

A Review on Detection of Arsenic in Water

Omay Naik and Prasanna Soparkar

Vidyalankar Institute of Technology
University of Mumbai
Wadala, Mumbai 400037, India

{naikomay & prasannasoparkar19}@gmail.com

Arbaz Khan, Sangram Navale and Sheetal Mapare

Vidyalankar Institute of Technology
University of Mumbai
Wadala, Mumbai 400037, India

{khan.firoz & [sheetal.mapare](mailto:sheetal.mapare@vit.edu.in)}@vit.edu.in

Abstract – For years, various methodologies to detect harmful content in water and the environment have been proposed. Arsenic is a naturally occurring element which is a contaminant as it is poisonous and carcinogenic. Humans are routinely exposed to arsenic through ingestion or contact with arsenic containing soil. Arsenic is found in two forms namely organic and inorganic. Inorganic arsenic is classified into two types namely As(III) and As(V). Industry also contributes to arsenic pollution in water. According to a survey, the largest reported population exposed to naturally occurring inorganic arsenic was found in West Bengal, India and neighbouring Bangladesh.

Keywords – Inorganic arsenic, Contaminants, Groundwater, Detection strategies

I. INTRODUCTION

Arsenic is a tasteless and odorless element which is naturally found in the earth's crust. It is a chemical element with symbol 'As' and atomic number 33[1]. There are several structural forms and oxidation states of arsenic because it forms alloys with metals and covalent bonds with hydrogen, oxygen, carbon, and other elements. Environmentally relevant forms of arsenic are inorganic and organic existing in the trivalent or pentavalent state [2]. It has two forms, organic and inorganic. Inorganic form of arsenic is more toxic

than organic form of arsenic. The mobility and toxicity of arsenic are determined by its oxidation state [3]. Exposure to arsenic can cause a variety of adverse health effects, including skin problems, respiratory, cardiovascular, gastrointestinal and carcinogenic effects [4]. Fish, seafood and algae have high concentration of arsenic. About one third of the arsenic in the atmosphere comes from natural sources, such as volcanoes, and the rest comes from man-made sources [5].

According to the World Health Organization, the Arsenic guideline value in groundwater is $10 \mu\text{g L}^{-1}$ [6]. The contamination of groundwater with arsenic has already been reported in 20 countries, out of which four major instances are from Asia. These include Bangladesh, India, Inner Mongolia and Taiwan. Fifty districts of Bangladesh and nine in West Bengal (India) have arsenic levels in drinking water above the World Health Organization's arsenic guideline [7-16]. By 1994, investigators estimated that over 800,000 people in West Bengal were exposed to elevated inorganic arsenic levels through drinking water retrieved from tube wells [17].

Several techniques have been found for detecting inorganic arsenic in water. These techniques will be studied in this review.

II. PRE-REDUCTION OF ARSENIC

This technique aims at conversion of all the arsenic species into As (III) form also known as

trivalent arsenic form. This is specially used in electrochemical techniques as pentavalent arsenic is electro-inactive [18]. The most popular pre reductant of As (V) to As (III) is potassium iodide, which can be used with ascorbic acid, in order to prevent the oxidation of iodide to triiodide by air [19].

III. INDUCTIVELY COUPLED PLASMA (ICP)

The ICP technique uses the plasma to ionise components, whereby the sample is acidified and sprayed into the plasma. The high temperature of the plasma atomises and ionises all forms of arsenic. ICP is used along with other analytical techniques, such as MS and AES [20]. ICP-AES is a less used technique and normally applied for a comparison and more accurate analysis of a multi-element sample. Whereas, the ICP-MS technique is one of the most widely applied analytical protocols for arsenic detection. The reason is that the main advantages of ICP-MS over ICP-AES are isotope analysis capability of high precession and lower detection limits. The possible drawback of ICP-MS equipped with a direct nebuliser is the possible interference from high levels of chloride due to the formation of argon chloride in the plasma, which has the same mass as arsenic [21].

For detection of non-volatile elements like arsenic, a coupled system of High pressure liquid chromatography (HPLC) and ICP-MS is used. This coupled technique is mainly used for detection of detection of single elements.

IV. NEUTRON ACTIVATION ANALYSIS (NAA)

NAA technique utilized neutron bombardment to detect the concentration of an element (or elements) present in a sample. It is

mainly used to detect trace amounts of an element. The basic principle is neutron capture.

