	[39]
	0.06	2			[41]
	0.3	2.5	110.7 for 5 μg L^{-1}	100	[42]
	0.026	2.2		20	[43]
		3.1		20	[46]
	0.05	5.3		25	[48]
	0.26	1.8 (RT)*		50	[54]
		5.3 (PA)*			
		6.1 (PH)*			
	54	1.8 (PA)*		0.05	[55]
		0.5 (PH)*			
	0.18	2.1		100	[59]
	0.035	0.69	99	100	[60]
	0.06	1.5	108	50	[52]

Table 5 (*Continued*)

Species	LOD [μg L^{-1}]	Precision [%]	Recovery [%]	Injection volume [μL]	Literature
	0.03		89 for 2 μg L^{-1}	15	[49]
	0.4	10	96 for 20 μg L^{-1}	20	[51]
	0.015 for pure water	2.8 for pure water	92	200	[77]
	0.083 for 2% Cl-solution	3.2 for 2% Cl-solution			
	0.022 for pure water	3.4 for pure water	94	200	[77]
	0.025 for 2% Cl-solution	7.3 for 2% Cl-solution			
	0.2	4–33 (ST)*		200	[79]
		11 (LT)*			
	0.2	1.4		50	[80]
	0.7	3.5			[81]
DMA	0.018	3.2	99 for 5 μg L^{-1}		[53]
	0.02	4.04	82 for 2 μg L^{-1}	100	[37]
	1.7	5.8		20	[38]
	0.06			200	[39]
	0.011			100	[40]
	0.06	2			[41]
	0.2	2.1	104.4 for 5 μg L^{-1}	100	[42]
	0.023	1		20	[43]
		3.8		20	[46]
	0.04	4.4		25	[48]
	0.48	1.2 (RT)*		50	[54]
		3.6 (PA)*			
		4.7 (PH)*			
	53	4.8 (PA)*		0.05	[55]
		2.8 (PH)*			
	0.17	1.9		100	[59]
	0.074	0.84	98	100	[60]
	0.1	0.3	112	50	[52]
	0.04		105 for 2 μg L^{-1}	15	[49]
	0.1	5.2	97 for 20 μg L^{-1}	20	[51]
	2	5 (ST)*		200	[79]
		5 (LT)*			
	0.25	2.7		50	[80]
	0.4	2			[81]
AsB	0.01	4.73	96 for 2 μg L^{-1}	100	[37]
	0.4	4.4		20	[38]
	0.024	1		20	[43]
		4		20	[46]
	0.75	2.8		100	[59]
	0.02	5.5	96 for 20 μg L^{-1}	20	[51]
	1	4–5 (ST)*		200	[79]
		6 (LT)*			
	0.067	1.3		5	[80]
AsC	0.6	3		20	[38]
	1	5–18 (ST)*		200	[79]
		12 (LT)*			
	0.19	1.7		50	[80]
TMAO	1	3.8		20	[38]
	0.14	2.7		50	[80]
MMA(III)	0.61	3.3		100	[59]
DMA(III)	0.44	2.1		100	[59]
TMAs	0.28	3.3		50	[80]
PAA		1.9–6.0			[83]
PAO		1.7–2.8			[83]
DPAA		1.8–3.2			[83]

* RT – retension time; PA – peak area; PH – peak height; ST – short-term precision; LT – long-term precision.

[51] in their research focused on arsenic speciation of the following compounds: As(III), As(V), MMA(V), DMA(V), MMA(III), DMA(III), AsB in human urine.

