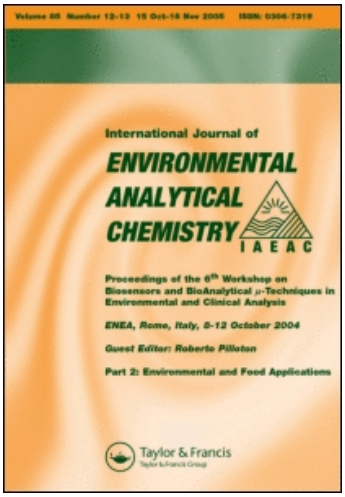

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Advances in arsenic speciation techniques

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To cite this Article Ali, Imran and Jain, Chakresh Kumar(2004) 'Advances in arsenic speciation techniques', International Journal of Environmental Analytical Chemistry, 84: 12, 947 — 964
To link to this Article: DOI: 10.1080/03067310410001729637
URL: http://dx.doi.org/10.1080/03067310410001729637

Intern. J. Environ. Anal. Chem.
Vol. 84, No. 12, pp. 947–964, 15 October 2004

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ADVANCES IN ARSENIC SPECIATION TECHNIQUES

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(Received 18 March 2004; In final form 30 April 2004)

The present review describes the speciation techniques of arsenic. The principal advanced techniques discussed are gas chromatography, reversed-phase liquid chromatography, ion chromatography, capillary electrophoresis. Some other techniques are also mentioned. The extraction procedures of arsenic species from unknown samples are also discussed. Arsenic speciation is summarized in tabular form and optimizing parameters are also discussed.

Keywords: Arsenic; Speciation; Sample preparation; Gas chromatography; Reversed-phase high-performance liquid chromatography; Ion chromatography; Capillary electrophoresis

INTRODUCTION

Metal ions are essential components of biological systems; nevertheless, even essential elements may have toxic or carcinogenic properties. Heavy metals occur in the environment in different physico-chemical forms. Simple hydrated species are generally the toxic ones, while strong complexes and species associated with colloidal particles are usually assumed to be non-toxic. Organometallic compounds are more toxic than their corresponding inorganic species except in the case of arsenic. Many metallic ions in the environment are differentiated not only by their physical and chemical forms, but also by diverse toxicities (speciation). The speciation affects the bio-availability and toxicity of elements and, hence, is important in the areas of toxicology and nutrition. The exploitation of speciation profiles in many environmental samples is widely unexplored [1].

The elements occur in the environment in different oxidation states and species, e.g., As as As(V), As(III) and As(0); Sb as Sb(V), Sb(III), Sb(0) and Sb(−III); and Se as Se(VI), Se(IV), Se(0) and Se(II). In an oxidized environment As, Sb and Se appear mostly as oxyanions. The valency state of an element plays an important role in its behavior in the aqueous system. For example, the toxicity of As(III) and Sb(III) is higher than that of their pentavalent species. Briefly, the toxicities of the different oxidation states (species) of a particular metal ion may be different and one

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ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/03067310410001729637

of the species may be more toxic. Arsenic is one of the oldest poisons used by man. International legislation concerning arsenic in food, environment and occupational health regulations are based on the total element contents, and are frequently given as maximum limits or guideline levels. But no regulation pays attention to the molecular species of arsenic in which the element is present. The present existing data on the toxicity due to the total concentration of a particular species is not sufficient to describe the exact toxicity, as the different species may have different toxicities. Therefore, to describe the exact toxicity of the metal, there is a great need to find out the toxicities of the different forms of arsenic [1].

OCCURRENCE OF ARSENIC

Arsenic contamination is a world-wide problem and has become a challenge for world scientists. Recently, it has been reported from several parts of the world including USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India [2–5]. Hering and Elimelesh [6] reviewed the international perspectives and treatment strategies on the problem of arsenic contamination in groundwater. Arsenic is distributed widely including ground and surface waters, soil, sediment, animals, humans, plants and some foodstuffs. Briefly, arsenic has been distributed into the lithosphere, atmosphere, pedosphere, hydrosphere, biosphere and anthroposphere [7]. Arsenic rarely occurs in the free state and is largely found in combination with sulphur, oxygen and iron. Arsenic occurs in the environment as a result of several inputs that contain the element in organic and inorganic forms [8]. The presence of arsenic in natural water is related to the process of leaching from arsenic-containing rocks and sediments [6]. Influx of arsenic from various anthropogenically induced sources may also contaminate both soils and groundwater, especially under anoxic conditions [9].

The presence of arsenic in groundwater is generally associated with geochemical environments such as basin-fill deposits of alluvial–lacustrine origin, volcanic deposits and inputs from geothermal sources and mining wastes [10,11]. Uncontrolled anthropogenic activities such as smelting of metal ores and the use of arsenical pesticides and wood preservatives may also release arsenic directly to the environment [12]. The occurrence of arsenic in natural water depends on the local geology, hydrology and geochemical characteristics of the aquifer. Furthermore, organic content in sediments as well as the land-use pattern may also play an important role in controlling the mobility of arsenic in alluvial aquifers. The oxidation of different mineral species causes arsenic to become soluble and enter the surrounding environment through drainage water. Knowledge of the geographical distribution of As(III) and As(V) species in the natural water system is important for the environmental consideration of the geochemical and biological cycling of the element. Furthermore, this will also provide insight into the geochemical processes responsible for elevated arsenic concentrations in some geological environments.

SAMPLE PREPARATION

Arsenic species are present in very low concentrations in the environment and biological samples and their speciation is therefore, a tedious job. Thousands of compounds

are present as impurities along with metal ions in unknown samples. Samples containing a high ionic matrix cause problems in capillary electrophoresis (CE) as the high ionic strength imparts a low electric resistance, resulting in very poor and broad peaks. In addition, electroosmotic flow (EOF) in the capillary is altered by the influence of the sample matrix, which may result in poor separation. Also, the detector baseline is usually perturbed when the pH of the sample differ greatly from the pH of background electrolyte (BGE). Samples containing UV-absorbing impurities may be problematic in the detection of metal ions by both chromatography and CE. Under such circumstances, sample preparation is essential before starting speciation analysis. Some review articles have appeared in the literature on this issue [13–19]. Gomez-Ariza *et al.* [16] have reviewed strategies for the extraction, concentration and derivatization of environmental samples before loading onto the chromatographic column. Basically, sample collection, storage, extraction, purification and pre-concentration are the main steps required in sample preparation. Most arsenic speciation was carried out in laboratory-synthesized samples (Table I) so only a few reports are available on sample preparation. However, a brief description of sample preparation techniques is given here.

