

AN OVERVIEW OF ARSENIC EXTRACTION AND SPECIATION TECHNIQUES IN SOIL AND WATER

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.

Key Words: 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 , 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) are 25-60 times more toxic As(V) [11, 12]. Correct estimation of As form in soil or water is important for understanding bioavailability of As and its effects on biota [13]. 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

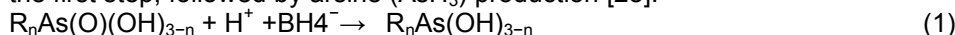
In case of soils and sediments the first step in As speciation is its extraction. An extraction procedure must meet three criteria: (i) the extracting solution must solubilize only the specific form, (ii) reduction of native As(V) to As(III) may not occur during the extraction, and (iii) oxidation of native As(III) to As(V) should not occur [14]. Four extraction procedures are commonly used (i) extraction with 10 M HCl in 1:30 soil to solution ratio shaken for 30 minutes [15], (ii) extraction

with 15% (v/v) H_3PO_4 in 1:200 soil to solution ratio heated at $95 \pm 3^\circ \text{C}$ for 1 h [16], (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), $(\text{C}_2\text{H}_5)_2\text{NCS}_2\text{Na} \cdot 3\text{H}_2\text{O}$ in 1:40 soil to solution ratio shaken for 60 minutes [17] and (iv) extraction with 1 M H_3PO_4 plus 0.5 M ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) using 1:150 soil to solution ratio kept at 60 W in microwave for 10 min [18, 19, 20]. Extraction with one molar H_3PO_4 + 0.5 M $\text{C}_6\text{H}_8\text{O}_6$ extracts maximum As while minimizing conversion of As(III) to As(V) [14]. Similarly, the 10 mM phosphate plus 0.5 % (w/v) NaDDC extractant also minimize reduction of As(III) [17].

Sodium diethyldithiocarbamate is also a good complexing agent for As(III) for water samples [21]. Water samples are stored in darkened polythene containers, and for longer preservation, samples are acidified HCl [22], HNO_3 [23], H_2SO_4 [24] and H_3PO_4 [25] increases the stability of As(III) and As(V) compared to unacidified samples.

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 [26, 27]. The derivitization process cause reduction of As(V) to As(III) in the first step, followed by arsine (AsH_3) production [28].



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:



The arsines production is pH sensitive [29]. Arsines ($\text{R}_n\text{AsH}_{3-n}$) arrive in atomic absorption spectrophotometer or ICP-MS for measurement driven by an inert gas N_2 [30].

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 [31], 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 [29, 32]. Sodium borohydride is now universally used for the synthesis of hydrides [33].

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 [34]. Due to different chemistry of As compounds both the techniques are sometimes used cumulatively [35].

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 [28]. 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 [36]. Liquid chromatography is attached with many other detection systems such as ICP-MS and HG-AFS. 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 can also be used for separation of As species [37]. 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 is most commonly used with ICP-MS [38]. Capillary electrophoresis has high separation efficiency for As speciation [39, 40, 41]. 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 [42].

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].

5.1 Atomic Absorption Spectrometry

Atomic absorption spectrometry gives high sensitivity and low detection limit only when coupled with arsine generator or different separation techniques [43]. 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 [33], unless coupled with hydride generation system [44, 45]. Similarly, for As speciation, AAS needs to be coupled with HPLC-HG for separation [44].

Graphite furnace atomic absorption spectrometry can be a stand alone facility without the need of AsH₃ because of low level interference [46] yet its performance is enhanced with hydride generation [47]. 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 [48].

5.2 Atomic Fluorescence Spectrometry

Atomic fluorescence spectrometry works on the principle of measuring fluorescence 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 [49]. Light scattering and background correction due to sample matrix is main problem solved by separating AsH₃ 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 [50, 51]. 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 [52].

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 [53] 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. Applications of HPLC–ICPMS for As speciation have been demonstrated [54].

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 auxiliary electrode [55]. 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 [56]. 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.

Arsenates are electroinactive while As(III) are electroactive. Arsenate 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 [57]. 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) (Terlecka, 2005). 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.

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 [58]. In case of anodic stripping voltammetry, the different types of electrodes used are bulk gold (Au) [57], thin Au film deposited on carbon (glassy carbon, graphite) [59], Hg (as hanging drop mercury electrode- HDME) [60]. Anodic stripping voltammetry is a leading technique in the determination of trace amounts of arsenic [61].

Cathodic stripping voltammetry with Hg electrode is classical technique [61]. Hg is best metal for cathodic scanning because of large overpotential that the hydrogen discharge undergo on this element [56]. 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 ($CuxSeyAsz$) on the hanging mercury drop electrodes (HMDE) during the deposition procedure [35]. 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) [62]. The introduction of pulse voltammetric techniques has provided much better detection limits [61].

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.

Gold, 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 limit of determination (LOD) 6.3×10^{-7} M [63]. A detailed method and protocol was developed for routine analysis of As(III) in 960 groundwater samples the using thin gold film on a glassy carbon electrode by ASV [59]. 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 gold-film glassy carbon electrode was prepared for As(III) and As(V) determination in sea water by ASV [64]. 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 gold 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 . It was found that 2.0 M HCl gave the best sensitivity for As(III) analysis and an LOD of $0.024 \mu\text{M}$ ($1.8 \mu\text{g L}^{-1}$) [65]. Kamenev et al., [66] employed ASV to study the effect of modifying a graphite electrode with copper and gold for the analytical determination of As(III). They reported arsenic best deposited at graphite electrodes modified with copper and gold in 0.1 M HCl and 0.05 M complexone III Y supporting electrolytes, respectively. They reported LOD ($17 \mu\text{g L}^{-1}$) for arsenic with graphite electrode modified with gold 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) [67]. They found As(III) LOD to be $3 \mu\text{g L}^{-1}$ As(III). Similarly Song and Swain [68] employed a Au-coated, boron-doped, diamond thin-film electrode (Au-BDDE) and detected $0.6 \mu\text{g L}^{-1}$ 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 $\text{Cu}_x\text{Se}_y\text{As}_z$ on Hg electrode has been reported [69]. 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 $\mu\text{g L}^{-1}$ for As(III) and As(V), respectively [70]. 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., [71] found higher sensitivity, lower detection limit, and lower deposition time (LOD at 0.004 $\mu\text{g L}^{-1}$ 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 $\mu\text{g L}^{-1}$ or less.

Carvalho et al., [72] 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 $\text{Na}_2\text{S}_2\text{O}_5/\text{Na}_2\text{S}_2\text{O}_3$ 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, [73]. 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 (74). Tongesayi and Smart, [75] 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 $\mu\text{g/L}$ in natural water samples [69]. 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% [57]. 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 [76]. SWSV and DPSV are more commonly used, due to their lower detection limits [61]. Determination of As(III) on a by DPASV in 1.0 M H_2SO_4 and 0.1 M HCl as electrolytes was reported [77]. The analysis showed a concentration range of 0.2–250 $\mu\text{g L}^{-1}$. A hanging copper amalgam drop electrode in the determination of As(III) using DPCSV was employed [71]. The method was tested by analyzing certified reference material and natural water samples for total As.

6. 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.

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