(b) *Limit of detection*. Detection limit was mainly calculated as three times the standard deviation of the background signal or replicate analyses of deionized spiked water samples. Sathrugan and Hirata [36] obtained the following LOD results: 0.08 μg L^{-1} for As(III) with RSD equal 3.7 and 0.07 μg L^{-1} for As(V) with RSD equal 2.7. Also Samanta et al. [37] obtained limits of detection with similar order of magnitude as authors abovementioned. Limits of detection for the following chemical species: AsB, DMA(V), As(III), MMA(V), As(V) amount to 0.01, 0.02, 0.03, 0.02, 0.04 μg L^{-1}; respectively. However, the 3δ detection limits obtained by Verdon et al. [38] were significantly higher than those discussed above. Limits of detection were as follows: As(V) – 1.0 μg L^{-1}, As(III) – 1.2 μg L^{-1}, DMA(V) – 1.7 μg L^{-1}, MMA(V) – 0.9 μg L^{-1}, AB – 0.4 μg L^{-1}, AC – 0.6 μg L^{-1}, TMAO – 1.0 μg L^{-1}. Duarte et al. [39] obtained the following LOD results: 0.02 μg/L for As(III), 0.06 μg L^{-1} for DMA(V), 0.04 μg L^{-1} for MMA(V) and 0.10 μg L^{-1} for As(V). Day et al. [60] studied robustness of an arsenic speciation method in application to drinking water samples. Detection limits received for As(III), DMA(V), MMA(V) and As(V) were 0.067, 0.074, 0.035 and 0.089 μg L^{-1}; respectively. Milstein et al. [41] tested different mobile phases for speciation of four arsenic compounds (As(III), As(V), MMA(V), DMA(V)) in drinking water samples. In the case of phosphate mobile

