Arsenic Detection Techniques and Their Drawbacks

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Abstract: The importance of arsenic detection techniques has received significant attention of researchers during recent years due to its carcinogenic effects on human health through drinking water even at low concentration. There are various arsenic detection techniques used in laboratory that have detection limit below 1µg/L viz., Hydride Generation Atomic Absorption Spectroscopy (HGAAS), Graphite Furnace Atomic Absorption (GFAA), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Atomic Fluorescence Spectroscopy (AFS). This paper gives an overview of various technologies with the potential to measure and monitor arsenic in the aquatic environment. The relative effectiveness of arsenic concentration detection techniques which have been discussed in this paper is based on sensitivity of the method, reliability (or bias and precision) of the analytical results, specificity or selectivity of the method in the presence of interferences, operating range of the method, availability of equipment and trained personnel, quick analysis to permit routine use, and cost of analysis. The selection of a suitable technique among available techniques to detect arsenic in water samples is presented in this paper. The GFAAS technique is the preferred method in absence of overwhelming interferences whereas HGAAS is used when interferences of trace metal elements are present. ICP-MS is considered to be more efficient with compared to all other methods mentioned above as it can determine the individual isotopes of each element and capable of multi elemental analysis, but it shows its limitations in detecting arsenic concentrations in presence of chloride. AFS technique is most efficient for detection of low arsenic concentration. Silver Di Ethyl Di Thio Carbamate (SDDC) method determines total inorganic arsenic when interferences are absent and sample contains no methyl arsenic compounds. When spectrometric methods are used in hyphenation with colorimetric methods, it becomes the most efficient technique for arsenic detection.

Keywords: Arsenic, Comparative Analysis, Cost Benefit Analysis, Detection Techniques.

1. Introduction

The presence of arsenic in groundwater and surface water has become one of the major environmental worries in the world as Royal Geographical Society reported that at least 130 million people across the globe are exposed to arsenic level greater than 0.01mg/l (WHO maximum permissible limit of arsenic in drinking water). Arsenic is a metalloid found in water, soil, sediment, and food stuff. Arsenic in natural systems is originated from both anthropogenic and geological sources. But mostly arsenic problems are the result of mobilization under natural conditions. Mining activities, combustion of fossil fuels, use of arsenic in pesticides and as semiconductor, are some anthropogenic activities which also create adverse impacts. In drinking water, it predominantly occurs as inorganic (arsenite, arsenate) and organic forms (methyl and dimethyl arsenic compounds) [20]. The order of toxicity of arsenic species are arsenite > arsenate > monomethyl arsenic acid (MMA) > dimethyl arsenic acid (DMA) [1]. The International Agency for Research on Cancer (IARC) defines arsenic as a Group I known human carcinogen that also induces a wide range of other non-cancer effects.

Now a days, surplus of arsenic detection methods in aqueous system have been developed and most of them have detection limit below WHO guideline for arsenic in drinking water i.e. 10µg/L. In this paper considering the parameters such as sensitivity; ability to detect chemical state of arsenic and potential interference, comparative analysis of different arsenic detection techniques will be reviewed.

2. Arsenic detection techniques

At present there are numbers of arsenic detection methods viz., spectrometric, electrochemical, chromatographic etc. Spectrometric methods for the determination of arsenic involve the use of various spectrometric techniques such as ultraviolet, visible, atomic absorption, atomic emission, and atomic fluorescence. Electrochemical method includes voltammetric technique such as polarographic, anodic stripping voltammetry, cathodic stripping voltammetry, and microlithographic fabricated arrays whereas chromatographic method includes high performance
liquid chromatography, gas liquid chromatography which often gives best results in combination of other methods [12].

2.1. Spectrometric methods

2.1.1. Atomic absorption spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) is one of the most common instrumental method for analyzing metals and some metalloids. This technique is based on Beer-Lambert Law and makes use of absorption spectrometry to assess the concentration of an analyte in a sample. Atomic absorption spectrometry quantifies the absorption of ground state atoms in gaseous state. The atoms absorb ultraviolet or visible light and make transition to higher energy level. The analyte concentration is determined from the amount of absorption [10].

