

Chapter 2

A Comprehensive Review on Various Analytical Methods for the Determination of Inorganic and Organic Arsenic in Environmental Samples

Nalini Sankararamakrishnan and Shruti Mishra

Abstract In natural environment, Arsenic (As) occurs in four oxidation states, namely, As(V), As(III), As(0), and As(−III). The oxidation state of As determines its toxicity and mobility in the environment. Thus, quantification and speciation of As are critical in assessing the overall risk. Further, As being a class A carcinogen, it is of interest to both environmental scientists and analytical chemists. Thus, sensitive and adept determination of As and speciation of different forms of As in various environmental matrices are indispensable. Most of the countries around the world have relevant official regulations on permissible levels of As in drinking water. In India, the permissible limit of As in drinking water is set at 10 µg/L by Bureau of Indian Standards (BIS) and WHO guideline value is also 10 µg/L. In this review, we focus on extraction of As from various environmental samples, As speciation, sample treatment, and determination of As in various matrices. Analytical methods for the determination of various forms of As like atomic absorption spectrophotometer (AAS), hydride generation AAS (HG_AAS), atomic fluorescence spectrometry (AFS), inductively coupled mass spectrometry (ICPMS), electrochemical methods, capillary electrophoresis (CE), high-performance liquid chromatography (HPLC), HPLC coupled with mass spectrometer (HPLC-MS), neutron activation analysis, and biosensors are also summarized. Determination of As in the field using various field test kits available in the market is also detailed.

Keywords Arsenic • Speciation • Extraction • Determination • Sensitivity

N. Sankararamakrishnan (✉) · S. Mishra
Centre for Environmental Science and Engineering, Indian Institute
of Technology Kanpur, Kanpur 208016, UP, India
e-mail: nalini@iitk.ac.in

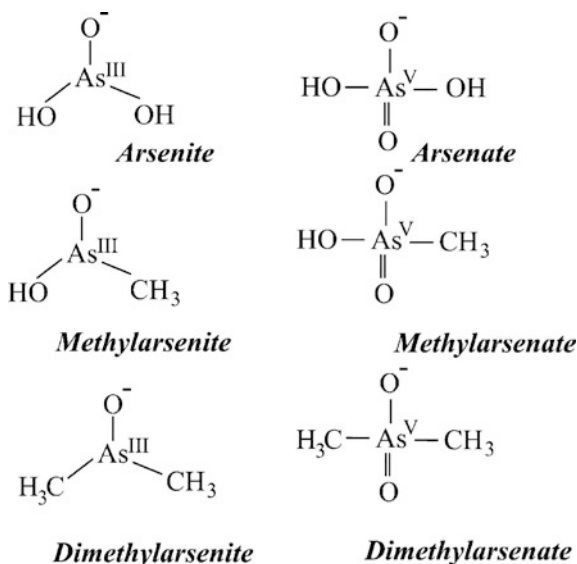
© Springer Nature Singapore Pte Ltd. 2018
T. Gupta et al. (eds.), *Environmental Contaminants*, Energy, Environment,
and Sustainability, https://doi.org/10.1007/978-981-10-7332-8_2

2.1 Introduction

Arsenic (As) is one of the most abundant elements in earth's crust (Ahmed 2009). As contamination in groundwater has been reported in more than 20 countries, out of which Bangladesh and India, inner Mongolia and Taiwan are severely affected (Chakraborti et al. 2002; Rahman et al. 2001). Around nine districts in West Bengal, India, and fifty districts of Bangladesh have reported to contain As levels above WHO permissible limit of 10 $\mu\text{g/L}$ in groundwater (World Health Organisation 1993). Long-term exposure to As leads to various kinds of cancer including skin, lung, liver, bladder, and kidney (World Health Organization 2001). The four predominant oxidation states of As found in natural environment are: As(III), As(V), As(0), and As(-3). The mobility of As in water and its toxicity toward living being is dependent upon the oxidation state of As (Meng et al. 2003). As predominantly exists as As(III) and As(V) with a minor amount of monomethyl arsenic (MMA) and dimethyl Arsenic (DMA) in groundwater (Fig. 2.1). Generally, inorganic As compounds are considered to be more acutely toxic compared to organic arsenicals and the toxicity of organic arsenicals decreases with methylation. Thus, the order of arsenic toxicity is As(III) > As(V) \gg MMA > DMA (Shiomi 1994).

Hence, it becomes extremely important to speciate arsenic and determine with sensitivity below 10 $\mu\text{g/L}$. Speciation of arsenic is reported using various techniques including hydride generation (HG) (Holak 1969), chromatographic techniques like ion chromatography (IC) (Ammann 2011), high-performance liquid chromatography (HPLC) (Jia et al. 2016), capillary electrophoresis (CE) (Qu et al. 2015) etc. The most commonly used detection method for As are inductively coupled mass spectrometry (ICP MS), graphite furnace atomic absorption spectrophotometer (GFAAS), hydride generation atomic absorption spectrophotometer

Fig. 2.1 Arsenic species found in water (Leermakers et al. 2006)



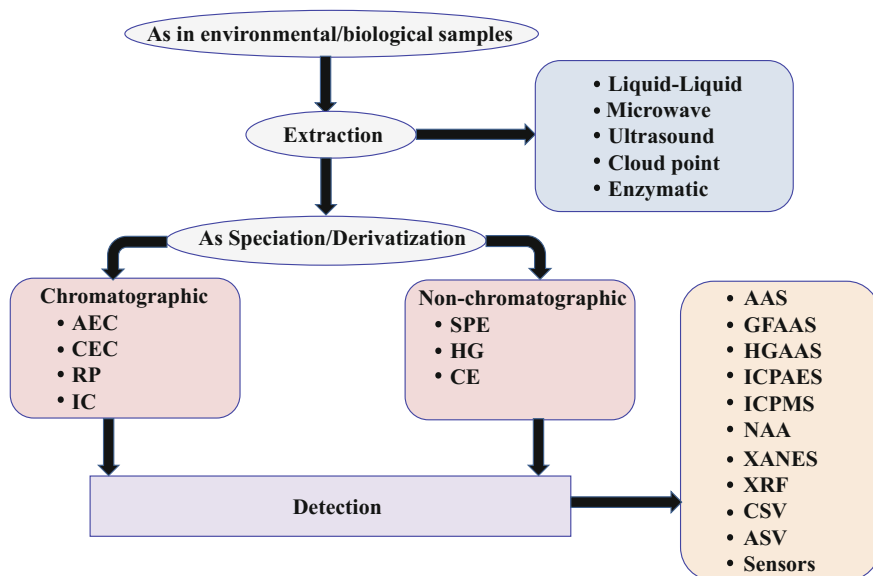


Fig. 2.2 Schematic representation of various stages for determination of different forms of As. *AEC* anion exchange chromatography, *CEC* cation exchange chromatography, *IC* ion exchange chromatography, *RP* reversed-phase chromatography, *HG* hydride generation, *CE* capillary electrophoresis, *SPE* solid-phase extraction, *AAS* atomic absorption spectroscopy, *GFAAS* graphite furnace atomic absorption spectroscopy, *HGAAS* hydride generation atomic absorption spectrophotometer, *ICPAES* inductively coupled plasma atomic emission spectrometry, *NAA* neutron activation analysis, *XANES* X-ray absorption near edge spectroscopy, *XRF* X-ray fluorescence, *CSV* cathodic stripping voltammetry, *ASV* anodic stripping voltammetry

(HGAAS), which have detection limits ranging from 0.5 to 50 $\mu\text{g/L}$ (United States Environmental Protection Agency 1999a). Thus, this chapter focuses on the comprehensive review of extraction of arsenic from various matrices, speciation, and detection using various methods. Determination of As in the field using various field test kits available in the market is also detailed. The schematic representation of various stages of As determination is detailed in Fig. 2.2.

