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Arsenic Toxicity and Speciation Analysis in Ground Water Samples: A Review of Some Techniques

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ABSTRACT

Growing interests in the determination of different arsenic species in ground waters is caused by the fact that toxic effects of arsenic are solely connected with its chemical forms and oxidation states. The toxicity and bioavailability of arsenic can only be determined if all its forms can be identified and quantified. In determinations of water samples inorganic arsenate (As (III), As (V)), methylated metabolites (MMAA, DMAA) and other organic forms such as AsB, AsC, arsenosugars or arsenic containing lipids have the most interest. Considerable analytical progress have been made toward arsenic speciation over the last few decades. Therefore, this research review the general description of the occurrence of arsenic in environment, its toxicity and measure techniques for speciation analysis. Methods based on high-performance liquid chromatography separation joined with inductively coupled mass spectrometry, hydride generation atomic spectrometry and electrospray mass spectrometry detection have shown most powerful methods for arsenic speciation in environmental and biological matrices. These methods provide strong reliability on understanding of arsenic metabolism and biological cycling.

Key words: Arsenic toxicity, speciation analysis, ground water, biological matrices

INTRODUCTION

Analytical chemistry is one of the most important part in science whole has carried a significant role in areas of research investigations. Additionally making of new analytical tools and techniques to assist experimental studies, analytical chemistry can also open up new areas of research in modern science. Examples include atomic absorption spectroscopy and its large impact on diverse fields covering from mineralogy to clinical analysis and the new research, particularly in the field of biological sciences, emanating from current advances in ionisation techniques for mass spectrometry.

In the field of arsenic research there are also significant advances in analytical chemistry to open new areas. Around 200 years back Dr. Marsh in 1830s firstly started the arsenic analysis process. Last few decades, arsenic research grew continuously in accord with the discovery of new arsenic species and the importance of their environmental and biological activities. Recently, the growing interest of arsenic is increased because of its carcinogenic and leukemic effects on human body due to the drinking of groundwater (Mahfuzar, 2007). So, advances in arsenic speciation analysis may provide the options to finally explore these toxicological mechanisms and other

important questions regarding arsenic's different roles in biological systems. This review presents a brief evaluation of the latest analytical methods for determining arsenic species in groundwater.

Arsenic (As) is the twentieth most common element in the earth's crust, fourteenth in the deep sea water and twelfth in the human body (Gong *et al.*, 2002; Munoz and Palmero, 2005). Arsenic mainly occurs naturally in a wide range of minerals, which, together with a once widespread use in pigments, insecticides and herbicides, represent the major sources of arsenic in ground water. Arsenic has received considerable interest now a days because the associated health problems it causes, with contamination of groundwater being found in many countries, such as Bangladesh, India, several parts of USA, China, Taiwan, Mexico, Argentina, Poland, Vietnam, Hungary and Japan (Sohel *et al.*, 2009; Mahfuzar, 2006; Munoz and Palmero, 2005; Frost *et al.*, 1993; Moncure *et al.*, 1992; Chakraborti *et al.*, 2003; Mosaferi *et al.*, 2003; Tendukar *et al.*, 2001; Berg *et al.*, 2001; Kim *et al.*, 2009; Peters *et al.*, 1999). It is necessary to know about the speciation of arsenic in natural water because the bioavailability, physiological and toxicological effects depends on its chemical form. During the transformation of the arsenic rich geological forms reactions, biological activity and volcanic emissions are another sources of arsenic in the ground water level (Garcia-Manyes *et al.*, 2002). Most of the environmental arsenic problems caused by the result of natural changes; but, man have had an important impact for instance, mining activity, manufacturing of glass, paper, semi conductors, pesticides and herbicides (Korte and Fernando, 1991).