2.1.1.1. Hydride generation atomic absorption spectroscopy (HGAAS)

Hydride generation atomic absorption spectroscopy (HGAAS) is available via an option for many modern AAS instruments. It only requires the hydride generation module. Metalloids like arsenic, antimony, selenium, and tellurium are now routinely analyzed by HGAAS. Many of the main parts of the HGAAS system are identical to that of AAS: a hollow cathode lamp, air/acetylene flame, and optical system but include (in most systems) an optical cell and the relatively complex hydride generation system. The nebulizer required in AAS is not used in HGAAS [10]. However the main drawback of using HGAAS is the interference of trace metals like iron but this problem can be overcome by using L-cysteine which is very useful for preventing iron interferences [13].

2.1.1.2. Graphite furnace atomic absorption (GFAA)

Graphite furnace atomization (also known as electro thermal atomization) is a technique for improving the sensitivity and limit of detection for atomic absorption measurements. A small amount of sample or standard solution is placed inside a hollow graphite tube. This is resistively-heated in a temperature to remove sample, burn off impurities, atomize the analyte to form a plume of free metal vapour, and finally clean the tube [4].

2.1.2. Inductively Coupled Plasma (ICP)

Inductively Coupled Plasma (ICP) is an analytical technique used for the detection of trace metals in environmental samples. The most important advantages of ICP are its multi-element detection capability and high sensitivity.

2.1.2.1. Inductively coupled plasma mass spectroscopy (ICP-MS)

Inductively coupled plasma mass spectroscopy (ICP-MS) is an analytical technique capable of achieving detection limits in the part per trillion (ppt) for most elements. In ICP, the energy in the plasma (an ionized gas at extremely high temperature) is transferred by collision of argon with the atoms of interest. Most metals are ionizable emitting in the UV range, non-metals do not form ions in the ICP (require a vacuum) [26].

2.1.2.2. Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) also referred as inductively coupled plasma optical emission spectrometry (ICP-OES), is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses argon plasma (6000-10000ºC) to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample. It determines approximately all the element except gases and also some of the non-metals(C, N, F, O, H) [22].

2.1.3. Atomic fluorescence spectroscopy (AFS)

Atomic Fluorescence Spectrometry (AFS) is an ideal detection technique for speciation studies concerning hydride forming elements (mainly As, Se, Hg and Sb). Atomic fluorescence involves photon excitation of atoms to produce excited atoms which undergo radiational de-excitation over a short period of time after excitation. The intensity of the fluorescence depends critically upon the intensity of the light source at the exciting wavelength and the concentration of analyte atoms [23].

2.2. Electrochemical methods

Due to its excellent sensitivity in parts per billion range and unique ability to detect the trace levels of elements in distinct oxidation states in aqueous system, stripping voltammetry analysis is best among all electrochemical methods [7].

2.2.1. Polarographic technique

Principle of polarography is the study of solutions or of electrode processes by means of electrolysis with two electrodes, one polarizable and one unpolarizable. The former formed by mercury regularly dropping from a capillary tube. Polarography is an outdated technique for arsenic determination due to its low sensitivity for arsenic detection at low concentrations in drinking water. Presently out of all existing electrochemical techniques differential pulse polarography is most sensitive one [16].
2.2.2. Anodic stripping voltametry

In this method the analyte of interest is electroplated on the working electrode during a deposition step, and oxidized from the electrode during the stripping step. The current is measured during the stripping step [5]. Now a days modification of electrode surfaces and materials by using metal nanoparticles and carbon electrodes and carbon nanotubes (other examples are Au nanoparticle modified glassy carbon electrode (GCE), Au modified boron doped diamond (BDD) electrode, Au nanoparticle modified carbon nanotubes) are being done to improve analytical ability for arsenic detection but these modified electrode also suffers from the problem of copper interference. It was reported that nano Pt-Fe (III)/Multivalved Carbon Nano Tube/Glassy Carbon electrode (nanoPt-Fe (III)/MWCNT/GCE) can be used without interference of copper in the determination of As (III) [19].

