Review Article

Detection of trace arsenic in drinking water: Challenges and opportunities for microfluids

Sarthak Jain

Student, Neerja Modi School, Shipra Path, Mansarovar, Jaipur, Rajasthan, INDIA.
Email: jainsarthak2000@gmail.com

Abstract

The Project talks about methods used for detection of arsenic in drinking water. Starting with understanding the harmful effects of arsenic and then exploring the detection techniques used for arsenic measurement. Through the project, we can understand the challenges in the detection methods and different types of sensors used for this problem.
Key Words: arsenic in drinking water, Micro Fluids, Drinking Water

Address for Correspondence:
Dr. Sarthak Jain, S-9, Adinath Nagar, JLN Marg, Jaipur, Rajasthan – 302018, INDIA.
Email: jainsarthak2000@gmail.com
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INTRODUCTION

Drinking water with the toxic levels of arsenic is a very serious problem in the world. It is challenging to measure the different types of field samples for arsenic. Arsenic is present in the nature and mostly available in the air, water and earth. It has highly toxic nature in inorganic form. Due to use of contaminated water in cooking, irrigation of food crops, use of contaminated meal, factory processes and tobacco, public is exposed to elevated levels of inorganic arsenic. It leads to chronic arsenic poisoning. Many harmful effect like skin cancer, developmental effects, cardiovascular disease, neurotoxicity and diabetes and skin lesions arises due to use of arsenic-rich water (unknown, WHO Fact Sheet)[1]. Unlike organic pollutants, arsenic cannot be transformed into a non-toxic material; it can only be transformed into a form that is less toxic when exposed to living organisms in the environment. Because arsenic is a permanent part of the environment, there is a long-term need for regular monitoring at sites where arsenic-containing waste has been disposed of and at sites where it occurs naturally at elevated levels (Zhong)[2]

Speciation of arsenic compounds in water: Generally, Arsenic presents in the form of typically arsenous acid and arsenic acid or their derivatives in the contaminated water. These species are merely the soluble forms of arsenic near neutral pH. These elements are feezed from the basic rocks that surround the aquifer. Arsenic acid is ionized and exists as the ions [HAsO4]2− and [H2AsO4]− in neutral water, whereas arsenous acid has non ionized characteristics (Yogarajah)[3].

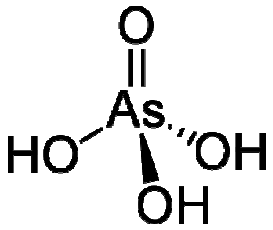

Figure 1: Arsenic acid (H3AsO4)

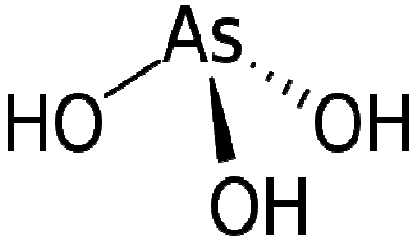

Figure 2: Arsenous acid (H3AsO3)

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Current Methods and Requirements for Measuring Arsenic in the Environment: Fixed laboratory assays are generally required to accurately measure arsenic in an environmental sample to parts per billion (ppb) levels, defined here as µg/L for water. The preferred laboratory methods for the measurement of arsenic involve pretreatment, either with acidic extraction or acidic oxidation digestion of the environmental sample. Pretreatment transfers all of the arsenic in the sample into an arsenic acid solution, which is subsequently measured using any one of several accepted analytical methods, such as Atomic Fluorescence Spectroscopy (AFS), Graphite Furnace Atomic Absorption (GFAA), Hydride Generation Atomic Absorption Spectroscopy (HGAAS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). These instruments are bulky, expensive to operate and maintain, and require fully equipped laboratories to maintain and operate. Field assays, in which lower sensitivities may be acceptable for purposes of sample screening or site surveys, strive for similar detection goals as fixed lab methods, are relatively inexpensive, and can produce a large number of screening results in a short time (Yogarajah)[4].