Acidification of water or other liquid samples is a common practice to stop adsorption and exchange processes but it is not suitable if the sample contains organometals, which may be degraded in acidic conditions. Feldmann *et al.* [20] investigated the effect of acid (HCl) and additives [sodium azide (NaN_3), benzyltrimethylammonium chloride ($BzMe_3NH_4Cl$), benzoic acid (BzAcid), cetylpyridinium chloride (Cetyl) and methanol (MeOH)] on arsenicals in urine samples. The authors reported the degradation of organoarsenicals in acidic samples with some additives. Since 1970, acid homogenization methods have been used for the extraction of metal ions from solid environmental and biological samples. Normally, concentrated nitric acid is used for homogenization of soil and sediment samples but, sometimes, mixtures of nitric acid, sulfuric acid, hydrochloric acid, perchloric acid, etc., are used to digest the samples. Toluene, methanol, etc. are suitable solvents for homogenization of biological samples but dilute acids may sometimes be used with the solvents under special conditions. Extraction follows filtration, in case of water or liquid biological samples, while it follows homogenization in case of solid samples. Liquid–liquid extraction, solid-phase extraction and liquid chromatographic techniques are all used.

The extraction of solid samples is started during the homogenization procedure, which involves the use of a variety of solvents. The most commonly used solvents are water, water–methanol or water–methanol–chloroform mixtures. Soxhlet extraction, sonication, microwave-assisted extraction, accelerated solvent extraction and supercritical-fluid extraction (SFE) are popular extraction methods nowadays. Sonication helps in the homogenization of solid samples and consequently can be used for the rapid and easy extraction of metal ions from the samples. Microwave-assisted extraction (MAE) involves heating of solid samples with a solvent or solvent mixtures using microwave energy, and the subsequent partitioning of the compounds of interest from the sample to the solvent. It has the potential to be a direct replacement for the conventional Soxhlet extraction technique for solid samples. Gomez-Ariza *et al.* [21] carried out microwave-assisted extraction for organarsenic species using methanol for 10 min at 150 W. Similarly, Dagnac *et al.* [22] also reported the microwave-assisted extraction of organoarsenicals using a methanol–water (1 : 1) mixture for 5 min at 50 W.

Soxhlet extraction was developed by the German scientist Franz von Soxhlet in 1879 and is a good extraction method for organometallic species from solid samples,

TABLE I Arsenic speciation by GC, RP-HPLC, IC and CE

Metal ions	*Matrix*	*Columns*	*Detection*	*Ref.*
Gas chromatography (GC)				
As(III), As(V), organic arsenic	–*	Fused silica	FID	39
Thioarsenites	–	–	MS-AES	40
MMA, DMA	Urine	–	MS (0.12–0.29 ng/mL)	33
As species	Soil	–	ICP-MS (ng to μg levels)	41–43
As species	–	HP-1	MS-PFPD (Det. Sen: 1 pg/s)	32,44
Reversed-phase High-performance liquid chromatography (HPLC)				
AsB $[(CH_3)_3As^+CH_2COOH]$, AsC $[(CH_3)_3As^+CH_2CH_2OH]$	–	Reversed phase	THG	47
As(III), As(V), MMA, DMA	Urine	C_{18} columns	ICP-MS, HGAFS (0.4–0.8 ng/mL)	48
As(III), As(V)	–	ICP-MS		41
AS(III), As(V)	Urban aerosol	Adsorbosphere SAX	HGAFS (0.12–0.63 ng/mL)	49
AS(III), As(V)	–	C_{18} column	HG-ICP-AES	50
Arsenosugars, a quaternary arsonium compound (arsenobetaine), DMA, dimethylarsinoylacetic acid	Algae	–	–	51
As species	–	ODS-3 RP	–	52
MMA, DMA	Urine	ODS-3 RP	HGAFS (sub to low μg/L)	53
As(III), As(V)	Mineral waters	–	HG-AFS	54
As(III), As(V)	–	Econosil C_{18}	UV/VIS (0.01–1.0 μg/mL)	1
MMA, DMA	Human urine	ODS column	ICP-MS	103
MMA, DMA	Wine	ODS column	ICP-MS	104
As(III), As(V), MMA, DMA	–	C_{18} column	ICP-MS (0.1 μg/L)	105
As(III), As(V), MMA, DMA	–	C_{18} column	UV-HG-QF-AAS	30
As(III), As(V), MMA, DMA	–	C_{18} column	ICP-MS	106
As species	–	C_{18} column	–	107
As species	Soil	Dionex AS 7, AG 7	ICP-MS (0.04-0.06 μg/L)	29
Ion chromatography (IC)				
As(III), As(V), MMA, DMA, AsB, AsC	Env. Samples	Hamilton	HG-AAS PRP-X-100	58
As(III), MMA, DMA, AsB, AsC, TMAO, tetramethylarsonium ion	–	Hamilton PRP-X-100 & Supelcosil SAX 1	HG-AAS	59
MMA, DMA, AsC, AsB, TMAO, TMA	–	IonoPac AS4-SC	ICP-MS	60
AcC, AsB, DMA, MMA, arsenous acid, arsenic acid	–	Hamilton PRP-X-100	ICP-MS	61
As(III), As(V), MMA, DMA	Aerosol	Adsorbosphere XAX	HG-AFS	49
As(III), As(V)	Water	Anion exchange	AAS-Graphite	62
As(III), As(V), MMA, DMA	–	Anion exchange	ICP-MS (2–13 ng/L)	63
As(III), As(V), MMA, DMA	–	IonPac AS11	ICP-MS	64