2.2 Extraction of Arsenic

With the advancement of various technologies, assessment of As in various environmental samples could be carried out directly without resorting to a preconcentration or extraction step. In general, HG techniques are quite selective as the interference from matrix elements are removed as the analyte is volatilized as gaseous arsine. However, the applicability of this method to seawater is a challenge due to the presence of high amounts of chloride ions. Reviews have been reported on As determination in environmental samples (Aker et al. 2005), water (Llorente-Mirandes et al. 2017), and food (Guell et al. 2010) samples.

2.2.1 Water

Guell et al. (2010) used Aliquat 336 in 4% dodecane to extract ppb levels of As(V) and As(III) at pH 13. It was found that As(V) extraction by aliquat-336 is kinetically more favorable, and the adsorbed As(V) was desorbed using 0.1 M HCl. Using this method, ppb levels of As(V) could be separated from As(III). Experiments were performed with As-spiked groundwater, and the results obtained were satisfactory. Preconcentration of trace amounts of As using ultrasonic bath and ionic liquid-based microextraction methodology has been reported (Amjadi et al. 2011). Initially, As(III) was extracted as ammonium pyrrolidine dithiocarbamate (APDC) complex into ionic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate, using an ultrasonic bath. Extracted As(III) was determined using electrothermal atomic absorption spectrophotometer (ETAAS). A detection limit (3s) of 0.01 $\mu\text{g/L}$ has been reported. For six replicate determinations of 0.2 $\mu\text{g/L}$ of As(III), the relative standard deviation was found to be 4.6%. As speciation in seawater was studied by collecting both As species in cobalt (III) oxide powder (Narukawa 2000). Quantitative extraction of both inorganic forms of As was achieved using cobalt (III) oxide powder as collector in the pH range of 1.0–11.0. Dimethyl arsine (DMA) was extracted from seawater into benzene after addition of potassium iodide. After extraction with benzene, the solution was acidified with 7.2 M HCl, and DMA was collected on cobalt (III) oxide powder.

2.2.2 Soils and Sediments

The main challenge is to extract both forms of inorganic arsenic quantitatively and minimize the conversion from one form to another. Georgiadis et al. (2006) reported that phosphate solutions with 0.5% sodium diethyldithiocarbamate trihydrate (NaDDC) could be used to extract arsenic species and restrict the transformation between As(III) and As(V) in the samples analyzed. Recoveries of As(III) spiked samples ranged from 80 to 120% which As(V) concentration remained constant. A similar procedure is reported by Garcia-Manyes et al. (2002) using the combination of ascorbic acid and phosphoric acid. Other extraction chemicals like 1,3-propanedithiol or 1,2-ethanedithiol (Szostek and Aldstadt 1998) are methanol/hydrochloric acid/water (Yehl and Tyson 1997), acetone and hydrochloric acid (Yehl et al. 2001) have also been reported. Extraction of phenyl arsenic compounds have been carried out using supercritical fluid extraction with carbon dioxide and methanol containing 15% dichloromethane as modifier. The efficiency of the method is reported to be 40% (Thurrow et al. 2002).

2.2.3 *Plants and Marine Organisms*

Kroukamp et al. (2016) recently reviewed speciation of As along with other metalloids in plants. Extraction of arsenic from biological samples is always carried out by shaking, heating, microwave digestion, or sonication. Generally, binary mixtures containing ethanol/water (Zhao et al. 2015), methanol/water, or methanol/chloroform are used (Alberti et al. 1995) for extraction purposes. Zhao et al. (2015) reported various extractants for the quantitative extraction of arsenic species from three different plants and subsequent determination by HPLC-ICP-MS. Satisfactory extraction of >78% was obtained using a mixture of 25% ethanol in water with sonication time of 0.5 h for fronds and 2.0 h for roots. Further, the method preserved the arsenic species during extraction. The three solvent systems, namely water, methanol, and 1:1 methanol-water were compared for the extraction of As from Molluscs (McSheehy et al. 2001). It was reported that the extraction of arsenic was found to be same in all the three systems. In marine organism, the kind of arsenic species is arsenobetaine (AB) and is completely soluble in water and >90% efficiency is found in all the three systems.

2.2.4 *Biological Samples of Humans*

To ascertain the seriousness of As contamination in human beings, As is analyzed in human nails, urine and blood samples. Ultratrace As determination was carried out in urine and blood samples by FI-HG-AAS after preconcentration and speciation using dispersive liquid-liquid microextraction (Shirkhanloo et al. 2011). Initially, As(III) was complexed with ammonium pyrrolidone dithiocarbamate at pH 4 and extracted with ionic liquid (IL). Then the extracted As(III) was back extracted from IL using HCl, and stripped As(III) was determined using FI-HG-AAS. Total As was determined by initially reducing As(V) to As(III) using KI and ascorbic acid in HCl solution. As(V) was determined by the difference between total As and As(III) concentration. The method reported a LOD of 5 ng/L. A good precision with RSD <5% was reported by using this method on biological samples of multiple sclerosis patients.

In another method, a water-miscible ionic liquid (IL) ([Hmim][BF₄]) was added to the sample followed by the addition of an ion exchange reagent (NaPF₆) to obtain the hydrophobic IL ([Hmim][PF₆]) (Howard 1997). The formed product acted as extractant to extract trace amounts of As(III) and As(V) which was then determined by ETAAS. In situ solvent formation microextraction exhibited a limit of detection (3s), and the enrichment factor were 6 ng/L and 198, respectively. The method was applied for the determination of total As in biological samples. Further, the application of this method was found successful in food salts and water samples as well.

2.3 Arsenic Speciation and Determination

2.3.1 Hydride Generation

Speciation of both inorganic forms of As was achieved by hydride generation technique. It is the most popular sample derivatization method used for determination of As(III) and As(V) (Howard 1997). Both sodium and potassium tetrahydroborate (III) are reliable reducing reagents for the conversion of As to volatile arsine (Holak 1969). The ability of As(III) to react with tetrahydroborate at a higher pH than As(V) was used for the differentiation of As(III) and As(V) species. Thus, total arsenic could be determined by the reduction to arsine at acidic conditions and at pH 4. As(III) was converted to arsine using tetrahydroborate. Concentration of As(V) was acquired from the difference between the total As and As(III) concentration. Inclusion of the flow injection technique along with HG decreased the interference from transition elements (Yamamoto et al. 1985). Gonzalez et al. (2009) reported a method for the determination of As(III) and As(V) in food samples using FI-HG-AFS. As(III) was measured directly by feeding the sample, and total As was determined by reducing it with KI and ascorbic acid for 30 min. The method reported a detection limit of 5.0 ng/g. Musil et al. (2014) reported a method for the speciation of inorganic As from organic As using HG-ICPMS. Initially, the samples were treated with HCl and NaBH₄ and the generated arsine was sent to ICPMS detector using Ar gas. Under these conditions, only inorganic As underwent reduction to volatile arsine gas. The method was applied to the determination of inorganic As from rice and marine organisms. HG is also used for pre-column or post-column derivatization. In the pre-column derivatization, initially, volatile arsine is formed which is cryogenically trapped and sequentially desorbed and carried to the detector (Gomez-Ariza et al. 2000). In the post-column method, separation of As species is carried out by HPLC followed by HG to improve the sensitivity of detection (Sloth et al. 2003; Wangkarn and Pergantis 2000).

2.3.2 Chromatographic Method

Chromatography is a very powerful tool to separate various forms of As. Further, coupling the chromatography with various element-specific detectors improves the sensitivity and selectivity of As determination. As speciation by various chromatographic methods are adequately reviewed (Larsen 1998; Ammann 2011; Feldmann et al. 2004). Among the various liquid chromatographic (LC) techniques, ion exchange chromatography (IEC) and ion interaction chromatography (IIC) have been widely used. In IEC, the analyte is transported into the column via a mobile phase where the various species compete for stationary phase containing oppositely charged functional groups and the separation of As species occurs by displacement

of mobile phase ions. The hyphenated IEC-ICPMS offers detection levels in the range of sub-nanogram levels, with great linear range.