2.2.3. Cathodic stripping voltametry

Cathodic stripping voltammetry is a voltammetric method for quantitative determination of specific ionic species [13]. Researchers have suggested that by use of mannitol, and L-cysteine sensitivity of this method can be increased which make it applicable for both laboratory and field [8, 9].

2.2.4. Microolithographic fabricated arrays

In this technique array of microelectrodes is fabricated by the use of photolithographic technique. The thin film of electrode materials viz., gold, iridium, platinum, and carbon has been fabricated on silicon wafer [6]. These arrays offer several benefits, such as low noise level, sensitivity, cost efficiency, and applicability for use in field portable or in-situ instrumentation [13].

2.3. Chromatographic method

Chromatographic techniques with hyphenation of element specific spectrometric detection have proven most beneficial for speciation of trace level of arsenic compounds. For ex. high performance liquid chromatography (HPLC) when used in combination with ICP-MS proved to be the most appropriate method for determination of non-volatile species of element like arsenic. There are various other combinations viz., HPLC-GFAA, HPLC-ICP-AES, HPLC-AAS but these are not sensitive enough and give poor detection limit.

Other chromatographic techniques used in separation of arsenic species are ion pair chromatography, ion exchange chromatography, ion exclusion and size exclusion chromatography, and multidimensional chromatography [24].

2.4. Standard arsenic detection method

At present variety of field arsenic measurement methods are commercially available. Some of these based on hydride generation techniques are described in standard method [31]. Silver di ethyl di thi carbamate (SDDC) is the standard method for arsenic detection which determines total arsenic when interferences are absent. Other arsenic detection methods such as field kits, colorimetric assays are not as reliable as aforesaid AAS but these are not sensitive enough and give poor detection limit. Other chromatographic techniques used in separation of arsenic species are ion pair chromatography, ion exchange chromatography, ion exclusion and size exclusion chromatography, and multidimensional chromatography [24].

| Table 1: Comparative analysis of existing arsenic detection techniques |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Techniques      | Working Principle                                                                                     | Detection Limit (in µg/l) | Advantages                                              | Disadvantages                                           | References     |
| Graphite furnace atomic absorption spectroscopy (GFAA) | Atomic absorption spectrometry quantifies the absorption of ground state atoms in gaseous state. The atoms absorb ultraviolet or visible light and make transition to higher energy level. The analyte concentration is determined from the amount of absorption. | 0.05                | Small sample size, moderate price, very compact instrument, little spectral interference. | Take more analysis time, Chemical interferences, Element limitations, 1-6 elements per determination, Limited dynamic range. | [4, 29]         |
| Hydride generation atomic absorption spectroscopy (HGAAS) | This technique based on production of volatile hydrides by chemical treatment of sample with a reducing agent viz, sodium borohydride. | 0.03                | Most widely used methods for arsenic speciation due to its high sensitivity, low detection limit | Applicable to only those arsenic species which give rise to volatile derivatives on reduction. | [2, 10, 11, 13, 15] |

Preferred method in the absence of overwhelming interferences.

