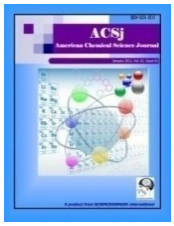

American Chemical Science Journal
6(1): 1-15, 2015, Article no.ACSj.2015.032
ISSN: 2249-0205

SCIENCEDOMAIN *international*
www.sciencedomain.org

An Overview of Arsenic Extraction and Speciation Techniques in Soil and Water

Shah Rukh[1*], Mohammad Saleem Akhtar[1], Mehruinsa Memon[2], Ayaz Mehmood[3] and Muhammad Imran[1]

[1]Department of Soil Science, Soil and Water Conservation, PMAS Arid Agriculture University, Rawalpindi (46300), Pakistan.
[2]Department of Soil Science, Sindh Agriculture University, Tando Jam (70060), Pakistan.
[3]Department of Agriculture Sciences, University of Haripur, Pakistan.

Authors' contributions

This work was carried out in collaboration between all authors. Authors SR and MSA conceived the idea. Authors MM, AM and MI critically reviewed the manuscript. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/ACSj/2015/13680
Editor(s):
(1) Nagatoshi Nishiwaki, Kochi University of Technology, Japan.
Reviewers:
(1) Anonymous, Portugal.
(2) Muhammad Ihsan Danish, Department of Environmental Science, Shaheed Benazir Bhutto University, Pakistan.
(3) Md Abdus Subhan, Department of Chemistry, Shah Jalal University of Science and Technology, Bangladesh.
(4) Anonymous, Mexico.
Complete Peer review History: http://www.sciencedomain.org/review-history.php?iid=899&id=16&aid=7596

Review Article

Received 28th August 2014
Accepted 8th December 2014
Published 1st January 2015

ABSTRACT

Arsenic toxicity and bioavailability are controlled by its chemical forms (e.g. exchangeable, sorbed on organic matter, Fe/Al bound pools and mineral phases) and oxidation states (As(III) and As(V)). High interest has been developed in measurement of arsenic species due to their hazardous nature. Little information is available on methods used for quantitative distribution of arsenic forms and species in contaminated soils and water. The aim of this article is to provide an understanding of available techniques for arsenic speciation and its extraction from soil. Various techniques used in arsenic speciation (spectrometric, chromatographic and voltammetric) are discussed. Research efforts are still needed to develop inexpensive, rapid, sensitive and reproducible methodologies for arsenic species capable of working in the low detection limits.

**Corresponding author: E-mail: shahishah_86jm@yahoo.com, shahrukhshah@hotmail.com;*

Keywords: Arsenic; speciation; extraction; techniques; soil and water.

1. INTRODUCTION

Arsenic (As) speciation may imply determination of its specific ionic forms in aqueous solution and of sequentially extracted As associated with various mineral phases [1]. Since the toxicity and bioavailability depend on oxidation state rather than its total content, speciation provides more useful information than the total element analysis [2]. In recent years As speciation is essential for understanding its distribution, mobility, toxicity and bioavailability in the natural system [3].

Arsenic forms a variety of inorganic and organic compounds in soils [4]. Inorganic As occurs dominantly as pentavalent arsenate (As(V)) and trivalent arsenite (As(III)). Redox potential (Eh) and pH control inorganic As speciation [5]. Pentavalent arsenate (oxyanions) viz., H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{-2}$ and AsO_4^{-3} are formed under low reducing conditions and high redox potentials while the trivalent arsenic species viz., $H_3AsO_3^0$, $H_2AsO_3^-$, $HAsO_2^0$, AsO_2^- are dominant under high reducing condition and low redox potential [6,7]. In contaminated soils, As(V) species are predominant over As(III), and organic arsenic may be upto 40% of total As content [8]. Transformation of As(V) to As(III) takes place due to bacterial activity which may be later methylated to less toxic organic species [9]. Organic As compounds are monomethylarsonic acid (MMA) and dimethylarsenic acid (DMA) formed by bacterial-mediated methylation processes of inorganic As under oxidizing conditions [10]. The inorganic As phases are 100 times more toxic than organic phases; and among the inorganic As forms As(III) is 25-60 times more toxic than As(V) [11,12]. Maximum permissible limit for As in drinking water is 10 µg L^{-1}, while for As species no limit values have been established [13,14]. Correct estimation of As form in soil or water is important for understanding bioavailability of As and its effects on biota [15]. This paper reviews recent development in measurement of total and various species of As in soil and water.

2. EXTRACTION AND PRESERVATION OF ARSENIC SPECIES

In case of soils and sediments the first step in As speciation is its extraction. An extraction procedure must meet three criteria: (i) the extracting solution must solubilize only the specific form, (ii) reduction of native As (V) to As(III) may not occur during the extraction, and (iii) oxidation of native As(III) to As(V) should not occur [16]. Four extraction procedures are commonly used (i) extraction with 10 M HCl in 1:30 soil to solution ratio shaken for 30 minutes [17], (ii) extraction with 15% (v/v) H_3PO_4 in 1:200 soil to solution ratio heated at 95±3ºC for 1 h [18], (iii) extraction with 10 mM phosphate (prepared from 0.5 M KH_2PO_4 and 0.5 M K_2HPO_4 in equal amount) + 0.5% (w/v) Sodium Diethyldithiocarbamate, (NaDDC), $(C_2H_5)_2NCS_2Na.3H_2O$) in 1:40 soil to solution ratio shaken for 60 minutes [19] and (iv) extraction with 1 M H_3PO_4 plus 0.5 M ascorbic acid ($C_6H_8O_6$) using 1:150 soil to solution ratio kept at 60 W in microwave for 10 min [20,21,22]. Extraction with one molar H_3PO_4 + 0.5 M $C_6H_8O_6$ extracts maximum As while minimizing conversion of As(III) to As(V) [16]. Similarly, the 10 mM phosphate plus 0.5 % (w/v) NaDDC extractant also minimize reduction of As(III) [19]. Sodium diethyldithiocarbamate is also a good complexing agent for AsIII for water samples [23].

In order to preserve the species information sampling and storage procedures are considered as a key requirement. Preservation should keep the chemical species of interest unchanged during all steps of analysis to avoid changes in the oxidation state, changes induced by microbial activity and losses by volatilization or adsorption. Water samples are stored in darkened polythene containers, and for longer preservation, samples are acidified HCl [24], HNO_3 [25], H_2SO_4 [26] and H_3PO_4 [27] increases the stability of As(III) and As(V) compared to unacidified samples. Using 10 mM H_3PO_4 as a preserving agent combined with keeping samples at 6ºC in dark, As species remain stable for 3 months, even with high concentrations of Fe and Mn. Stability procedures and reports are sometimes contradictory especially in case of complex solids matrices such as soils.

3. DERIVITIZATION OF TOTAL ARSENIC

Derivitization of total extracted As is carried out by sodium borohydride/hydrochloric acid for assay by AAS or ICP-MS [28,29]. The derivitization process causes reduction of AsV to AsIII in the first step, followed by arsine (AsH_3) production [30].

$$R_nAs(O)(OH)_{3-n} + H^+ + BH_4^- \rightarrow R_nAs(OH)_{3-n} \quad (1)$$

Where R is a methyl group and n ranges from 0 to 3. Subsequent reaction with the tetrahydroborate (III) takes the compound through to the corresponding arsine:

$$R_nAs(OH)_{3-n} + (3-n)BH_4^- + (3-n)H^+ \rightarrow R_nAsH_{3-n} + (3-n)BH_3 + (3-n)H_2O \quad (2)$$

The arsines production is pH sensitive [31]. Arsines (R_nAsH_{3-n}) produced during hydride generation (HG) step arrive in atomic absorption spectrophotometer or ICP-MS for measurement driven by an inert gas N_2 [32]. This improves the detection limits up to 100-fold over the commonly used liquid sample nebulization process [33]. It can eliminate spectral and chemical interferences encountered in the detection system as only gaseous hydrides are introduced into the detector. This technique strongly depends on type and concentration of the sample matrix.