As(III), As(V), MMA, DMA, PAA	–	Anion exchange	ICP-MS	65
As(III), As(V), MMA, DMA	–	AS11	HG-AFS	108
As(III), As(V), MMA, DMA, AsC, AsB, TMA, TMAO	–	Anion exchange	ICP-MS	25
As(III), As(V), MMA, DMA	–	Ion 120	ICP-MS (0.02–0.05 μg/L)	66
As(III), As(V), MMA, DMA	Water	Anion exchange	ICP-MS (40–60 ng/L)	67
As(III), As(V), MMA, DMA	–	Anion exchange	ICP-MS	68
As(III), As(V), MMA, DMA	–	Hamilton PRP-X-100	ICP-AES (0.34–0.56 mg/L)	69
As(III), As(V)	Seaweeds	Cation exchange	ICP-MS	70
As(III), As(V), MMA, DMA	–	Ionopac CS 10	AAS-Hyd. (1.0–1.4 μg/L)	30
As(III), As(V), MMA, DMA	Water	Anion exchange	–	71
DMA, AsB	Urine	Cation exchange	HG-AAS	72
As(III), As(V), MMA, DMA	Cold drinks	–	ICP-MS	108
As species	–	Cation exchange	UV	73
As(III), As(V), DMA, MMA, AsB, AsC	–	–	ICP-MS (0.5 μg/L)	74
As(III), As(V), DMA, DMA	–	–	ICP-AES	75
As(III), As(V), MMA, DMA	–	–	ICP-MS	76
As(III), As(V), MMA, DMA	Plants	–	HG-AFS	77
As(III), As(V), MMA, DMA, AsB, AsC, TMAO, TMA	Fish	–	ICP-MS	79
As(III), As(V), MMA, DMA	Water	Hamilton PRP-X-100	HG-QF-AAS	109
As(III), As(V), MMA, DMA	–	SAX & PRP-X	–	110
MMA, DMA	–	AG 50 W-X8	HG-AAS	111
As(III), As(V), MMA, DMA, AsB, TMA, AsC	–	Anion & cation	ICP-MS	112
As(III), As(V), MMA, DMA, AsB, TMAs, AsC	–	PRP-X100	ICP-MS	113
As(III), As(V), DMA, PhAs	–	ASGA	ICP-AES	114
As(III), As(V), DMA, AsB	Seaweed	Nucleosil-10	ICP-AES	115
As(III), As(V), DMA, AsB, AsC	River water	Anion exchange	ICP-MS	116
As(III), As(V), DMA, AsB, AsC	Biol. samples	Hamilton PRP-X-100	ICP-MS	117
Selenous acid, selenic acid, selonocystine, selenohomocystine, SeThr, $SeMe_3$	–	Supelcosil LC-SCX	ICP-MS	118
AsB, AsC, TMAs	–	Cation exchange	HG-AAS	47
As species	–	Cation exchange	ICP-MS	72
Capillary electrophoresis (CE)				
Arsenic species	Water	–	Conductivity (0.4 mg/L)	92
As species	–	–	Indirect UV (10^{-4} M)	94
As(III), As(V), MMA, DMA	–	–	ICP-MS (1 μg/L)	91
As(III), As(V), MMA, DMA	–	–	Direct UV (0.8 mg/L)	93
As(III), As(V), MMA, DMA	–	–	Indirect UV (0.4 mg/L)	27
As(III), As(V), MMA, DMA	–	–	ICP-MS (20–100 ng/L)	86
As(III), As(V), MMA, DMA	–	–	Direct UV (0.4 mg/L)	92
As(III), As(V), MMA, DMA	–	–	Direct UV	85
As(III), As(V), MMA, DMA, AsB, AsC	Sewage sludge	–	ICP-MS (15 μg/L)	89,90
As species	Drinking water	–	HG-ICP-MS ICP-MS (6 ng/L)	87,88
As species	Drinking water	–	Direct UV (0.8 μg/L)	93
As species	–	–	Proton induced X-ray emission (10^{-4} M)	94

*Information not available.

especially for organometallics having high volatility. Classical Soxhlet extraction is a simple and effective but relatively expensive method as it requires large amounts of organic solvents. Automatic Soxhlet assemblies are now available that involve the minimum amount of organic solvents (100–50 mL) [23]. Accelerated solvent extraction (ASE) works at elevated temperature and pressure using a small amount of solvent. The restrictions and limitations of this method are generally similar to those of Soxhlet extraction technology. Gallagher *et al.* [24] used an accelerated solvent extraction device for the extraction of arsenicals from ribbon kelp. The authors studied the effect of pressure, temperature, static time and solvent compositions on arsenic species, extraction. Supercritical-fluid extraction (SFE) is a selective technique of sample preparation, enabling the preparation of matrices by varying several parameters. Nowadays, it is considered as the best replacement for many extraction technologies such as accelerated solvent, Soxhlet solvent, microwave-assisted, etc.

Liquid–liquid extraction is a classical method carried out using a variety of solvents, but this technique is tedious and time consuming. Moreover, the wastage of large amounts of costly chemicals is a major drawback of this technique. Schmidt *et al.* [25] carried out the extraction of arsenicals using pressurized-liquid extraction (PLE) at different temperatures. The authors used 60–180°C as the working temperature, with water as the extracting solvent. The recoveries of arsenicals were higher at higher temperatures. Temperature is the most important experimental parameter for extraction and, hence, the maximum extraction can be achieved by varying the temperature and other experimental conditions. Yang *et al.* [26] used sodium hydroxide solution for the extraction of arsenic species from soil samples. Lin *et al.* [27] used an alkaline solution (pH 10) for the extraction of inorganic arsenic from coal fly ash. Schlegel *et al.* [28] carried out liquid–liquid extraction of arsenic species from lettuce samples using perchloric acid. Pongratz [29] extracted arsenic species from soil samples using water. Zhang *et al.* [30] used deproteinization and centrifugation methods to extract arsenic species from human serum.

The solid-phase extraction (SPE) technique is free from the drawbacks of liquid–liquid extraction and is very fast and sensitive with the recovery of metal ions ranging from 90 to 95%. SPE offers the advantages of convenience, cost saving and minimal consumption of solvents [31], and, hence, more than 50% analytical chemists are using this method for sample preparation. Various columns, disks and cartridges have been used for the extraction with the use of cartridges preferred as liquid flows more rapidly than in disks. Mothes and Wennrich [32] equilibrated arsenic metal ions on 100-μm PDMS solid support and reported the different equilibrium times indicating 50–60 min as the equilibrium. The authors also reported the effect of temperature, pH, headspace mode of sampling and the storage of the loaded solid support on the extraction of metal ions. Mester and Pawliszyn [33] used solid-phase micro extraction (SPME) fibers for the extraction of arsenicals from human urine samples.