Preferred method in absence of trace metals or in presence of interference preventing agents like L-cysteine for iron interference.
<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>Detection Limits</th>
<th>Main Advantages</th>
<th>Drawbacks</th>
<th>Applicable Conditions</th>
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<tbody>
<tr>
<td>Inductively coupled plasma mass spectroscopy (ICP-MS)</td>
<td>ICP MS measure ion produce by a radiofrequency ICP. From liquid analyte species nebulised and the resulting aerosol is transported by Ar gas into plasma torch. the ion thus produced are sorted according to their mass to charge ratio and quantified with a channel electron multiplier. ICP-MS can determine the individual isotopes of each element. Excellent detection limits, multi-element detection, very economical for many samples and/or elements.</td>
<td>0.002-0.06</td>
<td>Excellent detection limits, multi-element atomic spectroscopy technique, Excellent sample throughput, very wide analytical range, easy to use, little chemical interference.</td>
<td>Possible interference from high levels of chloride due to the formation of argon chloride in the plasma, which has the same mass as arsenic. Higher initial capital cost.</td>
<td>Applicable at lower concentrations, if chloride does not interfere.</td>
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<tr>
<td>Inductively coupled plasma atomic emission spectroscopy (ICP-AES)</td>
<td>This method describes multi-elemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry.</td>
<td>0.7</td>
<td>Best overall multi-element atomic spectroscopy technique, Excellent sample throughput, very wide analytical range, easy to use, little chemical interference.</td>
<td>Moderate to low detection Limits (but often much better than FAAS), spectrometric interferences possible, some element limitations.</td>
<td>Useful at higher concentrations (greater than 50 µg/L).</td>
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<td>Atomic fluorescence spectroscopy (AFS)</td>
<td>It is based on absorption of radiation of specific wavelengths by an atomic vapour with subsequent detection of radiationally deactivated states via emission in a direction orthogonal to the excitation source. Both the absorption and the subsequent atomic emission processes occur at wavelengths which are characteristic of the analyte atom.</td>
<td>0.05-0.5</td>
<td>Low detection limits (below the µg/L) and wide linear calibration range (from µg/L to mg/L) with further advantages simplicity, lower running costs for arsenic speciation.</td>
<td>Quenching and interferences.</td>
<td>In comparison to ICP it have additional advantages of low acquisition and low running cost, ease of operation but its ability to detect single element makes its use less widely.</td>
</tr>
<tr>
<td>Polarographic</td>
<td>Principle of polarography is the study of solutions or of electrode processes by means of electrolysis with two electrodes, one polarizable and one unpolarizable, the former formed by mercury regularly dropping from a capillary tube.</td>
<td>10</td>
<td>Low cost commercial instruments, Used for organic molecules and for metal ions which do not form amalgams easily, DPP (differential pulse polarography) is probably the most sensitive</td>
<td>Poor detection limits, use of toxic mercury can pose severe health effect.</td>
<td>Not preferred due to limited sensitivity.</td>
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<tr>
<td>Method</td>
<td>Description</td>
<td>Limitation</td>
<td>Improvement</td>
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<td>Anodic stripping voltammetry</td>
<td>Based on the deposition of metal arsenic on the electrode surface with subsequent anodic stripping.</td>
<td>Does not require expensive instrumentation, is easy to perform, provides very low detection limits by using modified electrodes, and can be performed in the field.</td>
<td>Modified electrodes such as nano Pt-Fe(III)/MWCNT/GC improves the analytical ability of ASV to detect arsenic without Cu interference.</td>
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<tr>
<td>Cathodic stripping voltammetry</td>
<td>The principle of arsenic speciation using CSV is to determine the electroactive AsIII species first and then sequentially to convert other arsenic species to for measurement.</td>
<td>These are cheap and can provide very accurate measurements with a rapid analysis time.</td>
<td>Copper interference, use of mercury is also a matter of concern.</td>
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<td>Microlithographic fabricated arrays</td>
<td>In this method microlithographic technique has been used and silica is most widely used to fabricate integrated circuits and physical sensors. These sensors are field deployable and can be modified chemically or coated with polymer or Hg film to provide selective response.</td>
<td>These arrays offer several benefits, such as small size, reproducibility, uniform ultra-microelectrode (UME) geometries, sensitivity, cost efficiency, and applicability for use in field portable or relatively inexpensive.</td>
<td>By overcoming interference (Cu) and use of solid electrode problem this technique can be used.</td>
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<tr>
<td>Silver di ethyl diithio carbamate (SDDC) Method</td>
<td>It is based on reduction of inorganic arsenic to arsine (AsH₃) by zinc in an acidic medium in a gutzeit generator. Arsine is absorbed in a chloroform solution of diethylthiocarbamate (DTC). Arsenic reacts with silver salt forming a soluble red complex which determines the amount of arsine evolved from the solution by spectrophotometer.</td>
<td>Simplicity of the instrumentation. Generates arsine gas and is prone to false positive and false negative readings, limited to water samples containing total metal ion concentration of more than 5000µg/l.</td>
<td>Relatively less expensive experimental set up and running cost. Applicable in determining total inorganic arsenic when interferences are absent and when the sample contains no methyl-arsenic compounds. This method also has the advantage of being able to identify and quantify arsenate and arsenite separately by generating arsine at different pH values.</td>
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3. Cost benefit analysis