Microfluidics and Sensing Systems: Microfluidic devices are used for small-scale manipulation of fluids. These are widely used for medical diagnosis purpose and environmental polluting elements detection. These are portable, low sample and reagent consumption, small sample size, low energy consumption, rapid detection, and very importantly, low cost. Two types of designs are generally used. One is micro-total analysis systems (µTASs) which is fully-integrated analytical device for onsite (Turdean)[4]. The micro-total analysis system (µTAS), mostly known as "lab-on-a-chip". It incorporates all necessary steps from sample pretreatment, dilution, calibration, separation, derivatization, and ultimate detection (Shukla). Another type is paper-based device having high portability and low-cost, to enable simple and rapid testing for either onsite applications or daily use. Classification of microfluidic devices is according to the signal acquisition methods or the detection methods used for this (Pumera, Merkoçi and Alegret)[5]. Signal acquisition comprises of optical measurement or electrochemical measurement by sensors. Various types of sensors like bio-, chemo- and electromechanical, are responsible for performance of the microfluidic devices (Pranjali Gautam)[6].

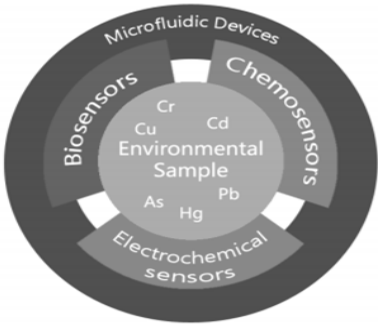

Figure 3: Different types of sensors used for arsenic detection

What is a Biosensor?: According to the International Union of Pure and Applied Chemistry (IUPAC) (namely Physical Chemistry and Analytical Chemistry Divisions) a biosensor is defined as "a self-contained integrated device that is capable of providing specific quantitative or semi-quantitative analytical information using a biological recognition element (biochemical receptor) which is in direct spatial contact with a transduction element" (D. R. Thévenot)[7]. Structure of biosensor is divided into three parts: a recognition element (enzyme, antibody, DNA, etc.), a signal transducing structure (electrical, optical, or thermal), and an amplification/processing element (unknown, wilkipedia). It also has permselective membrane which controls transport of analyte to the bioreceptor.

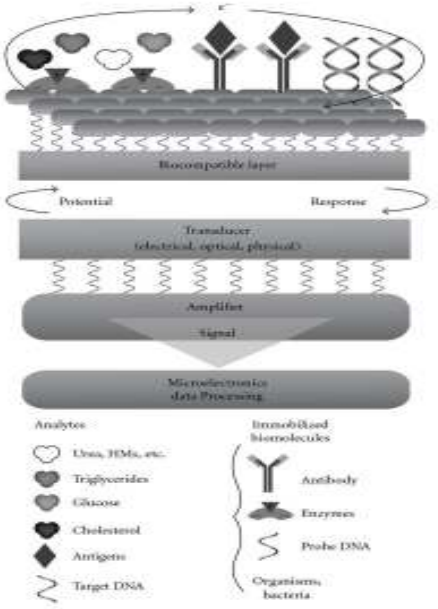

Figure 4: Schematic principle of operation of a biosensor

Characteristics of biosensors: Biosensors have highly sensitive behavior for small samples or we can say, very minimum sample prepration is required. Various types of biosensors are available according to transconduction

element and biorecogniton principle. Direct sampling and analysis is possible, giving way to automation. It has very attractive features like real time detection, minimal sample requirement, fast analysis, portability, cost-effective and on-site monitoring. It is also user friendly and can be used by non qualified personnel. It require very simple processing steps than bioassays or bio analytical systems, which require additional processing steps, such as reagent addition and where the assay design is permanently fixed in the construction of the device (Zhong)[8]. Biosensors are classified into various categories according to bio-recognition principle. A bio receptor can be a tissue, micro organism, organelle, cell, enzyme, antibody, nucleic acid and bio mimic etc. and the transduction may be optical, electrochemical, thermometric, piezoelectric, magnetic and micromechanical or combinations of one or more of the above techniques (Pumera, Merkoçi and Alegret).