Knowledge of the speciation of arsenic in natural water is important because the bioavailability, physiological and toxicological effects of arsenic depend on its chemical form. Arsenic is not found in free states, it is largely found in combination with sulphur, oxygen and iron (Jain and Ali, 2000; Kim *et al.*, 2009). Arsenic can be appear in the water as inorganic and organic forms (Bhattacharya *et al.*, 1997). The occurrence and origin of As in ground water depend on several factors for instance adsorption-desorption as well as precipitation-dissolution of unstable As minerals, subsurface redox condition, grain size of aquifer, organic contents, organic contents, biological activity and aquifer characteristics. Availability of As depends on the ground water depends on the process of leaching of As containing rocks and sediments. Generally As availability on the groundwater depends on the local geology, hydrology and geological characteristics of the aquifer materials. Moreover organic content in sediments as well as the uses of land properties depends on the natural transfer of arsenic in alluvial aquifers. Nickson *et al.* (1998) revealed that As in these alluvial sediments is derived from sulphide deposits in the Ganges basin. Due to the increase of using ground water for irrigation, other household works and increase use of phosphate fertilizers may involve in the mobilization of As in the ground water. Huge amount of water withdrawal from ground cause the mobilization of phosphate derived from fertilizers and from the decay of natural organic materials in shallow aquifers. This increase level of phosphate concentration promotes the growth of biota and desorption of arsenic from sediments. These combined microbiological and chemical processes might have increased the natural mobility of arsenic in groundwater (Acharyya *et al.*, 1999).

Luten *et al.* (1982) also showed that the highest level of arsenic contamination can be found in average all marine species. As also can be found in the crustaceans and shell fish. They also reported that the all the commercially available seafood contains 1.5 to 8.9 mg kg⁻¹ of arsenic. But high concentrations of As mainly found in conger cells (12-30 mg kg⁻¹), plaice (2-17 mg kg⁻¹), shrimp (0.4-12 mg kg⁻¹), sturgeon (0.7-12 mg kg⁻¹) and cod (2-10 mg kg⁻¹) (Luten *et al.*, 1982).

Generally arsenic naturally occurs in the environment in inorganic as well as organic forms. In the normal ground waters, As is mostly occurred in inorganic forms as trivalent arsenate (As(III)) or pentavalent arsenate as (As (V)), with a minor amount of methyl and dimethyl arsenic compounds being detected (Terlecka, 2005; Francesconi and Kuehnelt, 2004; Hung *et al.*, 2004). The (III) oxidation state is more toxic than the (V) state one; whereas, organoarsenic compounds for instance monomethylarsonic acid (MMA) and dimethylarsonic acid (DMA) are the least toxic (Sun *et al.*, 1997; Hymer and Caruso, 2004). The mobility and toxicity of arsenic are determined by its oxidation state and then the behavior of arsenic species will change depending on the biotic and abiotic conditions in water (Diesel *et al.*, 2009).

A wide variety of methods to determine arsenic have been used: ultraviolet spectrometry, atomic absorption spectroscopy methods (AAS), coupled with hydride generation (HG-AAS), electrothermal AAS in graphite furnace (ETAAS), Atomic Fluorescence Spectrometry (AFS), Atomic Emission Spectrometry (AES), usually coupled with inductively coupled plasma (ICP-MS), X-ray spectrometry, Neutron Activation Analysis (NAA), capillary electrophoresis, Collision Induced Dissociation (CID), Gas Chromatography (GC), Size Exclusion Chromatography (SEC), High Performance Liquid Chromatography (HPLC), Fourier transform ion cyclotron resonance-mass spectrometry (FTICR-MS), stripping potentiometry, electroanalytical detection on gold plate and gold film electrode preparation for anodic stripping voltametric determination of arsenic. Methods involved on these techniques require expensive instrumentation, complicated procedures and special sample pre-treatment. Overall, all these methods are essentially sensitive to total arsenic.

In this review we are trying to include recent developments and applications of analytical methods for the detection and speciation of ground water arsenic. It is speculated that the information will be accessible to and useful for, company or organisation to choose an analytical equipment for the establishment of a new research area. This review will also provide the comparison of different techniques for a given application and, at times, perhaps, dissuade them from less suitable techniques.