Sheppard et al. (1992) reported a method for the speciation of inorganic and organic As using ion chromatography(IC) coupled with ICP. A Wescan Anion/R-IC, 250~4.1 mm i.d. was used as the ion exchange column with 2% propan-1-ol and 50 mmol dm⁻³ carbonate buffer, pH 7.5 as eluants 1 and 2, respectively. A gradient elution program was used to resolve the various peaks. The order of the elution of various As species was As(III), DMA, MMA and As(V). Total run time of the program was 12 min. The method was used for the determination of As in urine, and limits of detection were found to be 4.9, 6.0, 1.2, 3.6 µg/L for As(III), As(V), DMA, MMA, respectively.

Reversed-phase ion pair HPLC with mobile phases such as tetramethylammonium cation or heptanesulfonate anion has also been reported. Seven As species have been separated using hexanesulfonate as mobile phase using C18 column as stationary phase (Le et al. 1996). Kohlmeyer et al. (2002) separated 17 organo-arsenical in single chromatographic run using ion exchange chromatography. Recently, Rasheed et al. (2017) assessed 228 samples of groundwater from Pakistan for inorganic and organic As using IC-ICPMS. It was found that As was present mainly as As(V) and the levels of MMA, DMA, and AB were well below the permissible limits.

Both inorganic and organic As species in various water samples were preconcentrated using on-line solid-phase extraction (SPE) (Jia et al. 2016). In this technique, phosphine functionalized polymer microspheres have been used as solid phase extractant. The inorganic and organic species, namely As(V), As(III), DMA, and MMA species, have been quantitatively retained on the solid phase column and were eluted with a mixed solution of ammonium nitrate and ammonium dihydrogen phosphate. After preconcentration and separation, speciation and determination of all the four As species were achieved using HPLC-ICP-MS technique. The enrichment factor of 28 was obtained for DMA and As(III) in 25 mL sample solution while a factor of 30 was obtained As(V) and MMA. The low detection limits of 0.91, 0.82, 0.96, 1.2 ng/L were obtained for As(V), MMA, DMA, and As(III), respectively.

Gas chromatography (GC) in conjunction with mass spectrometry (MS) (GC-MS) and GC-MS/MS has been used for the speciation of As. As speciation was achieved using derivatization agents like thiols, thioglycol methylate (TGM), thioglycol ethylate (TGE) and British anti-Lewisite (BAL; 1,3-dimercapto-1-propanol) (Namera et al. 2012; Campillo et al. 2008; Takeuchi et al. 2012; Kang et al. 2016). After derivatization, the samples were extracted in dichloromethane and injected in GC/MS in SIM mode to quantify the As species. Using GC-MS/MS technique, a very low detection limit of 0.08 pg was achieved with very high precision and accuracy.

2.3.3 *Capillary Electrophoresis (CE)*

CE is a robust separation technique possessing a high resolving power and used for the separation of various As species based on its charge (Qu et al. 2015). In CE, various separation processes are possible including capillary electrochromatography (CEC), micellar electrokinetic capillary chromatography (MECC), isotachopheresis (ITP), isoelectric focussing (IEF), and capillary zone electrophoresis (CZE) using the same instrument (Michalke 2003). The interaction between the analyte and the stationary phase is eliminated as the process is carried out without stationary phase. Coupling this technique to MS and ICPMS has been reported. Qu et al. (2015) reported a method for the quantification and speciation of As using CE-ICPMS technique. In this technique, α -amylase enzyme facilitated the water-phase microwave extraction of As species, including DMA, MMA, As(V), and As(III) from rice matrices. Usually, capillary columns are as the nebulizer to couple CE to ICP-MS. Some nebulizers may introduce backpressure which might affect the electrophoretic separation due to production of laminar flow in the capillary, hence the choice of the nebulizer is extremely important (Dressler et al. 2011). Yang et al. (2009) introduced an improved sheath flow interface to facilitate the coupling of CE to ICPMS. This sheath flow technique avoided laminar flow completely in the capillary and enabled stable electric supply in CE and efficient transport of the sample from CE to ICPMS. Sheath flow technique reduced the dead volume of interface to approximately zero which led to lower detection limit and better electrophoretic resolution. Thus, well-resolved peaks with lower detection limits (0.030–0.042 $\mu\text{g/L}$) were obtained. Using a 100 cm length_50 μm ID fused-silica capillary as the nebulizer, separation of various As species including As(III), As(V), DMA, MMA, AsB, AsC, 3-NHPAA, 4-NPAA, o-ASA (o-arsanilic acid), and p-UPAA was achieved using CE-ICPMS technique (Liu et al. 2013). To ensure quality control in CE, methods like internal standard, standard addition are often employed (Michalke 2003). Due to application of high voltage during electrophoresis, alterations of the chemical species may occur and the detection limits, reproducibility, and peak resolution are found to be inferior to LC (Liu et al. 2013).

2.3.4 *Detection Methods*

The USEPA has recently reviewed the methods available for monitoring As (United States Environmental Protection Agency 2004). Inductively coupled mass spectrometry (ICPMS), inductively coupled atomic emission spectrometry (ICP-AES), hydride generation atomic absorption spectrophotometer (HG-AAS), graphite furnace AAS (GFAAS) are the methods approved by USEPA. These methods report detection limit in the range of 0.5–50 $\mu\text{g/L}$ (United States Environmental Protection Agency 1999b). In the last six years, lots of comprehensive reviews have been

reported regarding arsenic speciation and analysis in various matrices (Radke et al. 2012; Ammann 2011; Leermakers et al. 2006; Akter et al. 2005; Llorente-Mirandes et al. 2017; Tyson 2013; Rajakovic et al. 2013; Chen et al. 2014; Sadee et al. 2015; Nearing et al. 2014; Quinaia and Rollemberg 2001).

The method chosen for the determination of arsenic depends on several factors including detection limit, precision, selectivity, cost-effectiveness. Usually, the sensitivity, selectivity, and speciation of arsenic are achieved by hyphenating the various detection techniques with solid phase extraction (SPE), flow injection, hydride generation, or liquid chromatography. Table 2.1 lists the various methods available for arsenic and their corresponding detection limits.

Table 2.1 List of various analytical methods and their detection limits for As

Analytical method	Detection limit (µg/L)	Strength/weakness of the method	References
HG-AAS	As(III) 0.6	Strength: low detection limits compared to AAS and GFAAS and speciation Weakness: single element analysis, strictly controlled reaction conditions, time consuming	Quinaia and Rollemberg (2001)
	As(V) 0.5		
FI-SE-HG-AAS	As(III) 0.05	S: very low detection limit. Applicable to seawater	Karthikeyan et al. (1999)
	As(V) 0.20		
FI-HG-AAS	As(III) 0.037	S: very low detection limit. Applicable to groundwater samples	Naykki et al. (2001)
FI-HG-AFS	As(III) 0.023	S: very low detection limit. Speciation	Yan et al. (2002)
SPE-GF-AAS	As(III) 0.11	W: high detection limits compared to other techniques	Hsieh et al. (1999)
	As(V) 0.15		
HG-ICP-AES	As(III) 0.7	S: multielement analysis W: high detection limits compared to other techniques	Hueber and Winefordner (1995)
TRXRF	As(III) 0.65	W: high detection limit, preconcentration and separation procedure is necessary	Cataldo (2012)
FI-ICPMS	As(III) 0.021	S: low detection limit, speciation, multielement analysis W: high operational cost	Yan et al. (1998)
	As(V) 0.029		