The cost of most of the instruments is well understood, but once we purchase any instrument, installation of these needs significant changes at installation place such as all these systems require fume extraction, ICP-MS or GFAAS sometimes require clean room conditions to operate at the parts per trillion levels. ICP-based systems (ICP-AES or ICP-MS) require high volume gas installation and even after installation to operate these instruments we need to purchase acetylene or nitrous oxide gas (compressed air source), hollow cathode lamps, reagents and standards power for FAAS, argon gas, quartz torches, reagents and standards pump tubing, cooling water for ICP-AES. Often we forget the actual cost of instruments that include capital cost, installation cost and operating cost too. There are many instruments available from a number of manufacturers, and because so many options and configurations are possible, it is difficult to put absolute values on capital costs. In Table 2, approximately relative cost of arsenic detection instruments is given.

**Table 2: Approximate estimation of purchase cost**

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Relative cost (x=$15,000)</th>
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<tbody>
<tr>
<td>Flame AAS</td>
<td>1x</td>
</tr>
<tr>
<td>Furnace AAS</td>
<td>2x</td>
</tr>
<tr>
<td>Sequential ICP-AES</td>
<td>4-5x</td>
</tr>
<tr>
<td>Simultaneous ICP-AES</td>
<td>5-7x</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>10-20x</td>
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</table>

*Source: An elementary overview of elemental analysis (Thermo Elemental).*

4. Discussion

ICP-MS is superior to ICP-AES owing to have better detection capability with the same sample throughput and have the ability to obtain isotopic information. Though ICP-MS have these qualities and capability of multi elemental analysis but its higher cost limits its widespread use as compared to GFAAS and HGAAS. But as per the review, AFS has been noticed to be advanced than AAS and equal to or greater than ICP MS regarding sensitivity, low detection limit, wide linear calibration range with further advantage of simplicity and lower running cost. AFS represents a suitable alternative to other atomic spectrometers commonly employed in speciation studies such as atomic absorption spectrometry (AAS) and inductively coupled plasma-mass spectrometry [18]. But AFS also have the limitation of quenching (which can diminish intensity of the atomic fluorescence by the collision between excited atoms and other molecules in the atomization sources) and interference. These lab based instrumentation such as ICP-MS and graphite furnace AAS applications provide accurate and reproducible results but if we consider SDDC method it only helps in detection of total arsenic. Field kits and colorimetric assays which offer rapid results and are cost effective but reliability and sensitivity is critical issue in case of these methods while electrochemical methods provide reliable results (under suitable laboratory condition) and are versatile and portable but it has the limitation of extensive field testing [13]. HPLC enhances the ability to detect different oxidation state of arsenic and ICP-MS provides comparatively higher detection limit with high productivity. When both of these coupled with HG then it increases the sensitivity of detection as well as reduces the interferences from sample matrix. After comparing HPLC-HG-ICP-MS and HPLC-HG-AFS it was concluded that limit of detection were similar for both. However, AFS has more advantage over ICP-MS as it provides lower running costs, shorter warm up time prior to analysis and ease in use [3].

5. Conclusions

As arsenic detection instruments are expensive, require fully equipped and skilled staffed laboratory to maintain and operate. Therefore before selecting any instrument for the arsenic detection, one must consider its detection limits, analytical working range, and sample throughput, data quality, cost, interferences, and ease-of-use. After reviewing most of the detection techniques it can be concluded that when spectroscopic method works in hyphenation with chromatographic method it can fulfill almost all the requirements to detect arsenic in water sample.

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References