However, the drawbacks of arsine are that firstly, it is limited to the materials that form volatile arsines and not suitable for non hydride forming As forms such as AsB, AsC, or arsenosugars [34], secondly, the reaction conditions must be strictly controlled, and thirdly the presence interfering elements such as copper (II), cobalt (II) and nickel (II) can reduce AsH_3 production efficiency [31,35]. Sodium borohydride is now universally used for the synthesis of hydrides [36].

For species determination usually at least two steps are followed: Separation and detection (Fig. 1). Nowadays, coupled techniques combining the separation technique with detection system are most applicable hyphenated techniques. Hyphenated techniques have many advantages such as high sensitivity, good reproducibility, short analysis time and reduced risk for species transformation. These are expensive systems used in scientific research rather than in routine analysis.

4. TECHNIQUES FOR SEPARATION OF ARSENIC SPECIES

Two common techniques used most frequently for separation of As species are chromatography (gas and liquid) and capillary electrophoresis [37,38]. Due to different chemistry of As compounds both the techniques are sometimes used cumulatively [39].

4.1 Liquid Chromatography

Liquid chromatography offers excellent possibilities for separation while gas chromatography is less common as most As compounds are non-volatile, and thus not applicable to environmental samples. Various liquid chromatography techniques commonly used are high performance liquid chromatography (HPLC), ion chromatography, and ion interaction chromatography [3]. Since As species form weak acids having different dissociation constants this difference in dissociation constant is used to speciate the acids by high performance liquid chromatography and ion chromatography [30]. Chromatographic separation can take place either by direct separation of metal ions using ion exchange columns or by adsorption (reversed- or normal-phase) liquid chromatography if the metal species are complexed with organic ligands. Ion chromatography is the advanced version of reversed-phase HPLC where the reversed-phase column is replaced by an ion-exchange column. With the development of various ion-exchange columns it becomes the best technique in metal ion speciation [40,41]. Liquid chromatography is attached with many other detection systems such as ICP-MS, HG-AFS, HG-AAS and GF-AAS [38]. The main advantage of liquid chromatography is that it eliminates the derivitization step, and allows waters and soil extracts to be analyzed directly [3]. Organic and inorganic species of As can be determined by using appropriate liquid chromatographic technique. However, organic solvents used as the mobile phase in liquid chromatography have limited UV transparency range which limits their use with a UV detector. Coelution of species having similar physicochemical properties is another problem related to liquid chromatographic techniques.

4.2 Capillary Electrophoresis

Capillary electrophoresis (CE) can also be used for separation of As species [42]. In capillary electrophoresis As species are separated on the basis of their charge to size ratio controlled by buffer constituents, concentration and pH. Capillary electrophoresis can be used with number of different detection systems [43] but most commonly used with ICP-MS [44]. Capillary electrophoresis has high separation efficiency for As speciation [45,46,47]. The use of CE has increased in recent years although not as prevalent as HPLC. Compared to chromatographic techniques, capillary

electrophoresis has advantage of simplicity, cost effectiveness, high speed of analysis and some degree of matrix independence. However, size of capillary limits path length for UV detection resulting in poor sensitivity [48]. Method development has addressed some traditional limitations associated with CE such as interfacing with detection systems [49,50].

5. DETECTION SYSTEMS

Speciation analysis demands sensitive and element specific detectors. Various detection instruments are atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GFAAS), atomic fluorescence spectrometry (AFS) and induced coupled plasma mass spectrometry (ICP- MS) which provide different level of specificity, cost effectiveness and detection limits [3,38].

5.1 Atomic Absorption Spectrometry

Atomic absorption spectrometry gives high sensitivity and low detection limit (for As(III) and As(V) <1 μg L^{-1}) only when coupled with hydride generation or different separation tachniques [51]. Atomic absorption spectrometry as alone stands facility constrained by position of As resonance lines (193.7 nm) in the low ultraviolet region of the spectrum where acetylene flame absorption is severe and spectral interferences from radicals in the flame [36], unless coupled with hydride generation system [52,53]. Similarly, for As speciation, AAS needs to be coupled with HPLC-HG for separation [52]. The use of HPLC-HG-AAS enabled the elimination of interference and the highly sensitive determination of As species at ng L^{-1} level [54,55]. For the detection of trace concentrations of As species HG-AAS is a more affordable and much less expensive technique than ICP-MS in soil and water samples [53].