(continued)

Table 2.1 (continued)

Analytical method	Detection limit ($\mu\text{g/L}$)	Strength/weakness of the method	References
SPE-ICPMS	As(III) 5.0×10^{-6}	S: low detection limit, speciation, multielement analysis W: high operational cost	Chen et al. (2009)
	As(V) 2.4×10^{-4}		
HG-ICPMS	AsB 0.0301	S: low detection limit, speciation of InAs and organic As, multielement analysis W: high operational cost	Sengupta and Dasgupta (2009)
	DMA 0.0022		
	As(III) 0.0021		
	MMA 0.0021		
	As(V) 0.00208		
FI-HG-ICPMS	AsB 0.0192	S: low detection limit, speciation of InAs and organic As, multielement analysis W: high operational cost	Sengupta and Dasgupta (2009)
	DMA 0.0145		
	As(III) 0.0177		
	MMA 0.0192		
	As(V) 0.0321		
Capillary microextraction-ICPMS	As(III) 0.0109	S: low detection limit, multielement analysis W: in environmental samples only As(V) could be detected	Zheng and Hu (2009)
	As(V) 0.0062		
PDC-NAA	As(III) 0.001	S: sample not destroyed W: preconcentration with PDC is necessary to achieve low detection limit	Sun and Yang (1999)
LC-NAA	As(III) 0.9	S: sample not destroyed W: preconcentration using liquid chromatography is necessary to achieve speciation and low detection limit	Sanchez et al. (2009)
	As(V) 1.7		
	MMA 1.6		
	DMA 3.8		
	Total As 16		

(continued)

Table 2.1 (continued)

Analytical method	Detection limit ($\mu\text{g/L}$)	Strength/weakness of the method	References
HG-Gas diffusion amperometry	As(Total) 5.0	W: high detection limit, matrix effect	Lolic et al. (2008)
HG-pervaporation-amperometry	As(Total) 1.0	W: high detection limit	Rupasinghe et al. (2009)
CSV	As(III) 0.035	S: low operational cost W: high detection limit, interference from matrix elements	Gibbon-Walsh et al. (2010)
DP-ASV	As(V) 0.07	S: low operational cost W: high detection limit, interference from matrix elements	AlvesGMS et al. (2011)
Modified Au electrode, CV	As(III) 0.047	S: low operational cost W: high detection limit, interference from matrix elements	Giacomino et al. (2011)

S strength; W weakness

2.3.5 AAS, AFS, ETAAS/GFAAS

In general, for the determination of arsenic in various environmental samples, both AAS and AFS are coupled with hydride generation technique. Hydride generation technique improves the selectivity as the analyte is separated from the matrix to volatile hydride, and further sensitivity of the analysis is also increased. By controlling the acidity of the reaction mixture during hydride generation, speciation is also achieved. A LOD of 12 ng/L was achieved for the determination of As(V) by HG-AAS (Tuzen et al. 2009) while HG-AFS reported LOD as 14 ng/L (Chen et al. 2013). The main interference in HGAAS technique is the interference from trace elements like iron which could conveniently overcome by the addition of L-cysteine (Howard and Salou 1996). Further, inclusion of flow injection technique eliminates the interference from transition metals (Yamamoto et al. 1985). Electrothermal or graphite furnace AAS (ETAAS/GFAAS) is based on the atomization of arsenic at very high temperature using electric furnace. In general, the LOD of As by GFAAS is 1 $\mu\text{g/L}$.

2.3.6 Total Reflection X-ray Fluorescence Spectroscopy (TRXRF)

The major advantages of TRXRF are high sensitivity, hence with very low detection limit, highly selective, and very low sample requirement. Sitko et al. (2015) recently reported a method for the preconcentration of Arsenic using mercapto-modified graphene oxide nanosheets and determination using TRXRF. A LOD of 0.064 $\mu\text{g/L}$ is reported for As(III). Speciation of As in cucumber (*Cucumis sativus* L.) xylem sap was achieved using synchrotron radiation-induced TRXRF. Arsenic speciation in xylem sap down to 30 $\mu\text{g/L}$ (30 ppb) was achieved using the above technique.

2.3.7 Electrochemical Methods

Several electrochemical methods are reported for the determination of arsenic. The main disadvantage of these methods is the interference from matrix elements. A detection limit of 20 $\mu\text{g/L}$ is achieved for arsenite determination using differential pulse polarography (Greschonig and Irgolic 1992). Higher sensitivity and selectivity is achieved by stripping voltammetric procedures. In this process, arsenic is electrochemically deposited on a suitable electrode followed by the oxidation to metal back to the solution by a reverse potential scan. The oxidation or stripping current is recorded as a function of the analyte concentration. Mays and Hussam (2009) reviewed the various voltammetric methods for the determination of arsenic. The most popular method for the determination of arsenic is anodic stripping voltammetry (ASV). It is reported that Au electrodes are more sensitive than Pt electrode, and a LOD of 0.2 $\mu\text{g/L}$ was achieved (Forsberg et al. 1975). The most commonly used method for the determination of As in ground waters of Bangladesh involves the ASV using thin gold film-deposited glassy carbon electrode. More than 950 samples of groundwater were analyzed using this method (Aggarwal et al. 2001). Similar to ASV, cathode stripping voltammetry (CSV) are also used for the determination of anions. Hanging drop mercury electrode (HDME) is the most commonly used electrode; however, Cu and Bi electrodes are also being used. A very low LOD of 0.01 and 0.02 $\mu\text{g/L}$ for As(III) and As(V), respectively, is reported using HBr as electrolyte by CSV (Profumo et al. 2005). Most of the electrochemical methods reported are applicable only for As(III).

2.3.8 Neutron Activation Analysis (NAA)

In this method, the analyte is bombarded with neutrons to form radioactive nuclides which further decay via β and/or γ emission. The γ rays emitted during the decay is

detected by a multichannel γ -ray spectrometer (Tulasi et al. 2013). Detection of As in seawater was found to be difficult using NAA owing to the spectral interference caused by the salt content of seawater (Shi and Chatt 2014). This interference was overcome by adding lead nitrate and titanium chloride as carrier and reducing agent, respectively, (Rottschäfer et al. 1972). Analysis of total As and As speciation was monitored in water and sediments from the Kwabrafo stream, in southwestern Ghana. Total As content was determined by NAA, and ion pair reverse phase high-performance liquid chromatography-neutron activation analysis (HPLC-NAA) was used for speciation of As species. A solvent extraction preconcentration method involving ammonium pyrrolidine dithiocarbamate (APDC) and 4-methyl-2-pentanone (MIBK) in conjunction with NAA was developed for the simultaneous measurement of low levels of inorganic arsenic along with antimony and selenium species in natural waters (Sun and Yang 1999). The LOD of As was in the range 0.026 $\mu\text{g/L}$. Sun and Yang (1999) used lead nitrate and titanium chloride as carrier and reducing agent in analysis of As in seawater by NAA. Sanchez et al. (2009) combined column chromatography with NAA to separate and analyze MMA, DMA, As(III), and As(V). The LOD for As(III), As(V), MMA, DMA, and total As was found to be 0.9, 1.7, 1.6, 3.8, and 16 $\mu\text{g/L}$.