The chromatographic techniques used for extraction are column chromatography (CC), high-performance liquid chromatography (HPLC), supercritical-fluid chromatography (SFC), gel-permeation chromatography (GPC), etc. The popularity of chromatographic techniques is due to their manifold developments and applications. Moreover, rapidity and low consumption of costly solvents are other assets of chromatographic methods. If metal ions present in solid samples are polar the extraction is normally carried out in aqueous solvents. If gas chromatography is required for

the analysis, the already extracted metal ions (in aqueous solvent or water) are further extracted into organic solvents. Contrary to this, metal ions present in an organic solvent are extracted into an aqueous solvent if the analysis is carried out by capillary electrophoresis.

Generally, a clean-up procedure is required only for those samples that are not clear or contain impurities. Mostly it is samples of blood, serum, food, plant extract and industrial and municipal effluents that require clean-up procedures. The maximum recovery of metal ion is very important. Clean-up of the extracted metal ions may be carried out by column chromatography, gel-permeation chromatography, sweep co-distillation, liquid–liquid partition, cartridges and disks. Generally, the concentration of metal ions in environmental and biological samples is below the detection limits of modern detectors, and pre-concentration of the extracted samples is required. The classical approach of solvent evaporation is used to concentrate the extracted metal ions. However, some other devices, such as purge and trap devices with cryogenically cooled capillary traps, have also been used for pre-concentration.

Recent advances in extraction have been techniques reported in the literature and these include the hyphenation of extraction methods with chromatographic and capillary electrophoretic techniques. Whang and Pawliszyn [34] designed an interface that enables the solid-phase micro extraction (SPME) fiber to be inserted directly into the injection end of a CE capillary. They prepared a semicustom-made polyacrylate fiber to reach the SPME-CE interface. Similarly, Huen and co-workers [35] developed SPE coupled with HPLC. Brinkman [36] has been a leader in applying column switching to the real world problem and has extended his work on the extraction of polar pollutants in river water using SPE coupled with liquid and gas chromatographic machines separately. Van der Hoff *et al.* [37] described automatic sample preparation with extraction column (ASPEC) coupled with a gas chromatographic (GC) system. The authors used a loop-type interface for coupling ASPEC to the GC machine. Yin *et al.* [38] reported solid-phase extraction pre-concentration, incorporated in a flow-injection (FI) system high-performance liquid chromatography (HPLC).

SPECIATION TECHNIQUES

UV-visible spectroscopic methods provide the classical approach to arsenic speciation. More recently atomic absorption spectrometry (AAS), inductively coupled plasma (ICP) and hydride generation (HG) have been introduced into spectroscopic methods. However, certain drawbacks prevented these methods achieving the status of routine laboratory analysis. The major problems associated with spectroscopic techniques are their ineffective coupling with some accessories, such as FIAS, HG, atomic furnaces, etc. The reproducibilities of these techniques for arsenic speciation are not good. Moreover, the conversion of one oxidation state into another is a tedious and time-consuming job, which also requires costly chemicals. Owing to these drawbacks, other chromatographic and capillary electrophoretic methods have emerged as the best alternatives for arsenic speciation. Nowadays, these modalities are considered to be the most advanced for investigating speciation. The intention of this article is to provide complete information on arsenic speciation, including extraction procedures, using the cited techniques.

Chromatographic Techniques

Chromatographic methods, such as gas chromatography (GC), reversed-phase high-performance liquid chromatography (RP-HPLC) and ion chromatography (IC), are currently being widely used for arsenic metal ion speciation. Among various versions of capillary electrophoresis, capillary zone electrophoresis (CZE) has been commonly used for arsenic speciation.

The speciation of arsenic by these techniques is discussed in the following sections.

Gas Chromatography

Gas chromatography is used for the speciation of metal ions that are volatile at the working temperature, so it has been successfully used for the speciation of organo-arsenicals. Non-volatile arsenic species are converted into the volatile ones by the derivatization process. GC has achieved a good status in arsenic speciation owing to its development and the use of modern detectors. The coupling of GC with flame ionization (FID), electron capture (ECD), flame photometric (FPD), mass spectrometer (MS), atomic absorption spectrometer (AAS), atomic emission spectrometer (AES), inductively coupled plasma (ICP), etc. detectors makes this technique a popular tool for arsenic speciation. The high separation power of GC columns with the excellent detection limits of modern detectors is an advantage in speciation technology. The speciation of arsenic by GC is controlled by a number of parameters. The most important factors are the nature of the stationary phase (column), mobile phase, temperature of the column, injector and detector, derivatization, amount of injection loading and the sensitivity of the detector.

Dix *et al.* [39] determined inorganic (arsenite, arsenate) and organic [monomethylarsonate (MMA), dimethylarsinate (DMA)] arsenic species by capillary gas chromatography on wide-bore borosilicate glass and fused-silica columns. Schoene *et al.* [40] converted various organoarsenic halogenides, oxides and hydroxides into the corresponding thioarsenites by reaction with thioglycolic acid methyl ester (TGM). The yields and the chemical structures of the TGM derivatives were evaluated by gas chromatography coupled with mass spectrometry and atomic emission spectrometry. Mester and Pawliszyn [33] analyzed DMA and MMA using solid-phase microextraction–gas chromatography–mass spectrometry (SPME-GC-MS) with a detection limit of 0.12 and 0.29 ng/mL, respectively. Prohaska *et al.* [41] used GC coupled to a double focusing sector field ICP-MS for the speciation of arsenic in liquid and gaseous emissions from soil samples, which were equilibrated in a microcosmos experiment. They described a home-built and laboratory-ready transfer line from GC to ICP-MS. Quantification of arsenic in gaseous emissions was performed by external calibration via hydride generation. The microcosmos experiment revealed only low production rates of organoarsenic compounds with a limited ability of the bio-volatilization experiment to simulate natural systems. Grüter *et al.* [42] improved the speciation technique for arsenic by enabling its identification and quantification in soil samples of municipal waste deposits. The hydride generation/low-temperature gas chromatography–inductively coupled plasma–mass spectrometry (HG/LT-GC/ICP-MS) apparatus containing a home-made gas chromatograph allowed satisfactory separation of arsenic species with a boiling point difference of 14°C. The absolute detection limit for the element was below 0.7 pg/L. Furthermore, the same group [43] used high-generation low-temperature gas chromatography–inductively coupled mass spectrometer coupling

for the efficient detection of arsenic species. The analyzed species were AsH_3, $(CH_3)AsH_2$, $(CH_3)_2AsH$ and $(CH_3)_3As$. Killelea and Aldstadt [44] developed a novel method for arsenic speciation using capillary gas–liquid chromatography with simultaneous quadrupole ion-trap mass spectrometric (MS) and pulsed flame-photometric detections (PFPD). The method coupled the sensitive arsenic selectivity of PFPD with the structure elucidation capability of molecular MS detection for the determination of trace levels of unknown organoarsenicals in complex matrices. The conditions that affected the PFPD response in the presence of interfering species were optimized using the sequential simplex algorithm for three key factors, i.e., gate delay (18.3 ms), gate width (9.1 ms) and combustion gas composition (16.6 mL/min H_2). Mothes and Wennrich [32] analyzed the species of arsenic on an HP-1 (25 m × 320 μm, 0.17 μm id) column using nitrogen as the mobile phase.