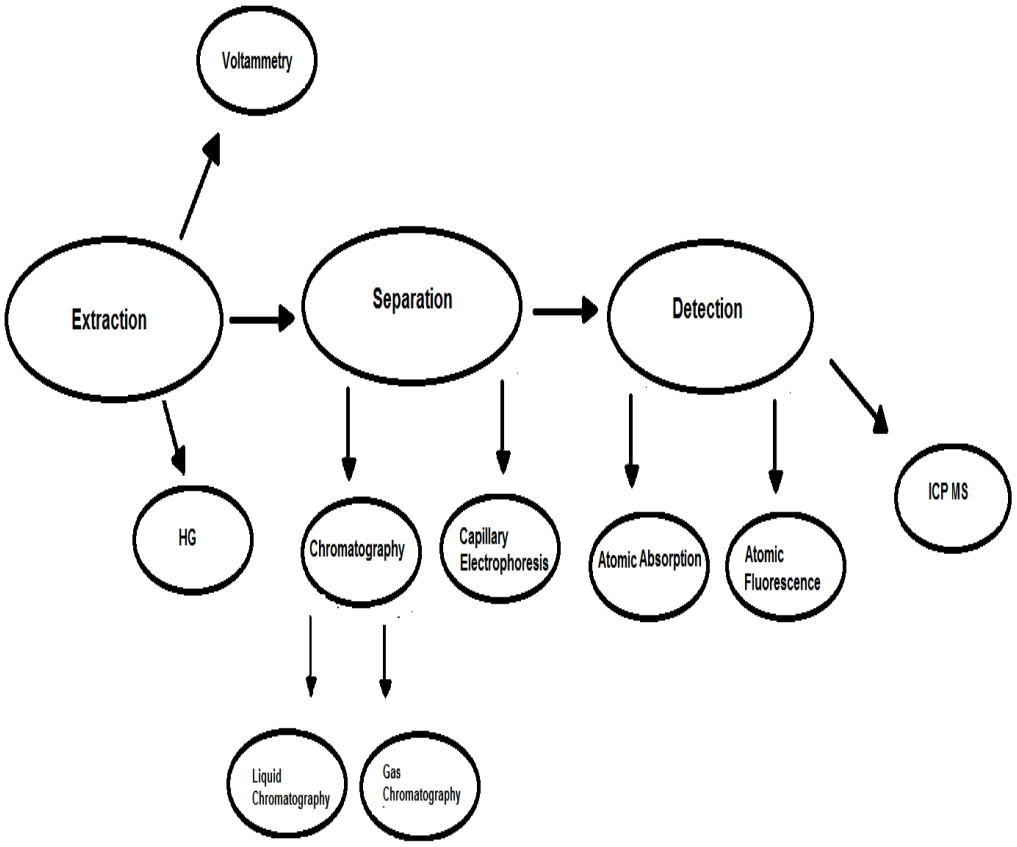

Fig. 1. Techniques involved in arsenic speciation analysis

Excellent and similar sensitivity in As speciation in groundwaters using HG-AAS and LC-ICP-MS was observed [56]. Limit of detection [LOD] in this method equal 0.07 for As(III), 0.10 for As(V), 0.10 for MMAA, 0.11 for DMAA, ngAs [57,58]. Akter et al. [56] determined As speciation with LOD from 0.10 (AsIII, AsT) to 0.19 (DMA) μg L^{-1}, while Maity *et al*., [59] achieved LOD up to 0.4 μg L^{-1} for As(III) in groundwater samples using HG-AAS method. Shraim et al. [30] found LOD to be 1.1 μg L^{-1} for total As, 0.5 μg L^{-1} for DMA, 0.6 μg L^{-1} for As(III) and 1.8 μg L^{-1} for MMA, respectively. Macedo et al. [60] determined total As and As(III) in phosphate fertilizers by slurry preparation with HCl, and they found LOD to be 0.1 μg L^{-1}. Apau and Enyemadze, [61] determine arsenic species (AsIII and AsV) in drinking water samples using HG-AAS and found that the procedure was precise and low time consuming as just a very simple sample treatment was required. Similarly, HG-AAS was used for the determination of ASIII and AsV in water and sediments and concluded that the precision for nine sample replicates was better than 3.1% for inorganic arsenic species [62]. A quantitative determination of methylated As-species (MMAA, DMAA) and arsenate (As(V)) with HG technique is only possible using standard addition procedures for calibration and not with external calibration. These problems do not occur when a detection system (e.g. ICP-MS) is used.

Graphite furnace atomic absorption spectrometry can be a stand alone facility without the need of AsH_3 because of low level interference [63] yet its performance is enhanced with hydride generation [64] but it may be attached with the chromatographic separation instrument. It has advantage of better limit of detection and low cost over many other detection techniques [65]. The use of a chemical modifier has become vital to reduce matrix interferences and to increase accuracy, for the stabilization of volatile elements during the pretreatment step. GFAAS is an efficient technique when coupled with different separation techniques and chemical modifiers, and can determine trace amounts of As(III), As(V), MMA, DMA and AsB with LOD 4–5 μg L^{-1} in fish and 0.02 μg L^{-1} in seawater. Due to simplicity of operation, rapidity, low consumption of organic solvents and high enrichment factors, this technique has been applied for the determination of As speciation in environmental samples with LOD of 9.2 ng L^{-1} and 0.01–0.12 μg L^{-1} in water [33]. Latif, [66] determined As species (AsIII and AsV) in water samples using GFAAS and achieved LOD 0.05 μg L^{-1}. A solid phase extraction coupled with dispersive liquid–liquid micro extraction based on the solidification of floating organic drop method, using diethyl dithiphosphate as a proper chelating agent, has been developed as an ultra preconcentration technique for the determination of inorganic arsenic in water samples prior GFAAS and found LOD 2.5 ng L^{-1} [67].

5.2 Atomic Fluorescence Spectrometry

Atomic fluorescence spectrometry works on the principle of measuring florescence emitted from excited atoms. The intensity of fluorescence is directly proportional to the concentration of atoms and hence has advantage over AAS or graphite furnace [68]. Light scattering and background correction due to sample matrix is main problem solved by separating AsH_3 from sample matrix through hydride generation. Arsenic speciation detection limit at μg L^{-1} level have been achieved when HG-AFS is attached to chromatographic separation techniques [69,70]. Atomic fluorescence spectrometry coupled with hydride generator is an attractive alternate to ICP-MS due to its low cost, low operating cost and high sensitivity [71].

Separation of various volatile arsenic species produced by sediments were performed by short packed cotton column which rapidly and effectively separated volatile arsenicals (AsH_3, CH_3AsH_2, $(CH_3)_2AsH$ and $(CH_3)_3As$). After separation on a cotton column, volatile arsenic species were sensitively detected by AFS [72]. Musil et al. [73] developed a method of selective hydride generation-cryotrapping (HG-CT) coupled to a simple in-house assembled and designed AFS including an advanced flame-in-gas-shield atomizer which was interfaced to HG-CT. A significant improvement both in sensitivity and baseline noise was found that was reflected in improved LOD for drinking water samples. The yielded LOD were 0.44, 0.74, 0.15, 0.17 and 0.67 ng L^{-1} for AsIII, total As, MMA, DMA and TMA, respectively. Limit of detection of 13 ng L^{-1} and 15 ng L^{-1} for AsIII and AsV was achieved in natural water samples by using method based on the generation of AsH_3 from the reaction between the arsenic species in the injected solution and tetrahydroborate immobilized on a strong anion-exchange resin prior to AFS detection [74]. A novel method for arsenic species in fresh water samples was developed in which after chromatographic separation of arsenic species HG-AFS was employed and

achieved LOD of 1.0, 3.0, 2.2 and 1.5 µg/L for As(III), DMA, MMA and As(V) respectively [75].

5.3 Inductively Coupled Plasma-Mass Spectrometry

Inductively coupled plasma-mass spectrometry is a detection technique with or without a separation technique. Liquid sample is pumped into a nebulizer converted into a fine aerosol and carried into argon plasma torch contained by a strong magnetic field causing excitation and release of specific energy as they return to ground state. It is a favored detection technique for arsenic analysis [76] and applied in many studies with all types of samples due to various advantages like ultra-sensitivity, multi-element capability and coupling it with various separation techniques for speciation. The coupling of chromatography with ICP-MS has advantages because of compatibility of the mobile phase with plasma torch behavior and carefully established mass detection interferences. It is necessary to maintain very low pressure in the spectrometer while separated analyte ions leaves the chromatographic column under comparatively high pressure is the main difficulty in using mass spectrometry detector coupled with chromatographic methods. Coupling of HPLC-ICPMS relies on matching chromatographic peaks to standards and provides no structural information about the separated compounds as the number of available standards is limited. These limitations stress on the use of complementary analysis methods for better understanding of arsenic chemistry occurring in the soil and water sample [43]. Applications of HPLC–ICPMS for As speciation have been demonstrated [77].

Limit of detection values in most of the published papers were several tens to several hundreds of µg L^{-1} [78]. The values calculated by particular authors varied because of the different sample injection volumes. At one of the lowest sample injection volumes, 20 µL, the DOL values were in the range of 0.017 to 1.2 µg L^{-1} for As(III), 0.026 to 1.0 µg L^{-1} for As(V), 0.026 to 0.9 µg L^{-1} for MMA, 0.023 to 1.7 µg L^{-1} for DMA and 0.024 to 0.4 µg L^{-1} for AsB [79,80]. However, by increasing the sample injection volume to 100 µL[81–85] or 200 µL, [86–88] almost none of the authors obtained similar results to those presented by Ronkart et al. [79]. Lowest values obtained with the use of a larger sample injection volume were 0.03 µg L^{-1} for As(III), [81] 0.027 µg L^{-1} for As(V), [85] 0.035 µg L^{-1} for MMA, [84] 0.011 µg L^{-1} for DMA, [85] and 0.01 µg L^{-1} for AsB [81]. Dissolves AsIII and AsV in the mineral soil extracts were quantified by using HPLC-ICPMS with DOL in the range of 1 to 75 ng As/g [89].