2.3.9 Inductively Coupled Plasma (ICP) Techniques

This technology was employed since the beginning of 1960s (Dickinson 1969). Plasma is used in this technique to atomize and ionize all forms of arsenic in the acidified sample. Generally, ICP is used in conjunction with atomic emission (AES) (Sansoni et al. 1988) or mass spectrometric (MS) detectors (Stetzenbach et al. 1994). ICP-AES is less commonly used technique compared to ICPMS. Low sensitivity for arsenic using ICP could be attributed to poor ionization efficiency. High precision, robust analysis, wide linear range, isotope analysis are the advantages of ICPMS over ICPAES. In ICPMS, during direct nebulization, possible interference from Ar arises due to the formation of dimer molecule ($^{40}\text{Ar}^{35}\text{Cl}$) in the plasma which coincides with the mass of As (^{75}As) (Colon et al. 2011). In recent years, these interferences are overcome by the use of collision cell or diffusion cell technology (Colon et al. 2011). In this technology, after the initial ion selection, the dimers are allowed to collide with small molecular weight gases such as He, H_2 , CH_4 , and O_2 to break the polyatomic species and a second quadrupole is employed to collect As species (Zhu et al. 2009).

Generally, ICPMS techniques are hyphenated with solid phase extraction (SPE) (Zhu et al. 2009; Chandrasekaran et al. 2010; Popp et al. 2010; Kempahanumakkagari et al. 2017; Profumo et al. 2006) capillary microextraction (Sun and Yang 1999), hydride generation (HG) (Zheng and Hu 2009; Popp et al. 2010), HPLC-IC (Popp et al. 2010).

2.3.10 Sensors

Generally, arsenic sensors are based on either stripping voltammetry or fluorescence or electrochemical detection with enzymatic inhibition. Recently, Kempahnumakkagari et al. (2017) have adequately reviewed the nanomaterial-based sensors for arsenic determination. Different electrode systems with surface modification have been developed to improve the detection limit and selectivity. As(V) is initially reduced to As(III) which is then electrochemically reduced to As(0). After deposition, the electrode potential is increased to oxidize and strip the deposited As(0) from the electrode. The oxidation current is used to quantify the arsenic oxyanions. Various electrode modifications are carried to facilitate the metal binding to the electrode and subsequent electron transfer. Nanomaterials like carbon nanotubes (Profumo et al. 2006), graphene oxide (Dreyer et al. 2010), metal nanoparticles (Aragay et al. 2011; Yavuz et al. 2016), and enzymes (Male et al. 2007) have been found useful as electrode material. In a study by Ramsesha and Sampath (2011), reduced graphene oxide–lead oxide composite has been used as the electrode to detect As(III) up to 10 nM. A selective and sensitive fluorescent sensor has been reported (Ezeh and Harrop 2012) for the determination of As(III) using ArsenoFluorI (AF1) as fluorescent chemical probe. The nonconjugated AF1 is non-fluorescent. However, on reaction with As(III) salts, leads to 25-fold increased fluorescent intensity owing to the formation of Coumarin C6-CF₃ (Scheme 2). The method reports a sub-ppb detection limit and selective for As(III) over other ions such as Fe²⁺, Zn²⁺, Na⁺, and Mg²⁺. Though progress has been made in arsenic sensors with very low LOD of 0.1 ppb (Xiao et al. 2008)

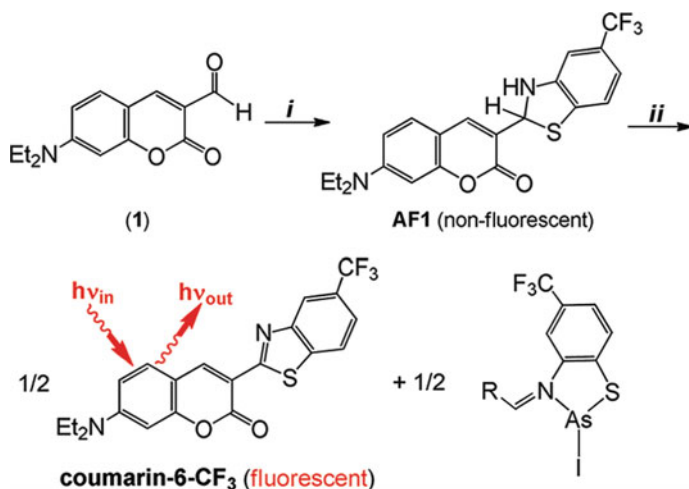


Fig. 2.3 Synthesis of AF1 and proposed As³⁺ response (Ezeh and Harrop 2012). (i) 4-(Trifluoromethyl)-2-aminothiophenol·HCl, EtOH, Et3N, 298 K, 6 h. (ii) AsI3, THF, Et3N, 298 K. R in the As³⁺ complex represents the (diethylamino) coumarin moiety

issues like cost-effectiveness, portability, reproducibility, and interference effect need to be addressed (Fig. 2.3).

2.3.11 Field Kits

Field kits developed for As are generally based on Gutzeit reaction. Initially, the sample is acidified and treated with powerful reducing agent like NaBH_4 , and As(V) is reduced to As(III) and the reduced As(III) further undergoes reduction to release arsine gas. The liberated gas is passed through a lead acetate-soaked cotton filter to remove H_2S followed by HgBr_2 impregnated test strip. The test relies on the color stain reaction of arsine generated with HgBr_2 impregnated test strip to give a yellow color that then becomes progressively browner as arsenic level increases. Though the method is inexpensive and portable, toxic Hg- and Pb-containing waste is generated and care must be taken to prevent arsine from leaking. Several brands are available in the market which uses this technology including Wagtech Arsenator,¹ Arsenic Quick,² EZ Arsenic,³ PurTest Arsenic,⁴ Merckoquant arsenic.⁵ Determination of arsenic by these kits is either based on color chart comparison or LED-based photometers calibrated to read the strip and provide a digital output. Recently, Bralatei et al. (2017) reported a method for rapid screening of inorganic As in seaweed samples. The method involved extraction using diluted HNO_3 to quantitatively extract inorganic As without decomposing the organoarsenicals to inorganic As followed by the selective volatilization of inorganic As to arsine and subsequent chemotrapping on a filter paper soaked in mercury bromide (HgBr_2) solution. The method reported a reproducibility with an average error of $\pm 19\%$, and further, the method was also validated with HPLC-ICPMS.

2.4 Conclusions

This review summarizes various available methods for extraction, speciation, and analysis of arsenic at ultra-trace levels. Various methods have been explored for speciation of various As compounds. With suitable extraction procedures, As determination with high sensitivity and precision is plausible in both environmental and biological samples. ICPMS coupled with HPLC or HG technique demonstrated

¹www.wagtech.co.uk. Accessed on 09/08/17.

²www.sensafe.com. Accessed on 09/08/17.

³<http://www.hach.com/arsenic-low-range-test-kit/product?id=7640217303>. Accessed on 09/08/17.

⁴<http://www.vitalus.net/purtest-arsenic-water-test-kit-1-test-kit>. Accessed on 09/08/17.

⁵http://www.merckmillipore.com/food-analytics/rapid-arsenic-tests/c_Hzib.s1OprIAAAEbFfcXP9oy. Accessed on 09/08/17.

separation, speciation, and robust analysis of As with high sensitivity. However, sample storage, preservation of various arsenic species during sample pretreatment is still a challenge. Though field kits offer the advantage of portability and cost-effectiveness, accuracy of determination is questionable.