In spite of having many advantages, GC suffers from certain drawbacks as the derivatization procedure of arsenic metal ions, particularly in the most contaminated environmental samples, is a major problem. Moreover, the derivatization is a tedious job, which consumes costly chemicals. In addition, the extraction of the samples requires specific attention, otherwise a problem/error may occur in the derivatization procedure. Scientists have therefore shifted their attention towards liquid chromatographic approaches (RP-HPLC and IC).

Reversed-phase High-performance Liquid Chromatography

Reversed-phase high-performance liquid chromatography (RP-HPLC) has emerged as a technique of choice in analytical science since 1980. It has been used widely for the speciation of many metal ions using a variety of reversed-phase columns and mobile phases. The hyphenation of electrochemical detection, ICP, MS, AAS, etc. is successful in RP-HPLC. This technique has the advantage of performing separations of non-volatile arsenic species; thus it has greater versatility than GC, which often requires a derivatization of inorganic arsenic species. Reversed-phase HPLC uses non-polar solids of high surface area with more polar aqueous solutions as the mobile phase. The most widely used columns are C_2, C_8 or C_{18} while the mobile phases used are buffers. Sometimes, a counterion is added to the mobile phase in reversed-phase HPLC and the technique is called reversed-phase ion-pair HPLC. Ion-pair chromatography is also known as soap chromatography, ion-interaction chromatography and dynamic ion-exchange chromatography. The counterion is typically referred to as the ion-pair reagent, consisting of a polar head and a non-polar tail. This method has also been used for the speciation of charged and uncharged arsenic species. If the counterion is a surfactant a micelle is formed and this sort of HPLC is referred to as micellar HPLC. A number of monographs and reviews have been published on the speciation of many metal ions by reversed-phase HPLC [45,46].

A detail study of the speciation of arsenobetaine, arsenocholine and tetramethylarsonium ion was carried out by Balis *et al.* [47]. The authors used AAS detection through a new on-line thermochemical hydride generation interface (THG) in HPLC. A novel high-performance liquid chromatography–atomic absorption spectrometry (HPLC-AAS) interface based on thermochemical hydride generation for the determination of arsenobetaine [$(CH_3)_3As^+CH_2COOH$], arsenocholine [$(CH_3)_3As^+CH_2CH_2OH$] and tetramethylarsonium [$(CH_3)_4As^+$] cations has been described [48]. Slejkovec *et al.* [49] used an analytical procedure for the speciation of arsenic in urban aerosol samples

using HPLC. The aerosols were collected by sequential filtration through membrane filters. Do *et al.* [50] used a C_{18} column in HPLC with hydride-generation–inductively coupled plasma–atomic emission spectrometry (HG-ICP-AES) for the speciation of four arsenic species, i.e., arsenite As(III), arsenate As(V), MMA and DMA. This analytical method allowed the sensitive determination of arsenic species in the sub-microgram per liter range. Pederson *et al.* [51] used a single quadrupole high-performance liquid chromatography electrospray mass spectrometry system, with a variable fragmentor voltage facility in the positive ion mode, for simultaneous recording of elemental and molecular mass spectral data for arsenic compounds. The method was applicable to seven organoarsenic compounds tested, i.e., four arsenic-containing carbohydrates (arsenosugars), a quaternary arsonium compound (arsenobetaine), DMA and dimethylarsinoylacetic acid. However, it was not suitable for the separation of two inorganic arsenic species, e.g., arsenite and arsenate. In the case of arsenosugars, qualifying ion data for a characteristic common fragment (m/z 237) was also simultaneously obtained. The method was used to identify and quantify the major arsenosugars in crude extracts of two brown algae. Saeki *et al.* [52] described the speciation of arsenic using an ODS reversed-phase column. Gong *et al.* [53] speciated MMA and DMA using an ODS-3 reversed-phase column with 4.7 mM tetrabutylammonium hydroxide, 2 mM malonic acid and 4% methanol (pH 5.85) as the mobile phase. Van Elteren *et al.* [54] speciated As(III) and As(V) in five bottled mineral waters from the Radenska and the Rogaska springs (Slovenia). A hyphenated technique (HPLC-HGAFS) and a more conventional technique, based on selective co-precipitation of As(III) with dibenzyldithiocarbamate prior to arsenic analysis (FI-HG-AFS), were used. The techniques yielded data that were not significantly different on the 5% level, with HPLC-HG-AFS being the least sensitive (detection limit of 1 μg/L), and the selective co-precipitation technique found to be suitable for sub-picogram per liter levels (with detection limit of 0.05 μg/L). The latter technique showed recoveries of $96.4 \pm 0.4\%$. Recently, Ali and Aboul-Enein [1] have achieved the speciation of the arsenic metal ion [As(III) and As(V)] on an Econosil C_{18} (250×4.6 mm id, particle size 10 μm) column. The authors used water–acetonitrile (80 : 20, v/v) as the mobile phase with detection by UV at 410 nm and AAS respectively and separately. High-performance liquid chromatography combined on-line with a quadrupole inductively coupled plasma mass spectrometer was used for arsenic speciation by D'Amato *et al.* [55]. Four species of arsenic detected: As(III), As(V), DMA and MMA at concentrations of 88.2 ± 7.1, 51.2 ± 3.5, 50.8 ± 5.0 and 15.2 ± 1.7 ng/g respectively. Rattanachongkiat *et al.* [56] described HPLC-ICP-MS methods for the speciation of As(III), As(V), AsB, DMA and MMA in biological and environmental samples.

To achieve the maximum speciation of arsenic by RP-HPLC in environmental samples, optimization of the experimental parameters is vital. Optimization may be achieved by using suitable reversed-phase columns and mobile phases. Other controlling factors are pH and the concentrations of the mobile phases. The detection, extraction of the environmental samples and amount injected on the RP-HPLC machine may also be used to control the speciation in reversed-phase HPLC.