6. VOLTAMMETRIC METHODS

Voltammetry is a simple and cost effective stand alone technique that can be used for arsenic speciation without separation and derivitization steps. A voltammeter consists of working electrode, a reference electrode (Ag/AgCl in saturated KCl) and an auxillary electrode [90]. A working electrodes makes contact with the analyte, apply controlled desired potential, and facilitates charge transfer to or from the analyte due to its oxidation or reduction. The reference electrode serves as a half cell of known potential and allows determining potential of the other half cell. An auxiliary electrode also known counter electrode balances the current at the working electrode. Working electrode is dipped in electrolyte solution containing analyte, electrons flow occurs (current in ampere) under oxidation-reduction and as potential (volt) E increase [91]. A voltammogram is an ordered pair graph of potential on abscissa and current on ordinate; and the peak position on abscissa identify the ionic species and area under a peak is proportional to the concentration of analyte (Fig. 2).

As(V) are electroinactivite while As(III) are electroactive. As(V) and As(III) are determined in two runs, first As(III) transformed to As by gain of $3e^-$. Second analysis is carried out after reducing As(V) to As(III) by chemical treatment to measure total inorganic As [92]. Sodium meta-bisulfite ($Na_2S_2O_5$)/sodium thiosulfate ($Na_2S_2O_3$) in H_2SO_4 is used as reducing agent for converting As(V) to As(III) [39]. The procedure is called direct voltammetry.

Stripping voltammetry is better suited then direct voltammetry. This technique consists of three steps: (i) metal ions are deposited onto an electrode held at a suitable potential while solution is being stirred to maximize its deposition, (ii) the stirring is stopped and the solution becomes quiet, and, (iii) metal deposits are stripped from the electrode $As \rightarrow As^{+3} + 3e$ by scanning the potential. Arsenic deposition on the electrode is related to its concentration in solution, the stripping peak current is proportional to the solution concentration.

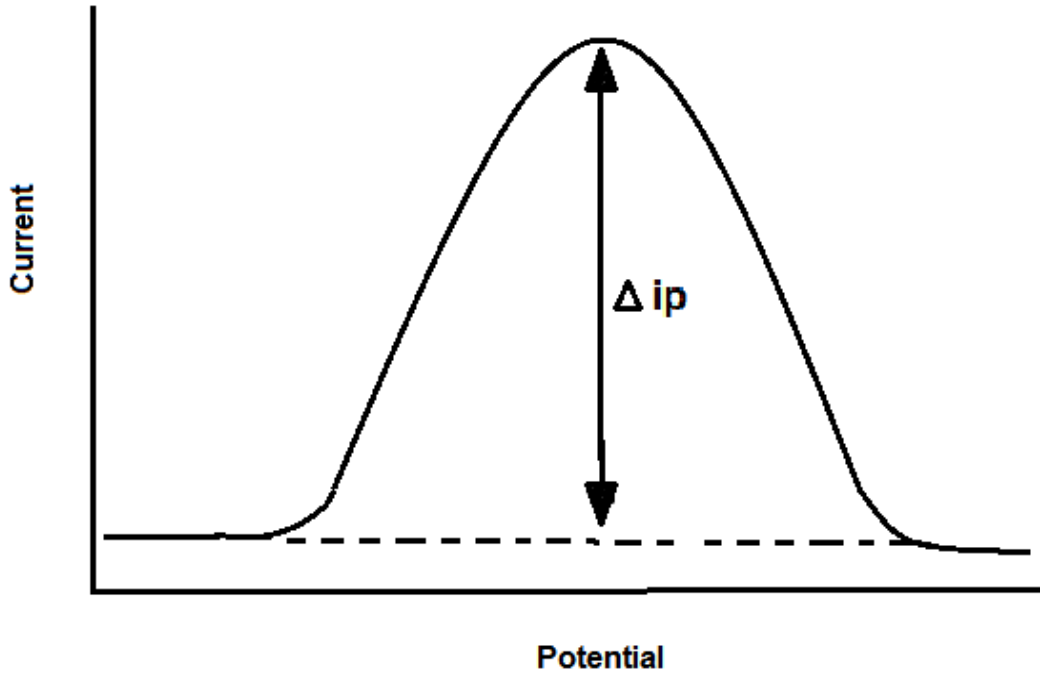

Fig. 2. A voltamogram having potential on y-axis and current on x-axis; and the peak position on abscissa identify the ionic species and area under a peak is proportional to the concentration of analyte

The stripping step may consist of a positive or a negative potential scan, creating either an anodic or cathodic current, respectively. Hence Anodic Stripping Voltammetry (ASV) and Cathodic Stripping Voltammetry (CSV) are specific stripping techniques [93]. In case of anodic stripping voltammetry, the different types of electrodes used are bulk gold (Au) [92], thin Au film deposited on carbon (glassy carbon, graphite) [94], Hg (as hanging drop mercury electrode- HDME) [95]. Anodic stripping voltammetry is a leading technique in the determination of trace amounts of arsenic [96].

Cathodic stripping voltammetry with Hg electrode is classical technique [96]. Hg is best metal for cathodic scanning because of large overpotential that the hydrogen discharge undergo on this element [91]. To improve the peak shape (sharp and symmetric) and the method sensitivity, Cu(II) and Se(IV) were used together to form intermetallic arsenic compounds (Cu*x*Se*y*As*z*) on the hanging mercury drop electrodes (HMDE) during the deposition procedure [39]. Another advantage of CSV with Hg electrode is that it does not suffer from the run-to-run reproducibility problems because each analysis is performed with a new Hg-drop.

In order to increase the speed and sensitivity, different forms of potential modules have been applied such as linear sweep voltammetry (LSV), normal pulse voltammetry (NPV), differential pulse voltammetry (DPV), staircase voltammetry (STCV) and square wave voltammetry (SWV) [97]. The introduction of pulse voltammetric techniques has provided much better detection limits [96].

LSV is the simplest technique in which a rapid potential that varies linearly with time is applied on working electrode. Oxidation or reduction of species produces a peak of current signal at the potential at which the species are oxidized or reduced. A graph is obtained when the variation in the current flowing through the electrode is plotted while a rapid and reducing potential scanning is applied.

NPV uses a series of potential pulses of increasing amplitude. The current measurement is made near the end of each pulse. It is usually carried out at either dropping mercury electrode or solid electrodes. Sampled current is plotted against potential.

In DPV series of periodical constant potential pulse of small amplitude is superimposed to a

linear scanning which result in as consistent signal. Current is measured at two points for each pulse; the first point is just before the application of the pulse and the second at the end of the pulse. At these points for each pulse the difference between current is determined and plotted against the base potential.

STCV is a derivative of LSV technique in which the potential sweep is a series of stair steps. The current is measured at the end of each potential change, right before the next.

SWV is further improvement of the staircase voltammetry. In SWV a symmetrical square-wave pulse superimposed on a staircase waveform where the forward pulse of the square wave coincides with the staircase step. The net current is obtained by taking the difference between the forward and reverse currents. The peak height is directly proportional to the concentration of the electroactive species.

Conditioning of electrode before and after the analysis of As(III) is often necessary for reproducible responses. Unexpected disappearance of stripping signal and loss of sensitivity are problems of ASV which corrected by repolishing and cleaning the electrode in batch experiments.