Plant and animal tissue based biosensor: Higher animals and plants have ability to detect important analytes like harmones, drugs. Neurotransmitters, amino acid and toxicants. These special tissues used in electrochemical transducers to construct biosensors. Nerve cells in animals and phloem cells in plants possess excitable membranes through which electrical excitations can propagate in the form of action potentials. action potentials respond to environmental irritants via intercellular and intracellular communication. adjacent excitable cells receive these impulses. electrochemical detection takes place mainly amperometric or potentiometric. optical techniques, such as chemiluminescence or fluorescence, also appeared for high degree of sensitivity. Work has been done on primary-source freshwater drinking samples from the Clinch and Tennessee Rivers using tissue based detection system that uses naturally occurring aquatic photosynthetic tissue as the sensing material for detection of chemical antagonists in the water. Sensor readout is based on well-known principles of fluorescence induction by living photosynthetic tissue. Plant tissues are mostly used in biosensors because of high stability, high level of activity, long lifetime, high reproducibility of the experimental results, availability, cheaper price, less time consumption and its diversity. There are several disadvantages like low specificityand long response times, due to the diffusion barrier (Pranjali Gautam)[10].

Microbial whole cell based biosensor: Whole cell based sensing techniques usually utilize engineered microbes with reporter genes or spores for detection of heavy metal targets. When a specific binding event occurs between a regulatory protein and its ligand analyte (As III or others), certain biochemical pathways in the engineered microbes can be activated to enable detection, usually through the expression of green fluorescence proteins, or the germination rate of spores can either be hindered or expedited. Certain parameter such as bioavailability, toxicity and genotoxicity can be assayed using whole cells only. They provide estimation for pollutant bioavailability. The use of whole cells as biocatalysts has several advantages as compared to isolated enzymes, the most important being increased stability and protection from interfering substances. Consequently, microbial biosensors are preferred for measurements in contaminated samples. Whole cell bioassays can be classified as turn off assay- degree of inhibition of a cellular activity that is continuous; or turn on assay – activation of a certain process by the target pollutant (ManjuPhadke)[11].

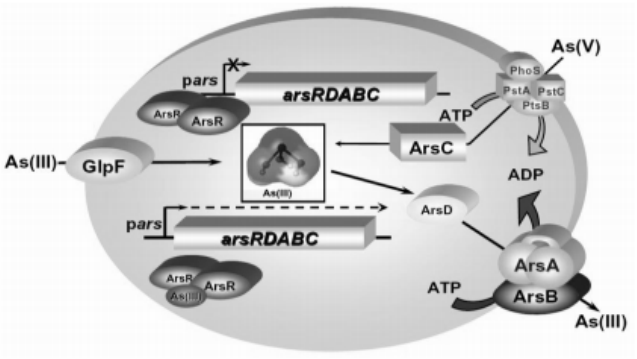

Figure 5:

Antibody and enzyme: In surface, ground, or drinking water other than regular pollutants, hormones, pesticides, endocrine disrupting compounds (EDCs) and antibiotics are also found to have an adverse and toxic effect on humans at low nanogram per litre levels. The first issue related to EDCs is removal of steroids from wastewater treatment process. EDCs did not draw much attention, because of the trace level concentration of detected EDCs and the lack of information on their significance in toxicity. EDCs are known as a class of chemicals which have xenobiotic and exogenous origins while mimicking or inhibiting the natural action of the endocrine system in animals and human, such as synthesis, secretion, transport, and binding. One of the effective methods to determine EDCs is usage of biologically based assays (Pranjali Gautam)[12]. The biological methods are intended to measure the levels of individual EDCs, based on the assumption that the target compound has been identified as an EDC and much is known about its chemical properties. However, traditional toxicity tests may not always be suitable for certain water samples. Several mechanisms are involved in the biological assays to determine EDCs, such as cell proliferation, ligand binding, luciferase induction, vitellogenin induction, or antigen–antibody interactions. Cell proliferation utilizes

the estimation for cell growth and reproduction in different samples. Ligand binding quantifies the number of specific estrogens binding sites. Luciferase induction measures the amount of luciferase induced from estrogens receptors and response elements with luminescence after cell lysing and the addition of luciferin. They maintain the homeostasis, reproduction, metabolism, development, and/or behaviour of living species. Vitellogenin induction quantifies the amount of vitellogenin in the plasma of female fish liver after extraction, which is secreted as a response to estrogens. In addition, the production of vitellogenin in male fish can be seen as an indication of endocrine disruption. Biologically based assays may be applied with whole organisms, cellular, or non-cellular materials, such as antibodies or estrogens receptors. Along with bioassay, immunoassay have become an important tool as automated immunosensor which is based on the principle of total internal reflection fluorescence (TIRFs) and antigen-antibody non covalent binding interaction, that can measure several organic compounds (antibiotics, hormones, pharmaceuticals, EDCs, pesticides) in parallel (Jokerst, Emory and Henry)[13].