References

- Aggarwal PK, Dargie M, Groening M, Kulkarni KM, Gibson JJ (2001) Draft report: an inter-laboratory comparison of arsenic analysis in Bangladesh, isotope hydrology section. International Atomic Energy Agency, Vienna, Austria. <http://www.iaea.org/programmes/aqcs/icpt/arsenicpt.pdf>
- Ahmed MF (2009) Periodic table. Chemical & Engineering News. <http://pubs.acs.org/cen/80th/arsenic.html>
- Akter KF, Chen Z, Smith L, Davey D, Naidu R (2005) Speciation of arsenic in groundwater samples: a comparative study of CE-UV, HG-AAS and LC-ICP-MS. *Talanta* 68:406–415
- Alberti J, Rubio R, Rauret G (1995) Extraction method for arsenic speciation in marine organisms. *Fresenius J Anal Chem* 351:420–425
- Alves GMS, Magalhães JMCS, Salaün P, Berg, CMG, Soares HMVM (2011) Simultaneous electrochemical determination of arsenic, copper, lead and mercury in unpolluted fresh waters using a vibrating gold microwire electrode. *Anal Chim Acta* 703(1):1–7
- Amjadi M, Manzoori JL, Abulhassani J (2011) Ultrasound-assisted ionic liquid-based microextraction for preconcentration of arsenic prior to its determination by electrothermal atomic absorption spectrometry. *Curr Anal Chem* 7:262–268
- Ammann AA (2011) Arsenic speciation analysis by ion chromatography—a critical review of principles and applications. *Am J Analyt Chem* 2:27–45
- Aragay G, Pons J, Merkoci A (2011) Recent trends in macro, micro, and nanomaterial based tools and strategies for heavy-metal detection. *Chem Rev* 111:3433–3458
- Bralatei E, Nekrosiute K, Ronan J, Rob A, Stengel DM, McGovern E, Krupp EM, Feldmann J (2017) A field deployable method for a rapid screening analysis of inorganic arsenic in seaweed. *Microchim Acta* 184:1701–1709
- Campillo N, Peñalver R, Viñas P, López-García I, Hernandez-Córdoba M (2008) Speciation of arsenic using capillary gas chromatography with atomic emission detection. *Talanta* 77:793–799
- Cataldo F (2012) Multielemental analysis of municipal landfill leachate with total reflection x-ray fluorescence (TXRF). A comparison with ICP-OES analytical results. *J Radioanal Nuc Chem* 293:119–126
- Chakraborti D, Rahman MM, Raul K, Chowdhury UK, Sengupta MK, Lodh D, Chanda CR, Saha KC, Mukherjee SC (2002) Arsenic calamity in the Indian subcontinent. What lessons have been learned? *Talanta* 58:3–22
- Chandrasekaran K, BalaramaKrishna MV, Karunasagar D (2010) On-line speciation of inorganic arsenic in natural waters using polyaniline (PANI) with determination by flow injection-hydride generation-inductively coupled plasma mass spectrometry at ultra-trace levels. *J Anal At Spectrom* 25:1348–1353
- Chen S, Zhan X, Lu D, Liu C, Zhu L (2009) Speciation analysis of inorganic arsenic in natural water by carbon nanofibers separation and inductively coupled plasma mass spectrometry determination. *Anal Chim Acta* 634:192–196
- Chen ML, Lin YM, Gu CB, Wang JH (2013) A green sorbent of esterified egg-shell membrane for highly selective uptake of arsenate and speciation of inorganic arsenic. *Talanta* 104:53–57
- Chen ML, Ma LY, Chen XW (2014) New procedures for arsenic speciation: a review. *Talanta* 125:78–86

- Colon M, Hidalgo M, Iglesias M (2011) Arsenic determination by ICP-QMS with octopole collision/reaction cell. Overcome of matrix effects under vented and pressurized cell conditions. *Talanta* 85:1941–1947
- Cosnier S, Mousty C, Cui X, Yang X, Dong S (2006) Specific determination of As(V) by an acid phosphatase-polyphenol oxidase biosensor. *Anal Chem* 78(14):4985–4989
- Dickinson GW (1969) Applications of the induction coupled plasma to analytical spectroscopy. Ames Lab, Ames, IA, USA, p 118
- Dressler VL, Antes FG, Moreira CM, Pozebon D, Duarte FA (2011) As, Hg, I, Sb, Se and Sn speciation in body fluids and biological tissues using hyphenated-ICP-MS techniques: a review. *Int J Mass Spectrom* 307:149–162
- Dreyer DR, Park S, Bielawski CW, Ruoff RS (2010) The chemistry of graphene oxide. *Chem Soc Rev* 39(1):228–240
- Ezeh VC, Harrop CT (2012) A sensitive and selective fluorescence sensor for the detection of arsenic(III) in organic media. *Inorg Chem* 51:1213–1215
- Feldmann J, Devalla S, Raab A, Hansen HR (2004) Analytical strategies for arsenic speciation in environmental and biological samples. In: Hirner AV, Emons H (eds) *Organic metal and metalloid species in the environment*. Springer, Heidelberg, p 41
- Forsberg G, O’Laughlin JW, Megargle RG (1975) Determination of arsenic by anodic stripping voltammetry and differential pulse anodic stripping voltammetry. *Anal Chem* 47(9):1586–1592
- Garcia-Manyes S, Jimenez G, Padro A, Rubio R, Rauret G (2002) Arsenic speciation in contaminated soils. *Talanta* 58(1):97–109
- Georgiadis M, Cai Y, Solo-Gabriele HM (2006) Extraction of arsenate and arsenite species from soils and sediments. *Environ Pollut* 141(1):22–29
- Giacomino A, Abollino O, Lazzara M, Malandrino M, Mentasti E (2011) Determination of As(III) by anodic stripping voltammetry using a lateral gold electrode: experimental conditions, electron transfer and monitoring of electrode surface. *Talanta* 83:1428–1435
- Gibbon-Walsh K, Salaün P, Berg CMG (2010) Arsenic speciation in natural waters by cathodic stripping voltammetry. *Anal Chim Acta* 662(1):1–8
- Gomez-Ariza JL, Sanchez-Rodas D, Giráldez I, Morales E (2000) Comparison of biota sample pretreatments for arsenic speciation with coupled HPLC-HG-ICP-MS. *Analyst* 125:401–407
- Gonzalez A, Llorens A, Cervera ML, Armenta S, Guardia M (2009) Non-chromatographic speciation of inorganic arsenic in mushrooms by hydride generation atomic fluorescence spectrometry. *Food Chem* 115:360–364
- Greschonig H, Irgolic KJ (1992) Electrochemical methods for the determination total arsenic and arsenic compounds. *Appl Organomet Chem* 6:565–577
- Guell R, Fontas C, Salvado V, Antico E (2010) Modeling of liquid-liquid extraction and liquid membrane separation of arsenic species in environmental matrices. *Sep Purif Technol* 72:319–325
- Holak W (1969) Gas-sampling technique for arsenic determination by atomic absorption spectrophotometry. *Anal Chem* 41(12):1712–1713
- Howard AG (1997) (Boro)Hydride techniques in trace element speciation. *J Anal At Spectrom* 12:267–272
- Howard AG, Salou C (1996) Cysteine enhancement of the cryogenic trap hydride AAS determination of dissolved arsenic species. *Anal Chim Acta* 333:89–96
- Hsieh CJ, Yen CH, Kuo MS (1999) Determination of trace amounts of arsenic(III) and arsenic(V) in drinking water and arsenic(III) vapor in air by graphite-furnace atomic absorption spectrophotometry using 2,3-dimercaptopropane-1-sulfonate as a complexing agent. *Anal Sci* 15(7):669–673
- Hueber DM, Winefordner JD (1995) A flowing electrolytic hydride generator for continuous sample introduction in atomic spectrometry. *Anal Chim Acta* 316:129–144
- Jia X, Gong D, Wang J, Huang F, Duan T, Zhang X (2016) Arsenic speciation in environmental waters by a new specific phosphine modified polymer microsphere preconcentration and HPLC–ICP-MS determination. *Talanta* 160:437–443