Au, Pt and Ag were compared and reported that Ag electrodes are certainly viable as working electrodes when HNO_3 is employed as the electrolyte vice HCl because of the lower deposition potential possible without hydrogen evolution. These conditions provide for a LOD 6.3×10^{-7} M [98]. A detailed method and protocol was developed for routine analysis of As(III) in 960 groundwater samples using thin Au film on a glassy carbon electrode by ASV [94]. Although the method is slow (20–30 samples/day), it is now a standard method for speciation of As(III) and As(V) in some parts of Bangladesh. A new method was described in which efficient rotating Au-film glassy carbon electrode was prepared for As(III) and As(V) determination in sea water by ASV [99]. For a deposition time of 4 min the determination limit was 0.19 ppb. The Proposed method had relatively high accuracy determined by analysis of certified references seawater and seawater samples spiked with arsenic standard solutions. In another method Au nano particles (10–40nm diameter) were electrodeposited on a glassy carbon substrate from a solution containing 1.0 mM $HClO_4$, 0.5 M H_2SO_4, and 0.1 mM KI. It was found that 2.0 M HCl gave the best sensitivity for As(III) analysis and an LOD of 0.024 μM (1.8 μgL^{-1}) [100]. Kamenev et al. [101] employed ASV to study the effect of modifying a graphite electrode with Cu and Au for the analytical determination of As(III). They reported As best deposited at graphite electrodes modified with Cu and Au in 0.1 MHCl and 0.05 M complexone III Y supporting electrolytes, respectively. They reported LOD (17 μgL^{-1}) for As with graphite electrode modified with Au was better than Cu- modified graphite electrode. They also reported a methodology for the determination of As in the presence of copper and in the presence of arsenic using 0.001–0.01 M EDTA and 0.01 M H_3PO_4 as the electrolyte combination. An improved ASV response using highly reactive gold coated, boron doped, diamond thin-film electrode (Au-BDDE) in 0.1M HNO_3 and 0.1M phosphate buffered saline (PBS) [102]. They found As(III) LOD to be 3 μgL^{-1} As(III). Similarly Song and Swain [103] employed a Au-coated, boron-doped, diamond thin-film electrode (Au-BDDE) and detected 0.6 μgL^{-1} As(III) in river water by using DPASV.

Modern hanging drop mercury electrode (HDME) and electronically controlled static mercury drop electrode (SMDE) which uses small amount of mercury have been used extensively. A procedure for the speciation of As in the field using DPCSV on a HDME based on the deposition of intermetallic species Cu*x*Se*y*As*z* on Hg electrode has been reported [104]. This method was applied to the measurement of As in Environmental Protection Agency superfund sites. A similar LSCSV method for the determination of As(III) was described in which HBr instead of HCl as the supporting electrolyte used because HBr required a shorter deposition time and less Cu and reported a LOD of 0.010 and 0.020 μgL^{-1} for As(III) and As(V), respectively [105]. Measurement of As(III) was also reported by using adsorptive CSV technique at HMDE in the presence of sodium diethyl dithiocarbamate (SDDC). Sodium diethyl dithiocarbamate (4 μM) is known to form a stable complex with As(III) on the Hg-electrode surface through adsorptive deposition in 0.01M HCl held for 100–300 s. Piech et al. [106] found higher sensitivity, lower detection limit, and lower deposition time (LOD at 0.004 μgL^{-1} with deposition times as short as 50 s using SDDC as a complexing agent for As(III) in several mineral water samples at 0.1 μgL^{-1} or less.

Carvalho et al. [107] later used the same adsorptive CSV for the speciation of As(III) and

As(V) in water and saline samples after a chemical reduction of As(V) with a mixture of $Na_2S_2O_5/Na_2S_2O_3$ at 2.5 and 0.5 mg mL^{-1}, respectively. A simple and fast method was developed for the determination of As(III) and total inorganic As in natural spring and mineral waters using SWCSV at a HMDE by Ferreira and Barros, [108]. Quantification limits of 0.2 ppb for As(III) and of 2 ppb for As(V) were obtained. In soil extracts determination of As(III) and As(V) was reported by using CSV procedure with HDME [109]. Tongesayi and Smart, [110] demonstrated that As(III) can be determined in the presence of dissolved organic matter (DOM) such as fulvic acid. The Cu–fulvic acid and As–fulvic acid complexes formed have higher affinity of adsorption than Cu(II) and As(III) on the Hg electrode thus enhancing the formation of intermetallic Cu–As–Hg. Real and synthetic samples spiked with fulvic acid were analyzed using Adsorptive SWCSV technique.

Differential pulse cathodic stripping voltametry has determination limit 0.5 µg/L in natural water samples [104]. SWASV was used for the measurement of As(III) and As(V) in seawater and fresh water. It was found that As(III) could be determined by ASV using a Au microwire electrode at any pH including that typical of natural waters. Multiple concentrations of supporting electrolyte were tested; the most stable was determined to be 0.01M HCl. Their LOD was 0.2nM for As(III) and 0.3nM for As(III) and As(V) at a pH of 1. Arsenic recovery was 96–103% [92]. Among Square Wave Anodic Stripping Voltammetry (SWASV), Differential Pulse Anodic Stripping Voltammetry (DPASV) and Normal Pulse Anodic Stripping Voltammetry (NPASV), SWASV technique is most selective and suitable [111]. SWSV and DPSV are more commonly used, due to their lower detection limits [96]. Determination of As(III) by DPASV in1.0 M H_2SO_4 and 0.1 M HCl as electrolytes was reported [112]. The analysis showed a concentration range of 0.2–250 μgL^{-1}. A hanging copper amalgam drop electrode in the determination of As(III) using DPCSV was employed [106]. The method was tested by analyzing certified reference material and natural water samples for total As. In surface water samples As(III) was determined by differential pulse polarography (DPP) in 1 mol L^{-1} HCl as supporting electrolyte. The obtained LOD was 2.7 µg L^{-1} [113]. Kempegowda et al. [114] proposed simple protocol for the chemical modification of graphene with platinum nanoparticles for determination of As using SWASV. This method showed linearity in the concentration range 10–100 nM with LOD of 1.1 nM.

7. CONCLUSION

Arsenic contamination is a worldwide problem and become a challenge for the scientists. Various techniques have been adopted for As speciation studies with its own advantages and disadvantages. However, research efforts are still needed to develop inexpensive, rapid, sensitive and reproducible methodologies for arsenic species capable of working in the low detection limits.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Tessier AP, Campbell GC, Bisson M. Evaluation of the APDC-MIBK extraction method for the atomic absorption analysis of trace metals in river water. Analytical Chemistry. 1979;7:41-54.
2. Apostoli P. The role of element speciation in environmental and occupational medicine. Journal of Analytical Chemistry. 1999;363:499-504.
3. Akter KF, David GO, Davey E, Naidu R. Arsenic speciation and toxicity in biological systems. Environmental Contamination and Toxicology. 2005;184:97-149.
4. Vaughan GT. The environmental chemistry and fate of arsenical pesticides in cattle dip sites and banana plantations. Investigation Report CET/LHIR 148. CSIRO, Divisions of Coal and Energy Technology, Centre for Advance Analytical Chemistry, Sydney, Australia; 1993.
5. Yan-Chu H. Arsenic distribution in soils. In: Arsenic in the environment. Part 1: Cycling and characterization. Nriagu JO (Ed.). Wiley, New York. 1994;17-49.
6. Mandal BK, Suzuki KT. Arsenic round the world: A review. Talanta. 2002;58:201-235.
7. Mehmood A, Hayat R, Wasim M, Akhter MS. Journal of Agriculture and Biological Sciences. 2009;1:59-65.
8. Giacomino A, Malandrino M, Abollino O, Velayutham M, Chinnathangavel T, Mentasti E. An approach for arsenic in a contaminated soil: Speciation,

fractionation, extraction and effluent decontamination. Environmental Pollution. 2009;158:416-423.