THE TOXICOLOGY OF ARSENIC

The toxicology of As is a complex phenomenon as it considered to be an essential element also. The acute As poisoning occurs due the consumption of contaminated food and water. The acute poisoning involves burning and dryness of the mouth and throat, dyspepsia, colicky abnormal pain, rashes, vomiting, profuse diarrhoea and hematuria. Sub acute arsenic toxicity mainly involves the respiratory, gastrointestinal (GIT) disorders, cardio-vascular, facial cramps, diabetes and haematopoietic systems (Mahfuzar *et al.*, 1998, 1999) Jain and Ali (2000) also found that chronic toxication by As can also cause skin dry, hair loss, brittle loose nails, eczema, discolour of skin and a horny condition of the palms and soles. A recent study on arsenic toxicity have shown that exposure to arsenic through drinking water has direct effect on the early stages of life when the brain is usually most vulnerable (Hamadani *et al.*, 2010). Another study by Tofail *et al.* (2009) have shown that exposure to contaminated drinking water during pregnancy is associated with low birth weight and fetal loss and there is concern that the infants' growth may be affected. The chemical form and oxidation state of arsenic is very important with regard to toxicity. Hymer and Caruso (2004) showed that acute toxicity also is dependent upon other factors including physical state, the rate of absorption into cells, the rate of elimination, the nature of chemical substituents in the toxic compound and the general state of patient. This study also suggested that methylated metabolites are partially responsible for the toxicity of arsenic. Arsenic also has that ability to

interrupt mitosis process and induce apoptosis in human skin fibroblasts. Arsenic also has that ability to act as a carcinogen in mice.

SPECIATION TECHNIQUES FOR GROUND WATER ARSENIC

Speciation analysis involves the use of analytical methods that can give information about the physico-chemical forms of the elements. Speciation techniques also involved the determination of the physical size or the physical properties of the metal and chemical speciation, which entails the differentiation among the various chemical forms (Fig. 1).

The elements occur in the environment in different oxidation states and form various species. Chemical and toxicological properties vary among the species. So, determination of the total concentration of an element may not provide information about the actual physico-chemical forms of the element, required for understanding its toxicity, metabolism. Therefore, in order to get information on toxicity and metabolism of elements in aquatic systems, quantification of individual species is needed.

There are different techniques are available for the speciation of arsenic compounds.

Spectrometric method: Spectrometric methods for the determination of arsenic compounds involve the different spectrometric techniques for instance, UV, visible, atomic absorption, atomic emission, hydride generation, graphite furnace etc. Arsenic determination procedure depends on the reduction of arsenic compounds into arsine compounds. This gas then used in the Atomic Absorption Spectroscopy (AAS) technique.

Atomic Absorption Spectroscopy (AAS): In 1980 AAS was firstly used for the determination of As (Terlecka, 2005). Presently it is used for arsenic speciation, because of its high sensitivity, selectivity and low detection limits when combined with other speciation techniques and is most