- Kang JH, Jung HJ, Jung MY (2016) One step derivatization with British Anti-Lewisite in combination with gas chromatography coupled to triple-quadrupole tandem mass spectrometry for the fast and selective analysis of inorganic arsenic in rice. *Anal Chim Acta* 934:231–238
- Karthikeyan S, Rao TP, Iyer CSV (1999) Determination of arsenic in sea water by sorbent extraction with hydride generation atomic absorption spectrometry. *Talanta* 49(3):523–530
- Kempahnumakkagari S, Deep A, Kim KH, Kumar Kailasa S, Yoon HO (2017) Nanomaterial-based electrochemical sensors for arsenic—a review. *Biosens Bioelectron* 95:106–116
- Kohlmeyer U, Kuballa J, Jantzen E (2002) Simultaneous separation of 17 inorganic and organic arsenic compounds in marine biota by means of high-performance liquid chromatography/inductively coupled plasma mass spectrometry. *Rapid Commun Mass Spectrom* 16:965–974
- Kroukamp EM, Wondimu T, Forbes PBC (2016) Metal and metalloid speciation in plants: overview, instrumentation, approaches and commonly assessed elements. *Trends Anal Chem* 77:87–99
- Larsen EH (1998) Method optimization and quality assurance in speciation analysis using HPLC with detection ICPMS. *Spectrochim Acta Part B At Spectrosc* 53(2):253–265
- Le XC, Mingsheng MA, Wong NA (1996) Speciation of arsenic compounds using high performance liquid chromatography at elevated temperature and selective hydride generation atomic fluorescence detection. *Anal Chem* 68:4501–4506
- Leermakers M, Baeyens W, De Gieter M, Smedts B, Meert C, De Bisschop HC, Morabito R, Quevauviller Ph (2006) Toxic arsenic compounds in environmental samples: speciation and validation. *Trends Anal Chem* 25:1–10
- Liu LH, Hen B, Yun Z, Sun J, Jiang GB (2013) Speciation analysis of arsenic compounds by capillary electrophoresis on-line coupled with inductively coupled plasma mass spectrometry using a novel interface. *J Chromatogr* 1304:227–233
- Llorente-Mirandes T, Rubio R, López-Sánchez JF (2017) Inorganic arsenic determination in food: a review of analytical proposals and quality assessment over the last six years. *Appl Spectrosc* 71:25–69
- Lolic A, Nikolic S, Mutic J (2008) Optimization of a flow injection system with amperometric detection for arsenic determination. *Anal Sci* 24:877–880
- Majidi B, Shemirani F (2011) In situ solvent formation microextraction in the presence of ionic liquid for preconcentration and speciation of arsenic in saline samples and total arsenic in biological samples by electrothermal atomic absorption spectrometry. *Biol Trace Elem Res* 143:579–590
- Male KB, Hrapovic S, Santini JM, Luong JH (2007) Biosensor for arsenite using arsenite oxidase and multiwalled carbon nanotube modified electrodes. *Anal Chem* 79(20):7831–7837
- Mays DE, Hussam A (2009) Voltammetric methods for determination and speciation of inorganic arsenic in the environment—a review. *Anal Chim Acta* 646:6–16
- McSheehy S, Pohl P, Lobinski R, Szpunar J (2001) *Analyst* 126:1055
- Meng X, Jing C, Korfiatis GP (2003) A review of redox transformation of arsenic in aquatic environments. In: *ACS symposium series 835*, Washington, pp 70–83
- Michalke B (2003) Element speciation definitions, analytical methodology, and some examples. *Ecotoxicol Environ Saf* 56:122–139
- Mondal P, Balomajumder C, Mohanty B (2007) Quantitative separation of As(III) and As(V) from a synthetic water solution using ion exchange columns in the presence of Fe and Mn ions. *Clean-Soil Air Water* 35:255–260
- Musil S, Petursdottir AH, Raab A, Gunnlaugsdottir H, Krupp E, Feldmann J (2014) Speciation without chromatography using selective hydride generation: inorganic arsenic in rice and samples of marine Origin. *Anal Chem* 86(2):993–999
- Namera A, Takeuchi A, Saito T, Miyazaki S, Oikawa H, Saruwatari T, Nagao M (2012) Sequential extraction of inorganic arsenic compounds and methyl arsenate in human urine using mixed-mode monolithic silica spin column coupled with gas chromatography-mass spectrometry. *J Sep Sci* 35:2506–2513

- Narukawa T (2000) Abstract of the 7th frontiers in education: computer science and computer engineering conference. Environ Sci Pollut Resvol 40
- Naykki T, Perämäki P, Kujala J, Mikkonen A (2001) Optimization of a flow injection hydride generation atomic absorption spectrometric method for the determination of arsenic, antimony and selenium in iron chloride/sulfate-based water treatment chemical. Anal Chim Acta 439:229–238
- Nearing MM, Koch I, Reimer KJ (2014) Complementary arsenic speciation methods: a review. Spectrochim Acta B 99:150–162
- Popp M, Hann S, Koellensperger G (2010) Environmental application of elemental speciation analysis based on liquid or gas chromatography hyphenated to inductively coupled plasma mass spectrometry—a review. Anal Chim Acta 668(2):114–129
- Profumo A, Merli D, Pesavento M (2005) Voltammetric determination of inorganic As(III) and total inorganic As in natural waters. Anal Chim Acta 539(1–2):245–250
- Profumo A, Fagnoni M, Merli D, Quartarone E, Protti S, Dondi D, Albini A (2006) Multiwalled carbon nanotubes chemically modified gold electrode for inorganic as speciation and Bi(III) determination. Anal Chem 78:4194–4199
- Qu H, Mudalige TK, Linder SW (2015) Arsenic speciation in rice by capillary electrophoresis/inductively coupled plasma mass spectrometry: enzyme-assisted water-phase microwave digestion. J Agric Food Chem 63:3153–3160
- Quinaia SP, Rollemberg ME (2001) Selective reduction of arsenic species by hydride generation-atomic absorption spectrometry. Part 2-sample storage and arsenic determination in natural waters. J Braz Chem Soc 12:37–41
- Radke B, Jewell L, Namiesnik J (2012) Analysis of arsenic species in environmental samples. Crit Rev Anal Chem 42:162–183
- Rahman MM, Chowdhury UK, Mukherjee SC, Mandal BK, Paul K, Lodh D, Biswas BK, Chanda CR, Basu GK, Saha KS, Roy S, Das R, Palit SK, Quamruzzaman Q, Chakraborti D (2001) Chronic arsenic toxicity in Bangladesh and West Bengal, India—a review and commentary. J Toxicol Clin Toxicol 39:683–700
- Rajakovic L, Todorovic Z, Rajakovic-Ognjanovic V, Onjia A (2013) Analytical methods for arsenic speciation analysis. J Serbian Chem Soc 78(10):1461–1479
- Ramesha G, Sampath S (2011) In-situ formation of graphene–lead oxide composite and its use in trace arsenic detection. Sens Actuators B 160:306–311
- Rasheed H, Kay P, Slack R, Gong YY, Carter A (2017) Human exposure assessment of different arsenic species in household water sources in a high risk arsenic area. Sci Tot Environ 584–584:631–641
- Rottschäfer JM, Boczkowski RJ, Mark HB Jr (1972) Preconcentration techniques for trace analysis *via* neutron activation. Talanta 19:163–172
- Rupasinghe TWT, Cardwell TC, Catral RW, Kolev SD (2009) Determination of arsenic in industrial samples by pervaporation flow injection with amperometric detection. Anal Chim Acta 652:266–271
- Sadee B, Foulkes ME, Hill SJ (2015) Coupled techniques for arsenic speciation in food and drinking water: a review. J Anal At Spectrom 30:102–118
- Sanchez WM, Zwicker B, Chatt A (2009) Determination of As(III), As(V), MMA and DMA in drinking water by solid phase extraction and neutron activation. J Radioanal Nucl Chem 282:133–138
- Sanson B, Brunner W, Wolff G, Ruppert H, Dittrich R (1988) Comparative instrumental multielement determination. I: comparison of ICP source mass spectrometry with ICP atomic emission spectrometry, ICP atomic fluorescence spectrometry for the analysis of natural waters from a granite region. Fresenius Z Anal Chem 331(2):154–169
- Sengupta MK, Dasgupta PK (2009) An automated hydride generation interface to ICPMS for measuring total arsenic in environmental samples. Anal Chem 81:9737–9743
- Sheppard BS, Carusot JA, Heitkenper DT, Wolnik KA (1992) Arsenic speciation by ion chromatography with inductively coupled plasma mass spectrometric detection. Analyst 117:971–976