9. Kumaresan M, Riyazuddin P. Overview of speciation chemistry of arsenic. Current Science. 2001;80:837-846.
10. Cullen WR, Reimer KJ. Arsenic speciation in the environment. Chemical Reviews. 1989;98:713-764.
11. Le XC, Lu X, Ma M, Cullen WR, Aposhian V, Zheng B. Speciation of key arsenic metabolic intermediates in human urine. Analytical Chemistry. 2000;72:5172-5177.
12. Jain CK, Ali I. Arsenic: Toxicity, speciation and occurrence. Water Research. 2000;34:4304-4312.
13. US EPA: United States Environmental Protection Agency, National primary drinking water regulations: Arsenic and clarification to compliance and new source contaminants monitoring, in: Final Rule, Code of Fedral Regulations, title 40, parts 141 and 142, USA; 2001.
14. WHO: World Health Orgination. Arsenic in Drinking Water, Geneva; 2001.
15. Ng CJ, Barry N, Bruce S, Crawley H, Moore MR. Bioavailability of metals and arsenic at contaminated sites from cattle dips, mined land and naturally occurring mineralization origins. In: Proceedings of the Fifth National Workshop on the Assessment of Site Contamination, EPHC, Adelaide. 2003;163-181.
16. Melanie G, Zagury JG, Deschenes L, Blouin J. Comparison of four extraction procedures to assess arsenate and arsenite species in contaminated soils. Environmental Pollution. 2009;158:1890-1898.
17. Chappell J, Chiswell B, Olszowy H. Speciation of arsenic in a contaminated soil by solvent-extraction. Talanta. 1995;42:323-329.
18. CEAEQ. Centre d'expertise en analyse environnementale du que´bec. De´termination des me´taux: Me´thode par spectrome´triede masse a` source ionisante au plasma d¢argon. MA. 200-Me´t.1.1; Ministe`rede l'Environnementdu Que´bec: Que´bec, QC, Canada. 2004;37.
19. Georgiadis M, Cai Y, Solo-Gabriele HM. Extraction of arsenate and arsenite species from soils and sediments. Environmental Pollution. 2006;141:22-29.
20. Garcia-Manyes S, Jimenez G, Padro A, Rubio R, Rauret G. Arsenic speciation in contaminated soils. Talanta. 2002;58:97-109.
21. Ruiz-Chancho MJ, Sabe R, Lopez-Sanchez JF, Rubio R, Thomas P. New approaches to the extraction of arsenic species from soils. Microchimica Acta. 2005;151:241-248.
22. Ruiz-Chancho MJ, Lopez-Sanchez JF, Rubio R. Analytical speciation as a tool to assess arsenic behavior in soils polluted by mining. Analytical and Bioanalytical Chemistry. 2007;387:627-635.
23. Alfassi ZB, Wai CM. Preconcentration of trace elements by solvent extraction, preconcentration techniques for trace elements. CRC Press, Boca Raton. 1992;100.
24. Mc Cleskey RB, Nordstrom DK, Meast AS. Peservation of water samples for arsenic (III/V) determinations: An evaluation of the literature and new analytical results. Applied Geochemistry. 2004;9:995-1009.
25. Hall GEM, Pelchat JC, Gauthier G. Stability of inorganic arsenic (III) and arsenic (V) in water samples. Journal of Analytical Atomic Spectrometry. 1999;14:205-213.
26. Nikolaos P, Nikolaidisa M, Gregory D, Chenc J, Lackovicc JA. Arsenic mobility in contaminated lake sediments. Environmental Pollution. 2004;129:479-487.
27. Daus B, Mattush J, Wennrich R, Weiss H. Preservation of arsenic species in water samples using phosphoric acid–limitations and long-term stability. Talanta. 2002;69:430-434.
28. Asghar U, Perveen F, Alvi SK, Khan FA, Siddiqui I, Usmani TH. Contamination of arsenic in public water supply scheme of Larkana and Mirpur Khas, District of Sindh. Journal of Chemical Society of Pakistan. 2006;28:130-135.
29. Arain GM, Aslam M, Majidano SA, Khuhawar MY. A preliminary study on the arsenic contamination of underground water of Matiari and Khairpur Districts, Sindh, Pakistan. Journal of Chemical Society of Pakistan. 2007;29:463-467.
30. Shraim A, Chiswell B, Olszowy H. Speciation of arsenic by hydride generation: Atomic absorption spectrometry (HG-AAS) in hydrochlororic acid reaction medium. Talanta. 1999;50:1109-1127.

31. Howard AG. (Boro) Hydride techniques in trace element speciation. Journal Analytical Atomic Spectrometry. 1997;12:267-272.
32. Goessler W, Kuehnelt D. Analytical methods for the determination of As and As compounds in the environment. In: Franjzenberzer WT (Ed.) Environmental Chemistry of Arsenic. Dekker, New York. 2001;27.
33. Anawar HM. Arsenic speciation in environmental samples by hydride generation and electrothermal atomic absorption spectrometry. Talanta. 2012;88:30- 42.
34. Lamble KJ, Sperling M, Welz B. Arsenic speciation in biological samples by online high performance liquid chromatography-microwave digestion-hydride generation-atomic absorption spectrometry. Analytical Chimica Acta. 1996;334:261-270.
35. Aggett J, Hayashi Y. Observations on the interference by copper (II), cobalt (II) and nickel (II) on the determination of arsenic by arsine generation. Atomic Absorption Spectrometry Analysis. 1987;112:277-282.
36. Campbell AD. A critical survey of hydride generation techniques in atomic spectroscopy. Pure and Applied Chemistry. 1992;64:227-244.
37. Leermakers M, Baeyens W, Gieter MD, Smedts B, Meert C, Bisschop HCD, Morabito R, Quevauviller P. Toxic arsenic compounds in environmental samples: Speciation and validation trends. Analytical Chemistry. 2006;25:1-10.
38. Rajakovic LV, Todorovic ZN, Rajakovic-Ognjanovic VN, Onija AE. Analytical methods for arsenic speciation analysis. Journal of the Serbian Chemical Society. 2013;78:1461-1479.
39. Terlecka E. Arsenic speciation analysis in water samples: A review of the hyphenated techniques. Environmental Monitoring and Assessment. 2005;107:259-284.
40. Imran AC, Jain K. Advances in arsenic speciation techniques. International Journal of Environmental Analytical Chemistry. 2004;84:947-965.
41. Tyson J. The determination of arsenic compounds: A critical review. ISRN Analytical Chemistry. 2013;2013:24.
42. Tomlinson MJ, Lin L, Caruso JA. Plasma mass spectrometry as a detector for chemical speciation studies. Analyst. 1995;120:583-589.
43. Nearing MM, Koch I, Reimer KJ. Complementary arsenic speciation methods: A review. Spectrochimica Acta. 2014;B99:150-162.
44. Barnes RM. Capillary electrophoresis and inductively coupled plasma spectrometry: Status report. Journal of Analytical Chemistry. 1998;361:246-251.
45. Timerbaev AR. Elemental speciation analysis by capillary electrophoresis. Talanta. 2000;52:573-606.
46. Sun B, Macka M, Haddad PR. Speciation of arsenic and selenium by capillary electrophoresis. Journal of Chromatography. 2004;1039:201-208.
47. Naidu R, Smith J, McLaren RG, Stevens DP, Sumner ME, Jackson PE. Application of capillary electrophoresis to anion speciation in soil water extracts: II. Arsenic. Soil Science Society of America Journal. 2000;64:122-128.
48. Li K, Li SFY. Speciation of selenium and arsenic compounds in natural waters by capillary zone electrophoresis after on-column pre-concentration with field-amplified injection. Analyst. 1995;120:361-366.
49. Hsieh MW, Liu CL, Chen JH, Jiang SJ. Speciation analysis of arsenic and selenium compounds by CE-dynamic reaction cell-ICP-MS. Electrophoresis. 2010;31:2272-2278.
50. Yang GD, Xu JH, Zheng JP, Xu XQ, Wang W, Xu LJ, Chen GN, Fu FF. Speciation analysis of arsenic in mya arenaria, linnaeus and shrimp with capillary electrophoresis-inductivley coupled plasma mass spectrometry. Talanta. 2009;78:471-476.
51. Capelo JL, Lavilla I, Bendicho C. Utlrasonic extraction followed by sonolysis–ozonolysis as a sample pretreatment method for determination of reactive arsenic toward sodium tetrahydroborate by flow-injection-hydride generation AAS. Analytical Chemistry. 2001;73:3732-3736.
52. Tsalev DL, Sperling M, Welz B. Flow-injection hydride generation atomic absorption spectrometric study of the automated on-line pre-reduction of arsenate, methylarsonate and dimethylarsinate and high-performance liquid chromatographic separation of their L-cysteine complexes. Talanta. 2000;51:1059-1068.