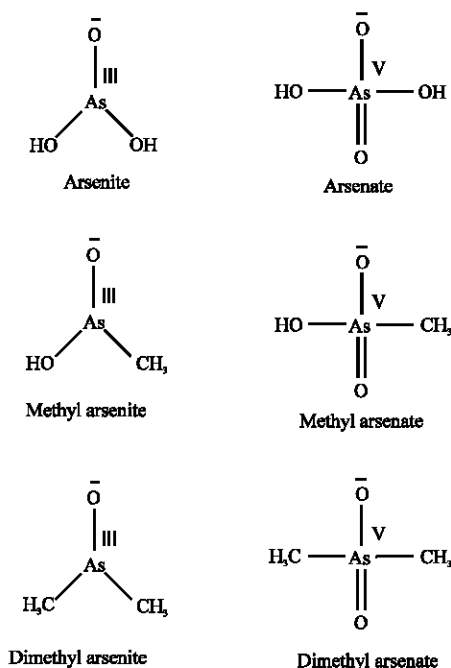


Fig. 1: Arsenic species found in water

frequently combined with Hydride generation (HG) (As(III) and As (V)<1 ng mL⁻¹) (Niedzielski and Siepak, 2005; Francesconi and Kuehnelt, 2004). HG-AAS also has some benefits over ICP-MS due to its low cost when consideration about ground water level. Terlecka (2005) also showed that As(III) -0.4 µL L⁻¹ for ground water samples with HG-AAS method with citric acid for selective hydride formation of As (III). Niedzielski and Siepak (2005) showed that AAS systems with hydride generation, the volatile hydrides are directed to the graphite tube and trapped in-situ on the walls of the tube covered with a modifier and heated. The use of the hydride generation technique for separation of the analyte from the matrix with *in situ* trapping on the walls of the graphite tube allows a determination of the total contents of element and its species (Bortoleto and Cadore, 2005). The method of AAS in combination with in-situ trapping in a graphite tube provides a significant (~10 times) decrease of the limit of determination compare to other AAS methods without the analyte concentration.

Atomic Emission Spectroscopy (AES): Determination of arsenic by inductively coupled plasma atomic emission spectrometry (ICP-AES) offered with a detection limit below 0.1 µg L⁻¹ (Jain and Ali, 2000). AES also coupled with HPLC and ICP. However, the spectral interferences is the most severe problem in ICP-AES method in the determination As in environmental sample (Terlecka, 2005). The interferences can be reduced by coupling with HG and HPLC. HG-ICP-AES using anion exchange chromatography for mineral or sea waters equals 35 for As (III) and 5 for As (V).

Atomic Fluorescence Spectroscopy (AFS): In 1990 AFS was first used with HG. Afterwards it showed that the highest sensitivity of As, almost rivaling that of ICPMS and because of its low purchase and operating costs, can proved the alternative method of MS techniques. One of the key features of this technique is that the inherent high sensitivity. While single molecule detection limit has been achieved with molecular fluorescence techniques, the amount was not able to get on the conventional atomic fluorescence based on liquid sample introduction. This happens due to the interferences effects that occur in AFS when consideration of real sample. But it is possible to solve this problem when it coupled with HG. Because in this process only gaseous arsines are introduced on the AFS detector and the sample matrix is removed, spectral interference encountered in the detection system is essentially eliminated. HG also provides increase of sensitivity for laser induced fluorescence and laser-enhanced ionization spectrometry detection of As (Gong *et al.*, 2002). For water analysis the samples the volatile arsines. Francesconi and Kuehnelt (2004) revealed that the AFS also can be used for more recalcitrant arsenicals when a pre HG decomposition step is included.

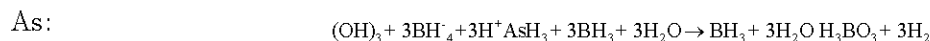
There are some drawbacks also have been reported (Akhter *et al.*, 2005) for this method, including: (1) Only work with volatile arsines; (2) reaction conditions have to be strictly controlled; (3) efficiency of HG can be reduced due to the presence of some interfering elements (4) laborious technique and single element detection technique.

Graphite Furnace Atomic Absorption Spectrometry (GFAAS): Graphite furnace absorption spectrometry (GFAAS) or electrothermal atomic absorption (ETAAS) spectrometry is one of the most important spectrometric methods without HG. This technique is based on the absorption of free atoms produced from the sample deposited in a small graphite tube, which can be heated by the introduction of high temperature (Hung *et al.*, 2004). In this method arsenic detection require pre-concentration in order to increase sensitivity. Soluble membrane filters technique used for the solid-

phase extraction of trace elements (Arsenic) in water before determination by ETAAS. Arsenic compounds converted into hydrophobic nature, which are retained on a membrane filter. In the next step, As can be collected from the membrane by dissolving with H₂SO₄. Finally the sample pre-concentrated and analyzed by ETAAS. Another approach is based on the formation and extraction of the As (III) -ammonium pyrrolidinethiocarbamate complex, with further dispersion in nitric acid containing Ni (II) species and injection of the obtained suspension to a graphite furnace (Hung *et al.*, 2004). By the modification of the matrix by salts of nickel and palladium can reduce the loss of As during experiment.