After the sample is irradiated, the elements present in the sample absorb a neutron in the nucleus of their atom. This created a compound nucleus, which is unstable. The atom decays rapidly into a lower energy state while emitting plank gamma radiation. The lower energy state which is obtained maybe radioactive. This radioactive state is achieved in certain elements. The radioactive decay of these atoms is of two types namely beta decay (where emission of a beta particle i.e. electron takes place) and gamma radiation which is also known as delayed gamma radiation. NAA measures this delayed gamma radiation, which is characteristic to each element, and the intensity of which reflects the amount of that element present in the sample [22].

V. SPECTROMETRIC METHODS

There many spectrometric methods developed to detect trace amounts of a material in a sample. Hydride generation coupled with AAS or Atomic Fluorescence Spectrometry (AFS) is a popular method of detecting arsenic in water. The reducing agents used are NaBH₄ and KBH₄ as they are reliable for converting the sample to volatile forms. This procedure can be used to measure both As(III) concentration and As(V) concentration separately, since As(III) reacts with tetrahydroborate at a higher pH level than As(V). This method of spectrometric detection allows for a higher level of sensitivity for arsenic as compared to colorimetric detection methods.

Graphite furnace atomic absorption spectrometry (GFAAS) or Electrothermal Atomic Absorption Spectrometry (ETAAS) is a detection method which can operate without the requirement of Hydride Generation. This technique works on the principle of absorption of free atoms produced from the sample which is contained in a graphite tube and

heated to high temperatures. However, in order to increase the sensitivity of this method, pre-concentration is required.

VI. ELECTROCHEMICAL METHODS

A. Polarography

Polarography is the oldest electrochemical technique for determination of trace inorganic metals [23-25]. It is a voltammetric measurement which is based on the principle of studying the sample using electrolysis and two electrodes, one is polarizable and the other is non-polarizable. Mercury is dropped on the polarizable electrode via a capillary tube. Since mercury falls on one electrode, the surface area changes. This causes capacitive current to flow through the system, thereby limiting the detection range [26].

In order to reduce the issue of capacitive current, Differential pulse polarography (DPP) is used. It has lower capacitive currents and high selectivity, thus providing better limits of detection [27].

B. Cathodic Stripping Voltammetry(CSV)

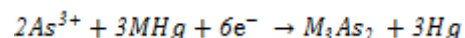
Cathodic Stripping voltammetry is a voltammetric determination method for detecting arsenic. It is done by using copper or selenium to react with arsenic in order to form favourable compounds at anode, that form arsenic hydride at the cathode. This increases the sensitivity of the system. It is based on the reduction of As(V) to arsenic hydride.

Generally this method is better suited for trace analysis, since the element to be detected is pre-concentrated on the working electrode.

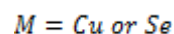
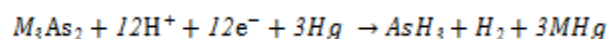
Most cathodic stripping techniques are carried out by using a HMDE which is a Hanging Mercury Drop Electrode, as this electrode does not suffer from the disadvantages of the solid electrodes. However, anodic stripping of arsenic

using a HMDE is not analytically useful due to interference from the oxidation of mercury [28]. In order to increase sensitivity most complex compounds of arsenic are stripped from the HMDE, whereby As(III) can react with copper or selenium to form relevant complex compounds which can be stripped from the cathode.

Deposition:



Stripping:



Scheme. 1 Processes occurring during Cathodic stripping voltammetry

C. Anodic Stripping Voltammetry(ASV)

Kaplin et al. [29,30] established the anodic stripping voltammetry technique for trace arsenic analysis, which is based on the deposition of metal arsenic on the electrode surface with subsequent anodic stripping (Scheme 2).

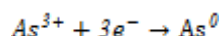
Anodic stripping is a voltammetric method which can detect $\mu\text{g/L}$ concentrations of a sample. This method has a very good detection limit (typically from 10^{-9} to 10^{-10} M).

Forsberg et. al. [31] investigated the detection of arsenic using Differential Pulse Anodic Stripping Voltammetry (DPASV) with different electrode materials (HMDE, Pt and Au).