53. Raessler M, Michalke B, Schulte-Hostede S, Kettrup A. Long-term monitoring of arsenic and selenium species in contaminated groundwater by HPLC and HG-AAS. Science of the Total Environment. 2000;258:171-181.
54. Hasegawa H, Masuti M, Okamura S, Hojo M, Iwasaki N, Sohrin Y. Arsenic speciation including 'hidden' arsenic. Applied Organometallic Chemistry. 1999;13:113–119.
55. Cabon JY, Cabon N. Determination of arsenic species in seawater by flow injection hydride generation in situ collection followed by graphite furnace atomic absorption spectroscopy. Stability of As(III). Analytical Chimica Acta. 2000;418:19–31.
56. Akter KF, Chen Z, Smith L, Davey D, Naidu R. Speciation of arsenic in ground water samples: A comparative study of CE-UV, HG-AAS and LC-ICP-MS. Talanta. 2005;68:406–415.
57. Guerin T, Astruc A, Astruc M. Speciation of arsenic and selenium compounds by HPLC hyphenated to specific detectors: A review of the main separation techniques. Talanta. 1999;50:1-24.
58. Chen S, Yeh SJ, Yang MH, Lin TH. Trace element concentration and arsenic speciation in the well water of the Taiwan area with endemic blackfoot disease. Biological Trace Element Research. 1995;48:263–274.
59. Maity S, Chakravarty S, Thakur P, Gupta KK, Bhattacharjee S, Roy BC. Evaluation and standardization of simple HG-AAS method for rapid speciation of As(III) and As(V) in some contaminated ground water samples of West Bengal, India. Chemosphere. 2004;54:1199–1206.
60. Macedo M, de Jesus RM, Garcia KS, Hatje V, de Queiroz AF, Ferreira SLC. Determination of total arsenic and arsenic (III) in phosphate fertilizers and phosphate rocks by HG-AAS after multivariate optimization based on box–behnken design. Talanta. 2009;80:974-979.
61. Apau J, Enyemadze I. Speciation of arsenic in drinking water at Amansie West District. International Journal of Development and Sustainability. 2014;3:431-440.
62. Abdel-Lateef AM, Mohamed RA, Mahmoud HH. Determination of As(III) and(V) in some environmental samples by atomic absorption spectroscopy. Advances in Chemical Science. 2013;3:110-113.
63. Schlemmer G, Radziuk B. Analytical graphite furnace atomic absorption spectrometry, a laboratory guide. Birkhauser, Basel, Switzerland. 1999;1-36.
64. Liang L, Lazoff S, Chan C, Horvat M, Wood JS. Determination of arsenic in ambient water at sub-part-per-trillion levels by hydride generation Pd coated platform collection and GFAAS detection. Talanta. 1998;47:569-583.
65. Gomez-Ariza LJ, Sanchez-Rodas D, Giraldez I, Morales E. A comparison between ICP-MS and AFS detection for arsenic speciation in environmental samples. Talanta. 2000;51:257-268.
66. Latif E, Umit D, Mustafa S. Inorganic arsenic speciation in various water samples with GFAAS with coprecipitation. Analytical Chemistry. 2008;88:711-723.
67. Shamsipur M, Fattahi N, Assadi Y, Sadeghi M, Sharafi K. Speciation of As(III) and AS(V) in water samples by graphite furnace atomic absorption spectrometry after solid phase extraction combined with dispersive liquid-liquid microextraction based on the solidification of floating organic drop. Talanta. 2014;130:26-32.
68. Featherstone AM, Boult PR, O'Grady BV, Butler ECV. A shipboard method for arsenic speciation using semi-automated hydride generation atomic fluorescence spectroscopy. Analytica Chimica Acta. 2000;409:215-226.
69. He B, Jiang G, Xu X, Arsenic speciation based on ion exchange high performance liquid chromatography hyphenated with hydride generation atomic fluorescence and on-line UV photo oxidation. Journal of Analytical Chemistry. 2000;368:803-808.
70. Bohari Y, Astruc A, Astruc M, Cloud J. Improvements of hydride generation of the speciation of arsenic in natural freshwater samples by HPLC-HG-AFS. Journal of Analytical Atomic Spectrometry. 2001;16:774-778.
71. Francesconi KA, Kuehnelt D. Determination of arsenic species: A critical review of methods and applications. Analyst. 2004;129:373-395.
72. Yuan CG, Zhang K, Wang Z, Jiang G. Rapid analysis of volatile arsenic species released from lake sediment by a packed cotton column coupled with atomic fluorescence spectrometry. Journal of

Analytical Atomic Spectrometry. 2010;25:1605-1611.