Ion Chromatography

Ion chromatography (IC) is the advanced version of reversed-phase HPLC, where the reversed-phase column of RP-HPLC is replaced by an ion-exchange column.

Earlier, it was known by the name of ion-exchange chromatography but with the development of various ion-exchange columns its name has been replaced by ion chromatography. It has been used widely for the speciation of all inorganic and organic metal ions, including ionized species. The development of a variety of ion-exchange columns makes it the best technique in metal ion speciation. In IC, anion and cation exchange columns are used but, nowadays, mixed (anion and cation) columns are also available, which have improved the separation efficiency. In cation exchange chromatography, the stationary phase is usually composed of resins containing sulfonic acid groups or carboxylic acid groups with negative charges and, thus, cationic metallic species are attracted to the stationary phase by electrostatic interactions. In anion exchange chromatography, the stationary phase is a resin generally containing primary or quaternary amine functional groups with a positive charge and, hence, these stationary phase groups attract solutes with negative charge. Generally, chromatographic separation of metal ions on anion exchange columns requires the presence of negatively charged complexes. The complexation can be obtained by off-line or on-line methods using a suitable ligand. The hyphenation of IC with advanced detectors in this technique is similar to RP-HPLC. Many detection devices such as electrochemical detection, conductometric detection, ICP, MS, AAS, etc. are used for the detection of metallic species.

The speciation of arsenic in seawater or brine is difficult by IC as the high ionic strength of seawater or brine samples swamps ion exchange columns. For these kinds of applications, the selectivity of the separation can be enhanced by using chelating reagents in the mobile phase and this modality is called chelation chromatography. In chelation chromatography, either the chelating reagent is chemically bonded to stationary phases; where complexation reactions in the stationary phase (ion exchange due to free or protonated chelating groups act as ion exchange resin sites) or chelating agents added to the mobile phase are responsible for the separation. Two main approaches can be followed to obtain an appropriate stationary phase: (i) chemical bonding of the chelating groups to the substrate and (ii) coating of a substrate with a ligand that is permanently trapped onto the substrate. This mode of chromatography is not popular owing to its limited application. However, a few reports are available on arsenic speciation using this method [57].

The speciation of arsenic metal ions mostly uses anion exchange columns. However, some reports are also available on arsenic speciation using cation exchange and mixed exchanger columns. Martin *et al*. [58] developed an on-line ion chromatography–microwave-assisted oxidation–hydride generation–atomic absorption spectrometric (HG-AAS) system (using columns of different kinds) for the determination of arsenite, arsenate, dimethylarsinate (DMA), monomethylarsonate (MMA), arsenobetaine (AsB) and arsenocholine (AsC) in environmental samples. The anion exchange Hamilton PRP-X100 anionic column has been proposed for the determination of six species. Tsalev *et al*. [59] coupled IC with continuous-flow hydride-generation atomic absorption spectrometry (HG-AAS) for the speciation of As(III), monomethylarsonate, dimethylarsinate, arsenobetaine, arsenocholine, trimethylarsine oxide and tetramethylarsonium ion. The authors used anion exchange columns, i.e., Hamilton PRP-X100 and Supelcosil SAX 1, and gradient elution with phosphate buffers containing KH_2PO_4–K_2HPO_4. Mattusch and Wennrich [60] reported the separation of MMA, DMA, arsenocholine (AsC), arsenobetaine (AsB), trimethylarsine oxide (TMAO) and tetramethylarsonium bromide (TMA) using an anion exchange (IonoPac AS4-SC)

column. The authors used 5 mM sodium carbonate, 40 mM sodium hydroxide and 4% methanol as the mobile phase with detection by ICP-MS. Zheng *et al.* [61] speciated six arsenic compounds in human urine samples, including arsenocholine, arsenobetaine, dimethylarsinic acid, methylarsonic acid, arsenous acid and arsenic acid on a Hamilton PRP-X100 anion exchange column using isocratic elution and detected by inductively coupled plasma mass spectrometry (ICP-MS). Slejkovec *et al.* [49] developed an IC-HG-AFS system for the speciation of arsenite, arsenate, MMA and DMA in aerosol samples using an anion exchange column, i.e., Adsorbosphere SAX. The authors used 10 mM KH_2PO_4 (pH 6.0) as the mobile phase. Miller *et al.* [62] used an anion exchange column for the separation of arsenate and arsenite species. Ion exchange separations were performed for four arsenic species common in drinking water sources. Gettar *et al.* [63] developed an analytical method for the specific determination of arsenite, arsenate, MMA and DMA using ion chromatography. Different types and sizes of anion exchange columns, silica and polymeric, were tested using EDTA as eluent. The method is based on an ion chromatographic separation coupled on-line to post-column generation of the gaseous hydrides by reaction with sodium tetrahydroborate in acidic medium. Bissen and Frimmel [64] speciated As(III), As(V), MMA and DMA arsenic species by IC with separation on anionic exchange column [IonPac AS11 (Dionex)] with NaOH as the mobile phase and detection by ICP-MS. The technique was successfully applied to analyze extracts of two contaminated soils sampled at tannery and paint production sites. Lindemann *et al.* [65] performed speciation analysis of As(III), As(V), AsB, MMA, DMA and phenylarsonic acid (PAA) by on-line coupling of anion exchange IC with inductively coupled plasma mass spectrometry (ICP-MS). Schmidt *et al.* [25] reported the speciation of As(III), As(V), MMA, DMA, AsC, AsB, TMA and TMAO species using an anion exchange column. The eluents used were 0.4 mM HNO_3 containing 0.05 mM benzene-1,2-disulfonic acid with detection by ICP-MS. Roig-Navarro *et al.* [66] reported the analysis of As(III), As(V), MMA and DMA using an Ion 12 column with 4 mM HNO_3–2% methanol and 0.3 M NH_4HCO_3–2% methanol as the mobile phases with detection by ICP-MS. Martinez-Bravo *et al.* [67] described a new method for the simultaneous chromatographic separation and determination of arsenite, arsenate, MMA, DMA, selenite and selenate in water. The speciation was achieved by on-line coupling of anion exchange IC and ICP-MS. The mobile phase used was NH_4NO_3 20 mM, pH 8.7–NH_4NO_3 60 mM, pH 8.7 with gradient elution. Day *et al.* [68] used an anion exchange column coupled to ICP-MS for the detection of As species [As(III), As(V), MMA and DMA]. The mobile phase containing 2.0 mM NaH_2PO_4 and 0.2 mM EDTA at pH 6.0 allowed adequate separation of these arsenic species. Schlegel *et al.* [69] reported the separation of As(III), As(V) and DMA species on an anion exchange Hamilton PRP-X100 column using ICP-AES as an atomic spectrometric detection technique. Van Hulle *et al.* [70] determined arsenic species in three common Chinese edible seaweeds, one brown (*Laminaria japonica*) and two red (*Porphyra crispata* and *Eucheuma denticulatum*) using anion and cation exchange columns with detection by ICP-MS.