The main reason for the introduction of flame less methods was to achieve a competitive analytical sensitivity by increasing the concentration of atoms of the elements being measured, i.e., of avoiding the dilution caused by the flame itself. However, the major problem of the graphite-furnace method has been the fact that the atoms of elements being measured are either too volatile and are lost during ashing period, or that chemical combination with carbon or minerals in the samples renders them too volatile for atomization (Shibata *et al.*, 1992).

HGAAS with *in-situ* trapping in graphite tube: Arsenic can be detected by using the AAS combined with HG and *in-situ* concentration on the inner walls of the graphite tube. The limits of detection were. 019 ng mL⁻¹ for total As and. 031 ng mL⁻¹ for As (III) at the preliminary analyte concentration for 60 sec. The optimized procedure of the analyte concentration on the inner walls of the atomizer tube (graphite tube) was applied for determinations of As in samples of ground water (Niedzielski and Siepak, 2005). They also found that the AASHG in combination with *in-situ* trapping in a graphite tube permits a substantial (~10 times) decrease of the limit of determination compare to other AAS methods without the analyte concentration.



Hydride generation reaction.

INDUCTIVELY COUPLED PLASMA (ICP) TECHNIQUES

ICP-AFS and ICP-Mass Spectrometry (MS): The ICP method was first introduced in early 1960. In compare to different analytical methods for the excitation of elements for emission spectrometry, ICP is one of the most efficient, is suitable for liquid samples and was widely recognized by the researcher (Baig *et al.*, 2010). A sample solution is nebulized and the resultant fine mist is carried out by an argon flow into a high temperature plasma generated by a radio frequency electric current running in an induction coil. The sample is decomposed in plasma, followed by atomized and excited and quantification of each compound is performed by monitoring a specific spectral line emitted by an atom (or ion). Continuous determination of arsenic is possible by monitoring the plasma with a polychromator. The most sensitive lines for arsenic lie in the UV region (193.7 nm) and an appropriate spectrometer would be used. However, there will be some interferences occurred due to the interferences with other compounds. The ICP technique uses the plasma to ionize components, whereby the sample is acidified and sprayed into the plasma. ICP is generally coupled with other analytical techniques, such as MS (Francesconi and Kuehnelt, 2004; Hung *et al.*, 2004; Gong *et al.*, 2002), LC (Akhter *et al.*, 2005) and AES (Kinniburgh and Kosmus, 2002).

The ICP-AES is a less used technique and normally applied for a comparison and more accurate analysis of a multi-element sample. There are also applied techniques coupled AES with HPLC and ICP. The spectral interferences is the most severe problem in ICP-AES method in ICP-AES method in the determination of As in environmental sample (Terlecka, 2005). The study also showed that the increase of sensitivity and reduction of interferences during the experiment can be solved by the incorporation of HG between HPLC and AES.

The ICP-MS is one of the most important and widely accepted analytical techniques for the detection of arsenic. ICP-MS can provide the analysis of isotopes with higher detection and lower detection technique ($1 \mu\text{g As L}^{-1}$) for the various species of arsenic with new single quadrupole instruments when it combined with HPLC. This detection limit can also be increased when it coupled with HG. The advantages of this HG-ICPMS system compared with ICPMS detection with direct nebulization, included increase sensitivity, reduce matrix interferences and additional selectivity due to the system can distinguish hydride active from non hydride active compounds. Francesconi and Kuehnelt (2004) showed that the advances have been made in terms of reducing interferences in ICPMS by use of reaction and collision cell technology. ICP-MS offered a wide range of sensitivity, multi-element capability, large range and can be combined with different separation techniques for separation techniques. However, some problems arise from the coupling of ICP-MS with separation techniques because many of them require a high ionic buffer strength (when complex sample matrix) (Terlecka, 2005). A recently published research paper by Villadangos *et al.* (2010) showed that the selective retention of arsenate at non-steady-state conditions can be obtained by using a double mutant strain of cyanobacteria. This study revealed that the developed analytical procedure based on the selective retention of As (V) on coal matrices, for example coal ashes, allowed the determination arsenic by ICP-MS, when a previous oxidation to As(V) is required.