73. Musil S, Matousek T, Currier JM, Styblo M, Dedina J. Speciation analysis of arsenic by selective hydride generation-cryotrapping – atomic fluorescence spectrometry with flame-in-gas-shield atomizer: Achieving extremely low detection limits with inexpensive instrumentation. Analytical Chemistry. 2014;86:10422-10428.
74. Wang N, Tyson J. Non-chromatographic speciation of inorganic arsenic by atomic fluorescence spectrometry with flow injection hydride generation with a tetrahydroborate-form anion-exchanger. Journal of Analytical Atomic Spectrometry. 2014;29:665-673.
75. Yu X, Deng T, Guo Y, Wang Q. Arsenic species analysis in freshwater using liquid chromatography combined to hydride generation atomic fluorescence spectrometry. Journal of Analytical Chemistry. 2014;69:83-88.
76. Szpunar J. Bio-inorganic speciation analysis by hyphenated techniques. Analyst. 2000;125:963-998.
77. Mandal BK, Ogra Y, Suzuki KT. Speciation of arsenic in human nail and hair from arsenic-affected area by HPLC-inductively coupled argon plasma spectrometry. Toxicology and Applied Pharmacology. 2003;189:73-83.
78. Komorowicz I, Baralkiewicz D. Arsenic speciation in water by high-performance liquid chromatography/inductively coupled plasma mass spectrometry–method validation and uncertainty estimation. Rapid Communications in Mass Spectrometry. 2014;28:159-168.
79. Ronkart SN, Laurent V, Carbonnelle P, Mabon N, Copin A, Barthelemy JP. Speciation of five arsenic species (arsenite, arsenate, MMAAV, DMAAV and AsBet) in different kind of water by HPLC-ICP-MS. Chemosphere. 2007;66:738-45.
80. Verdon CP, Caldwell KL, Fresquez MR, Jones RL. Determination of seven arsenic compounds in urine by HPLC-ICP-DRC-MS: A CDC population biomonitoring method. Analytical and Bioanalytical Chemistry. 2009;393:929-937.
81. Samanta G, Chowdhury UK, Mondal BK, Chakraboti D, Sekran NC, Tokunaga H, Ando M. High performance liquid chromatography inductively coupled plasma mass spectrometry for speciation of arsenic compounds in urine. Microchemical Journal. 2000;65:113-127.
82. Coelho NMM, Coelho LM, de Lima ES, Pastor A, de la Guardia M. Determination of arsenic compounds in beverages by high-performance liquid chromatography inductively coupled plasma mass spectrometry. Talanta. 2005;66:818-822.
83. Xie R, Johnson W, Spayd S, Hall GS, Buckley B. Arsenic speciation analysis of human urine using ion exchange chromatography coupled to inductively coupled plasma mass spectrometry. Analytica Chimica Acta. 2006;578:186-194.
84. Day JA, Montes-Bayon M, Vonderheide AP, Caruso JA. A study of method robustness for arsenic speciation in drinking water samples by anion exchange HPLC-ICP-MS. Analytical and Bio-analytical Chemistry. 2002;373:664-668.
85. Pouthieu M, Pinel-Raffaitin P, de Hecho I, Mazeas L, Amouroux D, Donard OFX, Potin-Gautier M. Speciation analysis of arsenic in landfill leachate. Water Research. 2007;41:3177-3185.
86. Duarte FA, Pereira JSF, Mesko MF, Goldschmidt F, Flores EMM, Dressler VL. Evaluation of liquid chromatography inductively coupled plasma mass spectrometry for arsenic speciation in water from industrial treatment of shale. Spectrochimica Acta B. 2007;62:978-984.
87. Milstein LS, Essader A, Pellizari ED, Fernando RA, Raymer JH, Levine KE, Akinbo O. Development and application of a robust speciation method for determination of six arsenic compounds present in human urine. Environmental Heath Perspective. 2003;111:293-296.
88. Castillo A, Roig- Navarro AF, Pozo OJ. Capabilities of microbore columns coupled to ICP MS in speciation of arsenic and selenium. Journal of Chromatography A. 2008;1202:132-137.
89. Huang JH, Kretzschmar R. Sequential extraction method foe speciation of arsenate and arsenite in mineral soils. Analytical Chemistry. 2010;82:5534-5540.
90. Hussam A, Douglas EM. Voltammetric methods for determination and speciation of inorganic arsenic in the environment-A review. Analytica Chimica Acta. 2009;646:6-16.

91. Protti P. Introduction to modern voltammetric and polarographic analysis techniques; 2001. AMEL online: Available:http://www.amelchem.com/download/items/voltammetry/manuals/eng/manual_eng.pdf
92. Salaun P, Planer-Friedrich B, Berg CMGVD. Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode. Analytica Chimica Acta. 2007;585:312-322.
93. Zima J, van den Berg CMG. Determination of arsenic in sea-water by cathodic stripping voltammetry in the presence of pyrrolidine dithiocarbamate. Analytica Chimica Acta. 1994;289:291-298.
94. Hussam A, Rasul H, Hossain SB, Munir Z, Alauddin AKM, Khan M. Electrochemical measurement and speciation of inorganic arsenic in groundwater of Bangladesh. Talanta. 2002;58:33-43.
95. Locatelli GT. Voltammetric trace metal determinations by cathodic and anodic stripping voltammetry in environmental matrices in the presence of mutual interference. Journal of Electroanalytical Chemistry. 2001;509:80-89.
96. Hussam A. Voltammetry: Dynamic electrochemical techniques in comprehensive analytical chemistry. S. Ahuja, N. Jesperen (Ed.), Elsevier B.V. 2007;47:663.
97. Fogg AG, Wang J. Terminology and convention for electrochemical stripping analysis. Pure and Applied Chemistry. 1999;71:891-897.
98. Smedley PL, Kinniburgh DG. A review of the source, behavior and distribution of arsenic in natural waters. Applied Goechemistry. 2002;17:517-568.
99. Sun Y, Mierzwa J, Yang M. New method of gold-film electrode preparation for anodic stripping voltammetric determination of arsenic (III and V) in seawater. Talanta. 1997;44:1379-1387.
100. Hossain MM, Islam MM, Ferdousi S, Okajima T, Ohsaka T. Anodic stripping voltammetric detection of arsenic (III) at gold nanoparticle-modified glassy carbon electrodes prepared by electrodeposition in the presence of various additives. Electroanalysis. 2008;20:2435-2441.
101. Kamenev AI, Orlov SE, Lyakhov AB. Electrochemical reconcentration of Arsenic (III) in Its Determination by stripping voltammetry at graphite electrodes modified with gold and copper. Journal of Analytical Chemistry. 2001;56:850-854.
102. Rassaei L, Sillanpää M, French RW, Compton RG, Marken F. Arsenite determination in phosphate media at electroaggregated gold nanoparticle deposits. Electroanalysis. 2008;20:1286-1292.
103. Song Y, Swain GM. Development of a method for total inorganic arsenic analysis using anodic stripping voltammetry and a au-coated, diamond thin-film electrode. Analytical Chemistry. 2007;79:2412-2420.
104. He Y, Zheng Y, Ramnaraine M, Locke DC. Differential pulse cathodic stripping voltammetric speciation of trace level inorganic arsenic compounds in natural water samples. Analytica Chimica Acta. 2004;511:55-61.
105. Profumo A, Merli D, Pesavento M. Voltammetric determination of inorganic As(III) and total inorganic As in natural waters. Analytica Chimica Acta. 2005;539:245-250.
106. Piech R, Bas B, Niewiara E, Kubiak WW. Determination of trace arsenic on hanging copper amalgam drop electrode. Talanta. 2007;72:762-767.
107. Carvalho D, Leandro M, Nascimento PCD, Bohrer D, Pilau EJ, Stefanello R, Lauer M. Voltammetric behavior of arsenic (III) in the presence of sodium diethyl dithiocarbamate and its determination in water and highly saline samples by adsorptive stripping voltammetry. Electroanalysis. 2006;18:1081-1089.
108. Ferreira MA, Barros AA. Determination of As(III) and arsenic (V) in natural waters by cathodic stripping voltammetry at a hanging mercury drop electrode. Analytica Chimica Acta. 2002;459:151-159.
109. Kowalska J, Chalko K, Stryjewska E. Speciation of arsenic (V) and arsenic (III) in soil extracts by cathodic stripping voltammetry. Electroanalysis. 2002;14:1508-1511.
110. Tongesayi T, Smart RB. electrochemical detection of arsenic (III) in the presence of Dissolved Organic Matter (DOM) by Adsorptive Square-Wave Cathodic Stripping Voltammetry (Ad-SWCSV). Electroanalysis. 2007;20:434-437.
111. Paul SC, Rahman MA, Siddique NA. Voltammetric study of arsenic (III) and arsenic (V) in ground water of Hajigonj and

Kalkini in Bangladesh. Pakistan Journal of Analytical and Environmental Chemistry. 2008;9:49-55.

112. Kopanica M, Novotny L. Determination of traces of arsenic (III) by anodic stripping voltammetry in solutions, natural waters and biological material. Analytica Chimica Acta. 1998;368:211-218.
113. Gamboa Jcm, Cornejo L, Acarapi J, Squella J. Determination of arsenic (iii) by differential pulse polarography in the waters of Camarones area, Chile. Journal of Chilean Society. 2013;4:2031-2034.
114. Kempegowda R, Antony D, Malingappa P. Graphene–platinum nanocomposite as a sensitive and selective voltammetric sensor for trace level arsenic quantification. International Journal of Smart and Nano Materials. 2014;5:17-32.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history.php?iid=899&id=16&aid=7596