Zhang *et al.* [30] reported the speciation of As(III), As(V), MMA and DMA on a cation exchange column (Dionex Ionopac CS 10) with detection by a UV photo-oxidation spectrometer. The mobile phase used was 100 mM HCl and 50 mM NaH_2PO_4. Johnson and Aldstad [71] described an improved method for the determination of inorganic arsenic in drinking water. The method is based on comprehensive optimization of anion exchange ion chromatographic separation of arsenite and arsenate with

post-column generation and detection of the arsenate molybdate heteropoly acid (AMHPA) complex ion. The arsenite capacity factor was improved from 0.081 to 0.13 by using a mobile phase composed of 2.5 mM Na_2CO_3 and 0.91 mM $NaHCO_3$ (pH 10.5, 2.0 mL/min). A post-column photo-oxidation reactor (2.5 m × 0.7 mm) was optimized using 0.37 μM potassium persulfate at 0.50 mL/min such that arsenite was converted to arsenate with 99.8 ± 4.2% efficiency. Multi-variate optimization of the complexation reaction conditions yielded the following levels: 1.3 mM ammonium molybdate, 7.7 mM ascorbic acid, 0.48 M nitric acid, 0.17 mM potassium antimony tartrate, and 1.0% (v/v) glycerol. A long-path-length flow cell (Teflon AF, 100 cm) was used to measure the absorption of the AMHPA complex (818 ± 2 nm). The merit for arsenite/arsenate include the limit of detection (1.6/0.40 μg/L), standard error in absorbance ($5.1 \times 10^{-3}/3.5 \times 10^{-3}$) and sensitivity ($2.9 \times 10^{-3}/2.2 \times 10^{-3}$) with absorbance units per μg/L. Successful application of the method to fortified surface and ground waters was also described. Cornelis *et al.* [72] speciated DMA and AsB in three candidate lyophilized urine reference materials. The measurements were based on cation exchange liquid chromatography coupled to hydride-generation atomic absorption spectrometry with on-line digestion of the samples. Sheppard *et al.* [73] developed an ion chromatographic method for the speciation of As(III), As(V), DMA and MMA in urine, club soda and wine samples. The detection was achieved by ICP-MS. Van Elteren and Slejkovc [74] described a novel separation for eight arsenic compounds on a polymer-based cation exchange column using 3-carboxy-4-hydroxybenzenesulfonic acid in the mobile phase. The method was also applied for testing the stability of arsenic compounds in aqueous media related to food treatment procedures. Pantsar-Kallio and Manninen [75] described an IC method in conjunction with ICP-MS for the speciation of As(III), As(V), DMA, MMA, AsB and AsC species using KNO_3 at pH 9.8 as eluent. Chausseau *et al.* [76] reported the separation of As(III), As(V), DMA and MMA by ion exchange chromatography coupled to an axially viewed sequential ICP-AES. Vela *et al.* [76] presented an IC-ICP-MS method for the speciation of As(III), As(V), MMA, DMA and AsB. Jackson *et al.* [78] used IC-ICP-MS for speciation of arsenic species, i.e., As(III), As(V), DMA and AsB using an AS7 column with HNO_3 as gradient eluent in liver and gill extract samples. Bohari *et al.* [79] developed an IC-AFS method for the determination of arsenic species (arsenite, arsenate, MMA and DMA) in plants. Kohlmeyer *et al.* [80] reported IC-ICP-MS as an effective method for the speciation of arsenite, arsenate, MMA, DMA, AsB, AsC, TMAO and tetramethylarsonium ion in fish, mussel, oyster and marine algae samples. Vela and Heitkemper [81] reported speciation of As(III), As(V), DMA and MMA by an ICP-MS method. Anion exchange chromatography was coupled with ICP for the speciation of DMA (106 ± 5 ng/g) and AsB (37 ± 4 ng/g) in chicken meat [82].

Capillary Electrophoresis

Various chromatographic methods discussed above have been used for the speciation of arsenic but still there is a need of fast and inexpensive methods for metal ion speciation at trace level. This demand is fulfilled by a newly developed technique called capillary electrophoresis (CE). Since the early 1990s, interest in using CE for speciation analysis has increased rapidly [27]. Mostly UV detection is used for the speciation of metal ions but CE has been hyphenated with element-specific detectors such as AAS,

ICP spectrometry, MS, etc. [83]. More recently, reviews on CE selectivity, sensitivity and applications for metal ion speciation have been published [17,84]. CE has certain advantages over the chromatographic techniques, including simplicity, inexpensive experimentation, high speed of analysis and degree of matrix independence. Under CE conditions, the migration of metal ions is controlled by the sum of the intrinsic electrophoretic mobility (μ_{ep}) and the electroosmotic mobility (μ_{eo}), due to the action of electroosmotic flow (EOF). In contrast to the large molecules, small cations have higher charge densities (q_i/r_i) ratio and, hence, larger ionic mobilities. As a very significant electrophoretic property, this should lead to rapid separation with high efficiency. In practice, this seldom occurs unless special precautions are taken. The mobilities of metal ion species in various oxidation states are different, and this may be considered as an advantage for speciation by CE. Moreover, the different charges on these species may again be a plus point for their speciation in CE, as the migration of cations in CE is controlled by the charges on the cations.

Owing to the great need of arsenic metal ion speciation extensive investigations have been carried [27,85–94]. Lin *et al.* [27] analyzed arsenate, arsenite, DMA and MMA in coal fly ash using sodium chromate as the background electrolyte (BGE). The authors also discussed the advantages of CE as an efficient and sensitive separation method. In the same year, Olesik *et al.* [91] coupled CE with ICP spectrometry for the speciation of As(III) and As(V) species using 0.06 M calcium chloride as the BGE. Michalke and Schramel [89,90] reported the speciation of DMA and MMA species. The authors used phosphate buffer as the BGE.