phase, obtained limits of detection were: 0.3, 0.6, 0.3, 0.3 for As(III), DMA(V), MMA(V), As(V); respectively. In the case of TRIS mobile phase obtained limits of detection were more less tenfold lower: 0.03, 0.03, 0.06, 0.06 for As(III), DMA(V), MMA(V), As(V); respectively. Both Coelho et al. [42] and Morita et al. [50] procedured similar limits of detection, which were more less 0.2 $\mu g\,L^{-1}$. Ronkart et al. [43] obtained LOD values, which were closely the same for all arsenic compounds – 0.5 $\mu g\,L^{-1}$. Aim of the work of Sloth et al. [48] was to perform an arsenic speciation analysis of human urine samples. Authors obtained the following values of LOD: for As(III) – 0.08 $\mu g\,L^{-1}$, As(V) – 0.2 $\mu g\,L^{-1}$, MMA(V) – 0.05 $\mu g\,L^{-1}$, DMA(V) – 0.04 $\mu g\,L^{-1}$. The next few authors, obtained similar limits of detection for arsenic compounds. For example Xie et al. [51] for the following compounds: As(V), MMA(V), DMA(V), As(III) and AsB, obtained limits of detection, which amount to: 0.05, 0.4, 0.1, 0.06 and 0.02; respectively. Aim of the work of Shraim et al. [52] was to perform an arsenic speciation in tube-well water samples. Detection limits for As(III), DMA(V), MMA(V) and As(V) were 0.07, 0.1, 0.06 and 0.09; respectively. Roig-Navarro et al. [53] in their research described speciation analysis of four chemical forms of arsenic: As(III), As(V), MMA(V), DMA(V). The results indicated low limits of detection: for As(III) – 0.05 $\mu g\,L^{-1}$, As(V) – 0.03 $\mu g\,L^{-1}$, MMA(V) – 0.025 $\mu g\,L^{-1}$ DMA(V) – 0.02 $\mu g\,L^{-1}$. Raml et al. [63] obtained instrumental detection limits for thio-DMA and thio-Gly about 0.6 $\mu g\,L^{-1}$. Xie et al. [59] obtained the following limits of detection: 0.11 $\mu g\,L^{-1}$ for As(III), 0.25 $\mu g\,L^{-1}$ for As(V), 0.18 $\mu g\,L^{-1}$ for MMA(V), 0.17 $\mu g\,L^{-1}$ for DMA(V), 0.61 $\mu g\,L^{-1}$ for MMA(III), 0.44 $\mu g\,L^{-1}$ for DMA(III) and 0.75 $\mu g\,L^{-1}$ for AsB. Significantly lower limits of detection were obtained by Nakazato et al. [77], even despite the fact of very rich matrix (seawter samples). Authors obtained the following limits: As(III) 0.025 $\mu g\,L^{-1}$ for pure water and 0.057 $\mu g\,L^{-1}$ for 2% Cl-solution, As(V) 0.012 $\mu g\,L^{-1}$ for pure water and 0.116 $\mu g\,L^{-1}$ for 2% Cl-solution, MMA(V) 0.015 $\mu g\,L^{-1}$ for pure water and 0.083 $\mu g\,L^{-1}$ for 2% Cl-solution. Worse LOD's values were obtained by Nakazato et al. [80] in the next paper: 0.089 $\mu g\,L^{-1}$ for As(III), 0.34 $\mu g\,L^{-1}$ for As(V), 0.20 $\mu g\,L^{-1}$ for MMA(V) and 0.25 $\mu g\,L^{-1}$ for DMA(V). Milstein et al. [79] obtained similar results, which were in the range of 0.2 $\mu g\,L^{-1}$ for As(III) to 2.0 $\mu g\,L^{-1}$ for As(V) and MMA(V). The following ranges of detection limits: 0.3 $\mu g\,L^{-1}$ for As(III) – 1.3 $\mu g\,L^{-1}$ for As(V), and 0.26 $\mu g\,L^{-1}$ for MMA(V) to 0.48 $\mu g\,L^{-1}$ for DMA(V) were achieved by Wangkarn et al. [81] and Lindermann et al. [54], respectively. Other authors tested different solutions. Castillo et al. [49] in their work tested capabilities of micro columns in speciation analysis. Application of micro columns enabled to obtain significantly lower limits of detection, which were below 0.05 $\mu g\,L^{-1}$ for all arsenic species. Brennan et al. [65] applied nano-HPLC–ICP-MS method for arsenic speciation of As(III), DMA(V), MMA(V), As(V) and *p*-ASA. Authors obtained very low detection limits: 5.4 $pg\,L^{-1}$, 2.7 $pg\,L^{-1}$ for DMA(V), 2.7 $pg\,L^{-1}$ for MMA(V), 0.4 $pg\,L^{-1}$ for As(V) and 4.4 $pg\,L^{-1}$ for *p*-ASA. Besides the most often determined arsenic species: As(III), As(V), DMA(V) and MMA(V), authors quite often determine arsenobetaine and arsenocholine. For AsB, authors obtained different results: 0.01 $\mu g\,L^{-1}$ [37], 0.02 $\mu g\,L^{-1}$ [51], 0.024 $\mu g\,L^{-1}$ [43], 0.067 $\mu g\,L^{-1}$ [80], 0.4 $\mu g\,L^{-1}$ [38], 0.75 $\mu g\,L^{-1}$ [59] and 1 $\mu g\,L^{-1}$ [79]. Similar research was provided by Brennan et al. [55]. The results were in the range of 7.8 $\mu g\,L^{-1}$ for As(V) to 108 $\mu g\,L^{-1}$ for As(III). Some authors focus on speciation of rather seldom arsenic species. They obtained very satisfying results: 1.0 $\mu g\,L^{-1}$ for TMAO [38], 0.14 $\mu g\,L^{-1}$ for TMAO [80], 0.61 $\mu g\,L^{-1}$ for MMA(III) [59], 0.44 $\mu g\,L^{-1}$ for DMA(III) [59], 0.28 $\mu g\,L^{-1}$ for TMAs [80].