- Shi Y, Chatt A (2014) Simultaneous determination of inorganic As(III), As(V), Sb(III), Sb(V), and Se(IV) species in natural waters by APDC/MIBK-NAA. *J Radioanal Nucl Chem* 299:867–877
- Shiomi K (1994) Arsenic in the environment. Part II: human health and ecosystem effects. In: Nriagu JO (ed) vol 27. Wiley, New York, pp 261–293
- Shirkhanloo H, Rouhollahi J, Mousavi HZ (2011) Ultra-trace arsenic determination in urine and whole blood samples by flow injection-hydride generation atomic absorption spectrometry after preconcentration and speciation based on dispersive liquid-liquid microextraction. *Korean Chem Soc* 32:3923–3927
- Sitko R, Janik P, Zawisza B, Talik E, MarguiE Queralto I (2015) Green approach for ultratrace determination of divalent metal ions and arsenic species using total-reflection X-ray fluorescence spectrometry and mercapto-modified graphene oxide nanosheets as a novel adsorbent. *Anal Chem* 87(6):3535–3542
- Sloth JJ, Larsen EH, Julshamn K (2003) Determination of organoarsenic species in marine samples using gradient elution cation exchange HPLC-ICP-MS. *J Anal At Spectrom* 18(5):452–459
- Stetzenbach KJ, Amano M, Kreamer DK, Hodge VF (1994) Testing the limits of ICP-MS: determination of trace elements in groundwater at the part-per trillion level. *Ground Water* 32(6):976–985
- Sun YC, Yang JY (1999) Simultaneous determination of arsenic(III,V), selenium(IV,VI), and antimony(III,V) in natural water by coprecipitation and neutron activation analysis. *Anal Chim Acta* 395:293–300
- Szostek B, Aldstadt JH (1998) Determination of organoarsenicals in the environment by solid-phase microextraction-gas chromatography-mass spectrometry. *J Chromatogr A* 807(2):253–263
- Takeuchi A, Namera A, Kawasumi Y, Imanaka T, Sakui N, Ota H, Endo Y, Sumino K, Endo G (2012) Development of an analytical method for the determination of arsenic in urine by gas chromatography-mass spectrometry for biological monitoring of exposure to inorganic arsenic. *J Occup Health* 54(6):434–440
- Thurrow K, Koch A, Stoll N, Haney CA (2002) Environmental aspects of converting CW facilities to peaceful purposes. In: McGuire RR, Compton JC (Eds) Kluwer Academic Publishers, Dordrecht, pp 123–138
- Tulasi D, Adotey D, Affum A, Carboo D, Serfor-Armah Y (2013) Speciation of As(III) and As(V) in water and sediment using reverse-phase ion-pair high-performance liquid chromatography-neutron activation analysis (HPLC-NAA). *Env Monitor Assess* 185:7979–7991
- Tuzen M, Citak D, Mendil D, Soylak M (2009) Arsenic speciation in natural water samples by coprecipitation-hydride generation atomic absorption spectrometry combination. *Talanta* 78:52–56
- Tyson J (2013) The determination of arsenic compounds: a critical review. *ISRN Anal Chem* 2013:1–24
- United States Environmental Protection Agency (1999a) Analytical methods support document for arsenic in drinking water. <http://www.epa.gov/safewater/arsenic/pdfs/methods.pdf>. Accessed on 09 Aug 17
- United States Environmental Protection Agency (1999b) Analytical methods support document for arsenic in drinking water. Standard and risk management division, Washington. <http://www.epa.gov/safewater/arsenic/pdfs/methods.pdf>. Accessed on 09 Aug 17
- United States Environmental Protection Agency (2004) Monitoring arsenic in the environment: a review of science and technologies for field measurements and sensors. http://www.epa.gov/tio/download/char/arsenic_paper.pdf
- Wangkarn S, Pergantis SA (2000) High-speed separation of arsenic compounds using narrow-bore high-performance liquid chromatography on-line with inductively coupled plasma mass spectrometry. *J Anal At Spectrom* 15:627–633
- World Health Organisation (1993) Guidelines for drinking-water quality, Geneva, Switzerland. <http://www.who.int/mediacentre/factsheets/fs372/en/>. Accessed on 09 Aug 17

- World Health Organization (2001) United Nations synthesis report on arsenic in drinking water. <http://www.bvsde.paho.org/bvsacd/who/arsin.pdf>. Accessed on 09 Aug 17
- Xiao L, Wildgoose GG, Compton RG (2008) Sensitive electrochemical detection of arsenic (III) using gold nanoparticle modified carbon nanotubes via anodic stripping voltammetry. *Anal Chim Acta* 620:44–49
- Yamamoto M, Yasuda M, Yamamoto Y (1985) Hydride-generation atomic absorption spectrometry coupled with flow injection analysis. *Anal Chem* 57:1382–1385
- Yan XP, Kerrich R, Hendry MJ (1998) Determination of (ultra)trace amounts of arsenic(III) and arsenic(V) in water by inductively coupled plasma mass spectrometry coupled with flow injection on-line sorption preconcentration and separation in a knotted reactor. *Anal Chem* 70 (22):4736–4742
- Yan XP, Yin XB, He XW, Jiang Y (2002) Flow injection on-line sorption preconcentration coupled with hydride generation atomic fluorescence spectrometry for determination of (ultra)trace amounts of arsenic(III) and arsenic(V) in natural water samples. *Anal Chem* 74 (9):2162–2166
- Yang GD, Xu JH, Zheng JP, Xu XQ, Wang W, Xu LJ, Chen GN, Fu FF (2009) Speciation analysis of arsenic in *Mya arenaria* Linnaeus and Shrimp with capillary electrophoresis-inductively coupled plasma mass spectrometry. *Talanta* 78:471–476
- Yavuz CTM, Yu JT, Prakash WW, Falkner A, Yean JC, Cong S, Shipley LL, Kan HJ, Tomson M, Natelson, Zhang X, Zeng T, Hu C, Hu S, Tian Q (2016) *Anal Methods* 8:1162–1169
- Yehl PM, Tyson JF (1997) Towards speciation of arsenic in a standard reference river sediment by high-performance ion chromatography coupled with plasma source mass spectrometry. *Anal Commun* 34:49–51
- Yehl PM, Gurleyuk H, Tyson JF, Uden PC (2001) Microwave-assisted extraction of monomethyl arsenic acid from soil and sediment standard reference materials. *Analyst* 126:1511–1518
- Zhao D, Li HB, Xu JY, Luo J, Ma LQ (2015) Arsenic extraction and speciation in plants: method comparison and development Science. *Sci Total Environ* 523:138–145-425
- Zheng F, Hu B (2009) Dual silica monolithic capillary microextraction (CME) on-line coupled with ICP-MS for sequential determination of inorganic arsenic and selenium species in natural waters. *J Anal At Spectrom* 24:1051–1061
- Zhu L, Chen S, Lu D, Cheng X (2009) Single-wall carbon nanotubes for speciation of arsenic in environmental samples by inductively coupled plasma mass spectrometry. *At Spectrom* 30 (6):218–222

Environmental Contaminants

Measurement, Modelling and Control

Gupta, T.; Agarwal, A.K.; Agarwal, R.A.; Labhasetwar,
N.K. (Eds.)

2018, XXII, 431 p. 140 illus., 97 illus. in color., Hardcover

ISBN: 978-981-10-7331-1