To achieve maximum speciation of metal ions by CE, optimization of the CE conditions is a very important aspect for the environmental chemist. Several parameters are required to control the speciation. The optimization factors may be categorized into two classes, i.e., the independent parameters that are under the direct control of the operator, including the choice of buffer, pH of the buffer, ionic strength of the buffer, voltage applied, temperature of the capillary, dimension of the capillary and BGE additives and the dependent parameters, which are directly affected by the independent parameters and are not under the direct control of the operator. These types of parameters are field strength (V/m), EOF, Joule heating, BGE viscosity, sample diffusion, sample mobility, sample charge, sample size and shape, sample interaction with capillary and BGE, molar absorptivity, etc.

Other Techniques

In addition to the above, some reports are also available on arsenic speciation by other methods such as electrochemical X-ray techniques, etc. Melitas *et al.* [95] reported arsenic speciation using an electrochemical method by investigating the redox reactions that occur on the surface of zero valent iron in arsenic solutions. The effect of arsenic on the corrosion rate of zero valent iron was investigated by analysis of Tafel diagrams for iron-wire electrodes in anaerobic solutions with As(V) concentrations between 100 and 20 000 μg/L. As(V) reduction in the absence of surface oxides was investigated by the analysis of chronoamperometry profiles for iron-wire electrodes in solutions with As(V) concentrations ranging from 10 000 to 106 μg/L. The effect of pH on As(V) reduction was investigated by analyses of chronopotentiometry profiles for iron-wire electrodes at pH values of 2, 6.5 and 11. For freely corroding iron, the presence of As(III) and As(V) decreased the iron corrosion rate by a factor of 5.0 compared to

that in a 3.0 mM $CaSO_4$ blank electrolyte solution. The chronoamperometry and chronopotentiometry experiments showed that elevated pH and increased As(III) to As(V) ratios near the iron surface decreased the thermodynamic favorability of As(V) reduction. Therefore, reduction of As(V) occurred only at potentials that were significantly below the apparent equilibrium potentials based on bulk solution pH values and As(III) to As(V) ratios. The potentials required to reduce more than 1% of the As(V) to As(III) were below those that are obtainable in freely corroding iron media. This indicates that there will be minimal or no reduction of As(V) in iron media filters under conditions relevant to potable water treatment. Feeney and Kounaves [96] developed on-site analysis of arsenic in groundwater using a small battery-powered unit in conjunction with a micro-fabricated gold ultramicro electrode array (Au-UMEA). The sensor, consisting of 564 UME disks with a unique gold surface created by electron beam evaporation, was demonstrated to be highly sensitive to low microgram per liter concentrations of As(III) using square-wave anodic stripping voltammetry. The influence of the square-wave frequency, pulse amplitude and deposition potential on the arsenic peak stripping current was investigated. The limit of detection was 0.05 μg/L As(III) with a S/N ratio of 3 : 1. Sancho *et al.* [97] analyzed arsenic in refined beet sugar at the microgram per kilogram level by anodic stripping voltammetry (copper) and cathodic stripping voltammetry (arsenic) in the differential-pulse mode (DPASV and DPCSV) at a hanging mercury drop electrode (HMDE). DPCSV measurements of arsenic were based on its accumulation on the HMDE as an inter-metallic Cu–As compound followed by the reduction of As(0) to arsine in hydrochloric acid medium. The measurements were directly carried out on untreated sugar solutions. The performance of the procedures was compared with electrothermal AAS and stripping voltammetry, which showed a better accuracy.

Sbarato and Sanchez [98] used an X-ray fluorescence (XRF) technique using an energy-dispersive spectrometer for the analysis of arsenic in water samples. The samples were excited with a 3-kW X-ray tube and measured using a reflecting geometry with 45° incident and take-off directions. Pre-concentration techniques were employed for the preparation of the samples in order to obtain an adequate signal-to-noise ratio. Farquhar *et al.* [99] studied the mechanisms of As(III) and As(V) determination in aqueous solution (pH 5.5–6.5) by interaction with the surfaces of goethite, lepidocrocite, mackinawite, and pyrite using As K-edge EX-AFS and XA-NES spectroscopy. Also, Ng *et al.* [100] used a hydride cold-trapping technique for the measurement of urinary arsenic metabolites. The analytical precision of the method was found to be 6.1, 4.0 and 4.8% ($n = 5$) for inorganic and organic arsenic species with recoveries close to 100%. The detection limits for these species were 1.0–3.0 ng/L. The method was used to analyze urine samples obtained from three groups of workers for occupational exposure in three companies where copper chrome arsenate was used for timber treatment. Arsenic species were determined either by energy dispersive X-ray fluorescence (EDXRF) directly or by inductively coupled plasma optical emission spectrometry (ICP/OES) after microwave digestion by Moll *et al.* [101] Arsenic species studied were arsenite, arsenate, MMA, DMA, AsB and AsC. The authors claimed the method as validated by means of inter-comparison studies within the measurements and testing programme of the European Community. The isotopic dilution technique has been coupled with chromatographic and mass spectrometry for arsenic [As(III) and As(V)] speciation in soil–water systems [102].

CONCLUSION

Owing to the different toxicities of arsenic species its speciation is a very important and urgent need of today. Spectroscopic methods of arsenic speciation have been replaced by the newly developed chromatographic methods. Gas chromatography is a fairly good technique for arsenic speciation but the derivatization it involves is a serious drawback. On the other hand, liquid chromatographic approaches do not require derivatization and, hence, are popular in this field. RP-HPLC has also been used for arsenic speciation but the development of ion exchange columns (IC) makes the arsenic speciation job easy even in highly polluted environmental samples. Recently, CE has been introduced as a newly developed technique with fast and inexpensive arsenic speciation. Unfortunately, this could not achieve the status of routine arsenic speciation owing to the poor detection and the lack of reproducibility. The precision linearity, sensitivity and reproducibility of CE methods for arsenic speciation are not superior to those of the chromatographic methods. But scientists are working to improve CE applications and it seems that in the near future CE will be realized as a widely recognized method of choice for speciation of arsenic and other metal ions. All the capabilities and possibilities of CE have not yet been fully explored but they are underway. No doubt CE will prove itself as the best technique for the speciation of arsenic and will achieve the status of the technique of routine speciation in most laboratories.

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