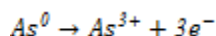
This method incorporates three electrodes namely, working, auxiliary and reference electrode. The sample being analyzed usually has an electrolyte added to it. A bismuth or mercury film electrode is used in most standard tests. In case the sample being tested has an oxidising potential above that of mercury or in cases that mercury

electrode is unusable, a solid, inert metal such as silver, gold or platinum is used as an electrode [32].

Deposition:



Stripping:



Scheme. 2 Processes occurring during Anodic stripping voltammetry

D. Microlithography fabricated arrays

This technique employs an array structured electrode. This results in a defined structure and increases reproducibility. Various materials can be used to create the electrode and has a low cost of chip.

Feeney et. al. [33] implemented a rapid on-site analysis of arsenic in groundwater using a microfabricated gold ultramicroelectrode array (Au-UMEA) used with a small battery powered unit. The advantages offered by such arrays are reproducibility, good sensitivity, low noise level, amplification of the signal while keeping UME behaviour, background current rejection and capability of implementation in portable detection systems.

Unlike colorimetric field kits presently in use, voltammetric techniques can yield precise quantitative data when careful analytical methods are used [34].

VI. NANO-MATERIALS

Most methods for detection of trace amounts of elements in water have a serious limitation on selectivity and sensitivity. Improvements in performance can be done by using different

electrode systems based on nanomaterials. Nanomaterials used are mainly carbonaceous nanomaterials, metallic nanoparticles, metal nanotubes. Gold nanoparticles have been tested to improve the detection capability of arsenic sensing systems [35].

However, practical application in the field i.e. to make the system cost efficient and portable, further innovation is required. Nano-material systems are projected to become an important option of monitoring hazardous pollutants in both environmental and biological fields [36].

VII. BIOSENSORS

Advancement in biology has allowed scientists to configure enzymes. Enzymes for detection of arsenic have been developed. Enzymatic Catalysis is a technique which utilizes the properties of enzymes for detection of trace amounts of a material. In this case, arsenic in water. The technique employed an enzyme that produced fluorescent compounds as per the concentration of arsenate compounds in water. The light emitted by this fluorescent compound can be measured to determine the arsenic concentration. This method is capable of detecting arsenic concentrations below the allowable level adopted by the World Health Organisation (WHO) which is 10 ppb (in drinking water). The technique achieved a detection range of 0-200 ppb. Calibration curves made at a set time interval allows for accurate determination of unknown arsenic samples [37].

VIII. CONCLUSION

There are multiple techniques with which contaminants like arsenic can be detected. However, each technique has its advantages and

disadvantages. Some techniques are accurate and rapid, however they can only be carried out in a laboratory environment. Other techniques, which can be deployed on-site are rapid however are not always accurate. Advancements in technology has resulted in nanomaterials and biosensors. These techniques provide novel methods for detection of arsenic level in the environment. However, the cost effectiveness of these detectors have to be addressed in order to make them practical. Currently there is a need of affordable and field portable arsenic sensing systems.

ACKNOWLEDGMENT

We hereby are very grateful to and wish to thank our guide and institute to give us this opportunity who supported us greatly and were willing to help us.