For the detection of low concentrations of arsenic in real samples suffers from low sensitivity because of its poor ionization ability. In order to overcome this problem different ICP applications combined with HG (Gomez-Ariza *et al.*, 2000; Hung *et al.*, 2004) and a cold vapour mercury sample introduction technique have been applied for arsenic determination. A system developed to maintain continuous flow HG system without the conventional gas-liquid phase separator as a sample introduction device for flow injection ICP-MS analysis to detect As(III) simultaneously with Bi, Sb and Hg.

Liquid Chromatography (LC) and ICP-MS: The combination of LC with an element selective detector ICP-MS is one of the most popular techniques for As speciation in environmental sample. Among the various LC techniques, ion chromatography (IEC), ion interaction chromatography (IIC) has frequently been used. IEC separation was often used in jointly with ICP-MS detector owing to its multi-elemental capabilities, low detection levels and greater linear range.

High Pressure Liquid Chromatography (HPLC) and ICP-MS: High sensitivity has been achieved using ICP-MS in combination with HPLC (Jain and Ali, 2000; Gong *et al.*, 2002; Terlecka, 2005; Hung *et al.*, 2004; Hymer and Caruso, 2004; Hirata *et al.*, 2006). The coupling of mass spectroscopy with ICP is the most effective detector in HPLC speciation studies. According to Jain and Ali (2000), Arsenite, arsenate, DMA and MMA have been speciated by HPLC using the coupling MS with ICP. The HPLC-ICP-MS offers high level of detection limits in comparison to

HPLC-AAS method. Moreover, the choice of HPLC column offered the increase of sensitivity of this assay. However, Francesconi and Kuehnelt (2004) showed that the HPLC-ICPMS is expensive and time consuming technique.

Liquid chromatography coupled with ionspray tandem mass spectroscopy: Ionspray mass spectroscopy, a well established organic analysis technique, has been coupled to HPLC for detection and speciation of arsenic compounds. Tandem mass spectroscopy increases the selectivity. Electrospray and ionspray (IS) are closely related atmospheric pressure ionization techniques which produce gas phase analyte ions directly from preexisting ions in solution and hence are particularly suitable for providing the interface between liquid separation technique and MS (Corr and Larsen, 1996).

X-RAY SPECTROSCOPIC TECHNIQUES

The X-ray spectroscopic methods such as EXAFS and XANES are being increasingly used for arsenic speciation analysis (Francesconi and Kuehnelt, 2004). The possibility of associating the elements of a sample with their characteristic fluorescent emission allows establishing relationships among the intensity of the spectral lines and the weight fraction of the constituent elements (Sbarato and Sanchez, 2001). EXAFS can provide precise inter atomic distances (± 0.01 nm) and hence by comparison by the standard samples, the technique can say which atoms are bound with arsenic.

ELECTROCHEMICAL METHODS

Polarographic techniques: Polarographic is one of the old electrochemical method for the determination of trace inorganic metals. But this method is not suitable due to high capacitive currents followed by low detection limits. Differential Pulse Polarography (DPP) offers the same benefits of selectivity as well as lower capacitive currents and as a result improved limits of detection. DPP was popular of trace metals due to high sensitivity for a wide range of elements (Hung *et al.*, 2004).

Another method by Vukovic *et al.* (2004) showed that the capability of ozone used as a digesting agent in the trace analysis of arsenic in natural water when it incorporated with DPP and spectrophotometric methods. No significant differences were found when it compared with ICPMS technique.