(c) *Limit of quantification*. Majority of the authors do not explain in their papers, the way of designation limit of quantification. Probably it was assumed as value corresponding to triple limit of detection, as it is the most often applied way. Only few authors placed details. Sathrughnan and Hirata [36] evaluated limit of quantification as a 6 standards deviations of standard addition into sample extracts. Also Wrobel et al. [46] calculated quantification limit from the 6 standard deviations of the noise level and obtained LOQs for: As(V) – 44 $ng\,L^{-1}$, MMA(V) – 56 $ng\,L^{-1}$, As(III) – 94 $ng\,L^{-1}$, DMA(V) – 64 $ng\,L^{-1}$ and AsB – 66 $ng\,L^{-1}$. However, Ronkart et al. [43] evaluated limit of quantification by analyzing ten samples containing an arsenical concentration close to the expected LOQ values: As(III) – 0.056 $\mu g\,L^{-1}$, As(V) – 0.085 $\mu g\,L^{-1}$, MMA(V) – 0.088 $\mu g\,L^{-1}$, DMA(V) – 0.076 $\mu g\,L^{-1}$, AsB – 0.08 $\mu g\,L^{-1}$. Higher LOQ's values, in the range of 0.6 $\mu g\,L^{-1}$ for MMA(V) to 3 $\mu g\,L^{-1}$ for As(V) were obtained by Milstein et al. [41]. Pouthieu et al. [40] obtained similar limits of quantification: 0.036 $\mu g\,L^{-1}$ for DMA(V), 0.09 $\mu g\,L^{-1}$ for As(V). However, results higher of about order of magnitude were received by Milstein et al.: As(III) – 0.8 $\mu g\,L^{-1}$, As(V), DMA(V), AsC – 5 $\mu g\,L^{-1}$, MMA(V) – 0.6 $\mu g\,L^{-1}$, AsB – 4 $\mu g\,L^{-1}$.

(d) *Precision*. Precision was most often determined as a value of relative standard deviation. As a rule, authors obtained low RSD values, the maximum value did not exceed 20% [39]. Usually, RSD values occurred on the level of 6 or 7% [37,38]. Milstein et al. [41] checked differences in precision between types of mobile phases. Short-term precision for phosphate buffer did not exceed 7%, however long-term precision was about 20% for phosphate mobile phase. For TRIS mobile phase short-term precision did not exceed 7%, however long-term precision was about 6%. Other authors [79] also investigated differences between short and long-term precision, the results were distinct, from 2% for As(III) to even 45% for As(V). Nakazato et al. [77] tested differences between precision for pure water and 2% Cl-solution, higher values of precision were obtained for chloride solution, the maximum for MMA(V). Coelho et al. [42] obtained relative standard deviations for As(III), DMA(V), MMA(V), As(V) were 1.2, 2.1, 2.5 and 3.0%, respectively. Next authors obtained similar RSD values in the following ranges: 2.0% for As(V) – 5.3% for MMA(V) [48] and 1.0% for DMA(V) – 5.9% [43]. Low values of precision obtained Wrobel et al. [38], maximum values was 5.3%. Lower relative standard deviations (less than 2%) were calculated by Morita et al. [50]. Another authors evaluated different RSD values depending on peak area and peak height. The maximum relative standard deviation for the retention time was below 2%. In the case of peak area and peak height precision, the highest values of precision obtained for peak height did not exceed 7% [54]. Precision values based on peak area did not exceed 5%, however precision values based on peak height were less then 7% [55]. Xie et al. [51] obtained the reproducibility ranged from 2% for As(V) to 10% for MMA(V). Good values of repeatability achieved by Roig-Navarro et al. [53] did not exceed 3.2%. Similar values of repeatability defined as relative standard deviation obtained Xie et al. [59], the maximum RSD value was 3.3%. Close precision values were obtained by few authors [36,46,48,49,51,52,60,80,81,83]: 1.7–3.7% for As(III), 1.15–3.9% for As(V), 0.69–3.5% for MMA(V), 0.84–5.2% for DMA(V), 1.3–5.5% for AsB. Also, in case of AsC and TMAO, results obtained by Verdon et al. and Nakazato et al. [38,80] were similar, and did not exceed 3.0% for AsC and 3.8% for TMAO. Equally good precision values were obtained for rarely determined arsenic species: 3.3% for TMAs [80], 1.9–6.0% for PAA [83], 1.7–2.8% for PAO [83], 1.8–3.2% for DPAA [83].