REFERENCES

- [1] <https://en.wikipedia.org/wiki/Arsenic>
- [2] <https://academic.oup.com/toxsci/article-abstract/123/2/305/1685876>
- [3] X. Meng, C. Jing, G.P. Korfiatis, ACS Symp. Ser. 835 (2003) 70
- [4] B.K. Mandal, K.T. Suzuki, Talanta 58 (2002) 201.
- [5] <https://www.greenfacts.org/en/arsenic/index.htm>
- [6] http://www.who.int/water_sanitation_health/dwq/chemicals/arsenic.pdf
- [7] P.C. Ray, J. Forensic Med. Toxicol. 16 (1999) 30
- [8] D. Chakraborti, B.K. Mandal, R.K. Dhar, B. Biswas, G. Samanta,
- [9] K.C. Saha, Ind. J. Environ. Protec. 19 (1999) 565.
- [10] D. Chakraborti, M.M. Rahman, K. Raul, U.K. Chowdhury, M.K. Sengupta, D. Lodh, C.R. Chanda, K.C. Saha, S.C. Mukherjee, Talanta 58 (2002) 3.
- [11] A. Chatterjee, D. Das, B.K. Mandal, T.R. Chowdhury, G. Samanta, D. Chakraborti, Analyst 120 (1995) 643.
- [12] D. Das, A. Chatterjee, B.K. Mandal, G. Smanta, D. Chakraborti, Analyst 120 (1995) 917.
- [13] R.K. Dhar, Curr. Sci. 73 (1997) 48.
- [14] B.K. Mandal, T.R. Chowdhury, G. Samanta, G.K. Basu, P.P. Chowdhury, C.R. Chanda, D. Lodh, N.K. Kuran, R.K. Dhar, D.K. Tamili, Curr. Sci. 70 (1996) 976.
- [15] D.N.G. Mazumder, Curr. Sci. 72 (1997) 114.
- [16] M.M. Rahman, U.K. Chowdhury, S.C. Mukherjee, B.K. Mandal, K. Paul, D. Lodh, B.K. Biswas, C.R. Chanda, G.K. Basu, K.S. Saha, S. Roy, R. Das, S.K. Palit, Q. Quamruzzaman, D. Chakraborti, J. Toxicol. Clin. Toxicol. 39 (2001) 683.
- [17] <https://academic.oup.com/ije/article/29/6/1047/659236>
- [18] H. Greschonig, K.J. Irgolic, Appl. Organometal. Chem. 6 (1992) 565.
- [19] H. Chen, I.D. Brindle, X. Le, Anal. Chem. 64 (1992) 667.
- [20] Q. Hung, Dang & Nekrassova, Olga & G Compton, Richard. (2004). Analytical methods for inorganic arsenic in water: A review. Talanta. 64. 269-77. 10.1016/j.talanta.2004.01.027. Page: 4
- [21] U. Bose, M. Rahman and M. Alamgir, 2011. Arsenic Toxicity and Speciation Analysis in Ground Water Samples: A Review of Some Techniques. International Journal of Chemical Technology, 3: 14-25.
- [22] <https://www.youtube.com/watch?v=en8tO3dtZ28>
- [23] M. Brezina, P. Zuman, Polarography in Medicine, Biochemistry and Pharmacy, Interscience, NY, 1958, p. 883.
- [24] P. Zuman, I.M. Kotloff (Eds.), Progress in Polarography, Inter-science, New York, 1962, pp. 1-2.
- [25] P. Zuman, L. Meites, I M. Kotloff (Eds.), Progress in Polarography, Interscience, New York, 1972, p. 3.
- [26] <https://en.wikipedia.org/wiki/Polarography>
- [27] Q. Hung, Dang & Nekrassova, Olga & G Compton, Richard. (2004). Analytical methods for inorganic arsenic in water: A review. Talanta. 64. 269-77. 10.1016/j.talanta.2004.01.027. Page: 5
- [28] D.J. Myers, J. Osteryoung, Anal. Chem. 45 (1973) 267.
- [29] L.F. Trushina, A.A. Kaplin, Z. Anal. Khim. 25 (1970) 1616.
- [30] A.A. Kaplin, N.A. Veits, A.G. Stromberg, Z. Anal. Khim. 28 (1973) 2192.
- [31] G. Forsberg, J.W. O'Laughlin, R.G. Megargle, S.R. Koirtyihann, Anal. Chem. 47 (1975) 1586.
- [32] https://en.wikipedia.org/wiki/Electrochemical_stripping_analysis
- [33] R. Feeney, S.P. Kounaves, Anal. Chem. 72 (2000) 2222.

- [34] R. Feeney, S. Kounaves, *Talanta* 58 (2002) 23.
- [35] K. Gibbon-Walsh, P. Salaün, C. M.G.van den Berg. Analysis of arsenic(V) by cathodic stripping voltammetry. *Analytica Chimica Acta*, ISSN: 0003-2670, Vol: 306, Issue: 2, Page: 217-223 Publication Year: 1995
- [36] S. Kumarkempahanumakkagari, A. Deep, Ki-Hyun Kima, S. K. Kailasa, Hye-OnYoon. Nanomaterial-based electrochemical sensors for arsenic - A review. *Biosensors & bioelectronics*, ISSN: 1873-4235, Vol: 95, Page: 106-116 Publication Year: 2017
- [37] Liu, Y.; Yu, C.; Cao, Z.; Shvarts, D.; Trogler, W.C. A highly sensitive enzymatic catalysis system for trace detection of arsenic in water. *Chem. Eur. J.* 2017, 23, 10289–10292. [CrossRef] [PubMed]