Cathodic Stripping Voltammetry (CSV): Stripping analysis is better suited than direct polarography for trace determinations in real samples because the substance of interest is preconcentrated on the working electrode. Cathodic stripping analysis of As at the HDME is based on arsenic pre-concentration in highly acidic media with further scanning in the cathodic direction to obtain peak due to formation of arsine (Hung *et al.*, 2004). This method is mainly based on the potentiostatic enrichment of analytes on an electrode surface and the subsequent re-oxidation or re-reduction of analytes by means of their spontaneous chemical reactions or by a combination of such reactions and an applied constant current. According to As(III) has been reduced electrochemically to the element, while As(V) has been chemically or electrochemically reduced at As(III). The flow systems have also used with stripping potentiometry for arsenic determination. Recently published research work by Gibbon-Walsh *et al.* (2010), showed that CSV method specifically for the determination of As(III) in freshwater including groundwater level. They

showed that this method is novel in that no sample pre-treatment or reagent addition is required, enabling the determination of arsenite, *in situ* in the unaltered water at the original pH and in the presence of air. Mixture of inorganic arsenic (As (III)+As(V)) can be analyzed subsequently by CSV after acidification of a sample aliquot to p^H 1, as a result speciation process can be done in a single sample aliquot. Interferences were found to have only minor effect, major anions and metals causing the peak potential to shift, whereas very high iron levels in originally reducing conditions can cause problems upon sample storage due to coprecipitation of As(V). However, in some cases a potential interference for some waters may be due to sulphide.

MISCELLANEOUS TECHNIQUES

Baghel *et al.* (2007) developed a rapid colorimetric method for the detection of As. Different reagents containing Mg turnings in combination with a series of acids were tested for arsine generation. In the next step arsine is allowed to react with auric chloride on Whatman filter paper No. 3, which in turn changed color. The detection time and detection limit were measured for each acid. Another colorimetric method developed by Dhar *et al.* (2004) showed that the method is relatively fast and the detection limit is below WHO guideline value for As in drinking water of $13 \mu\text{mol L}^{-1}$, even if a portable and moderately priced single-beam spectrophotometer is used. Gold nanoparticles are also incorporating with the simple colorimetric and ultrasensitive Dynamic Light Scattering (DLS) assay to improve the detection limit of arsenic in groundwater level. Study conducted by Kalluri *et al.* (2009) have showed that the As can be detected at the ppt level quickly and accurately without any leveling and with significant characteristic against other heavy metals. This technique is a rapid and takes less than 10 min from As binding to detection and analysis.

Polarographic and voltametry techniques have also been used for the speciation of arsenic. Anodic pulse voltameter, with a detection limit of 2 ppb, has been used to differentiate between arsenite and arsenate (Jain and Ali, 2000).

The electroanalytical detection of As on a gold electrode is investigated in the presence and absence of ultrasound (Simm *et al.*, 2005). The use of ultrasound assisted As deposition was found to significantly reduce accumulation times when compared to silent methods which lowering the detection limit and increasing the sensitivity of As detection.

Capillary Electrophoresis (CE) offers high separation efficiency and rapid analysis (Akhter *et al.*, 2005). Small amount of samples (nano-litres) were required and the cost is low. However, the availability of pure solution and matrix interferences made this process is not suitable. But sample stacking or on-column pre-concentration method has been introduced to increase the detection sensitivity and has been employed for As detection.

Instant on-site analysis of arsenic in groundwater can be done by the use of a small battery powered unit in conjunction with a microfabricated gold ultramicroelectrode (Au-UMEA) array. Use of portable equipment in conjunction with Au-UMEAAs provided rapid analysis of arsenic in groundwater with measured Limit of Detection (LOD) of 0.05 ppb (Feeney and Kounaves, 2000).

CONCLUSIONS

Arsenic contamination in ground water is a worldwide problem and has become a challenge for the world scientists. The toxic effects of As depends on its oxidation state, resulting in increasing interests in the quantitative determination of individual species. The techniques used for the determination of As sample in environmental samples should be more selective and sensitive. The most popular analytical techniques for the determination of arsenic have been described in this

review. It was clearly indicated that there is a plethora of analytical techniques available for the detection of arsenic in groundwater sample. Methods involved on HPLC separation with ICP, HG-AAS and electrospray mass spectroscopy determination techniques have been the most useful As speciation in environmental samples. There are also different methods available for the speciation studies of As with its own advantages and limitations. However, more research efforts are needed for the development of inexpensive, rapid, sensitive and reproducible methodologies for As species capable of working in the range of drinking water limits.

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