(e) *Recovery*. Recoveries estimated from the spiking of the urine samples with arsenic species were in the range of 82–101% [37]. Coelho et al. [42] for the analysis of beverages samples obtained recovery percentages in the range of 90.8–116.0%. Better recoveries for almost the same species were obtained by

Ronkart et al. [43] and they were ranging from 95 to 108%. The similar recoveries (between 90 and 110%) were obtained by Xie et al. [59]. Rabieh et al. [45] calculated recoveries from the sum of the species, the results were in the limit from 83.1 to 94.9%. Similar recoveries were obtained by Samantha et al. [37]. Recoveries better than 95% for all analyzed species were obtained by Xie et al. [51]. Similar recoveries (from 96 to 99%) were received by Day et al. [60]. Obtained by Shraim et al. [52], percentage recoveries for arsenic species were: 112% for As(III), 112% for DMA(V), 108% for MMA(V) and 97% for As(V), however Bednar et al. [57] procedured the following percentage recoveries: 112% for As(III), 99% for As(V). Milstein et al. [41] calculated recovery to be 93 ± 2%, which was expressed as the method accuracy, however recovery expressed as the instrument accuracy ranged from 102 ± 5% to 108 ± 3%. Roig-Navarro et al. [53] obtained good recoveries: 97% for As(III), 107% for As(V), 98% for MMA(V), 99% for DMA(V). However Castillo et al. [49] received the following recoveries: 95% for As(III) and As(V), 89% for MMA(V) and 105% for DMA(V). Quite similar results were obtained by Nakazato et al. [77]: As(III) – 87–104%, As(V) – 104–105%, MMA(V) – 92–94%.

(f) *Traceability*. Pouthieu et al. [40] focused on separation of six arsenic species (As(III), As(V), MMA(V), DMA(V), AsB, AsC, TMAO) in landfill leachate. Because of the lack of liquid certified material, validation process only concerns the analytical procedure not the whole protocol, as samples are prepared in different way. Authors of the paper validated the analytical separation and quantification by using certified reference material BCR-627, which have certified values for AsB and DMA(V). They obtained values comparable with certified values. The rest of the authors, whose paper works are included in this article, did not designate the traceability of particular species, because of the lack of certified reference material of chemical forms. However majority of papers contain traceability designated for total arsenic, and they are in good agreement with certified values.

The most important in arsenic speciation analysis, analytical performance parameters, such as: limit of detection, precision, recovery were assembled in Table 5. Additionally, injection volumes are placed to Table 5, as there exist strong dependence between these parameters. Noticeable is a rule, that very low value of precision accompanies also low limit of detection. In the articles, where recoveries were calculated, authors obtained good results, mostly recoveries were in the range of: 90–110%. No significant differences in limits of detection and precision values were ascertained.

9. Conclusion

Complete characterization of arsenic compounds is necessary due to its different toxicological effects demonstrated by particular arsenic species. In turn, the toxicity is directly related to arsenic mobility in water. As Table 2 suggests, arsenic imposes significant risk to the health of people all over the world. It is most often consumed with drinking water. Such species of arsenic regulations in water must be enforceable. For the control of the provisions there is a need for validated routine control methods. The main problem during determination of arsenic by ICP-MS is occurrence of interferences descended from sample matrix, especially from chlorides, which appear in every water sample. As arsenic is a monoisotopic element, another non-interfering isotope cannot be used. For that reason elimination of interferences may be carried out through using DRC or mathematical equation.

HPLC separation with ICP-MS detection represents the most popular combination of separation and detection technique for arsenic studies today. One of the most important advantages of LC is the extended range of separation mechanisms available using different mobile and stationary phases, which provide nearly all combinations necessary for the separation of arsenic species. Also application of ICP-MS gives great capabilities as it can be used as a highly sensitive and element-specific detector.

One of the most important problems concerning arsenic speciation analysis is difficulty in establishing traceability. Due to lack of certified reference materials, which have certified values of particular arsenic compounds and impossibility of using isotope dilution technique, the only way of establishing traceability is standard addition method.

Summarizing, HPLC–ICP-MS technique is recently the best one for arsenic speciation analysis. This kind of instrumentation provides, simple and reliable way to monitor and enforce legislation in water, if introduced, more reliable arsenic species data can be generated. This would facilitate the necessity and relevant progress in determining arsenic species and developing appropriate legislation.

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