Nucleic acid based biosensor: Nucleic acid-based biosensors are finding increasing use for the detection of environmental pollution and toxicity. A nucleic acid-based biosensor employs as the sensing element an oligonucleotide, with a known sequence of bases, or a complex structure of DNA or RNA. Nucleic acid biosensors can be used to detect DNA/RNA fragments or either biological or chemical species. In the first application, DNA/RNA is the analyte and it is detected through the hybridization reaction (this kind of biosensor is also called a genosensor) (Palchetti I)[14]. In the second application, DNA/RNA plays the role of the receptor of specific biological and/or chemical species, such as target proteins, pollutants or drugs. New trends in nucleic acid research include development of aptamers and aptazymes as affinity ligands and potential coupling to transduction technologies. Deoxyribonucleic acid (DNA) biosensors (genosensors) have been exploited for their inherent physico-chemical stability and suitability to discriminate different organism strains (Teles)[15]. The main principle of detection among genosensors relies on specific DNA hybridization, directly on the surface of a physical transducer. Surface plasmon resonance and piezoelectric sensing are reported as transduction principles for DNA-based devices. Mussels adjust their functions to ordinary environmental changes, e.g. temperature fluctuations and emersion-related hypoxia, and react to various contaminants, accumulated from the surrounding water and define a potential health risk for sea-food consumers. Despite the increasing use of mussels in environmental monitoring, their genome and gene functions are largely unexplored. The transcriptional footprints and discriminating capacity of different mussel tissues have to be taken into account in the microarray analysis. In the digestive gland, numerous gene probes discriminated biologically relevant doses of two contaminant mixtures and about half of them appear potential markers of real exposure to heavy metals and persistent organic pollutants (Venier)[16]. Moreover, among nucleic acids, aptamers represent a new promising recognition element for biosensor development. RNA, has opened new perspective in the development of new analytical and diagnostic methods. The coliform Escherichia coli were used as a model fecal indicator. DNA probecoated magnetic beads in combination with the electrochemical monitoring of the oxidation state of guanine nucleotides should allow for direct detection of bacterial RNA. In vitro evolution from random sequence libraries makes it possible to build nucleic acids that specifically recognise and bind to virtually any kind of target, such as ions, metabolites, drugs, toxins, peptides and proteins. The quickly growing area of genomics, ribonomics, proteomics and metabolomics requires the development of high-throughput and massive-parallel analysis of biological samples. DNA sensors are being used to detect salmonella enteric using keypad user interface to operate a nucleic acid sensor with fluid handling and real-time polymerase chain reaction (PCR) capabilities. Biosensors and micro-array chips that are based on detection of hybridisation/interaction of short strands of nucleic acids offer platforms for applications such as screening of genomes, detection of pathogenic organisms, and efficient searching of compound libraries for detection of potential therapeutic agents (H.Tsai)[17].

Protein or DNA Based Biosensors: Sensors using nucleic acids for the recognition and monitoring of toxic compounds are useful because many toxins, such as arsenic, have high affinity for nucleic acids or for DNA binding proteins, and specific sequences can be detected rapidly and at low cost. An electrochemical DNA-based biosensor for the detection of arsenic trioxide (As2O3) has been reported. It should be pointed out that arsenic trioxide forms inorganic As(OH)3 (As(III)) when dissolved in solution at neutral pH. A voltammetric signal that reflects guanine oxidation decreases with exposure time and the concentration of As2O3, presumably as a result of a reaction between guanine and As2O3 that damages purine bases. The interaction of As2O3 with double-stranded DNA (dsDNA), single-stranded DNA (ssDNA) and 17-mer short oligonucleotide was observed electrochemically using differential pulse voltammetry (DPV) with a carbon paste electrode (CPE) at the surface. Potentiometric stripping analysis (PSA) was employed to

monitor the interaction of As2O3 with dsDNA in the solution phase using a renewable pencil graphite electrode (PGE) (Melamed)[18]. Changes in experimental parameters, such as the concentration of As2O3 and the accumulation time of As2O3, were assayed using DPV. However, the carbon paste electrode (CPE)-based DNA biosensor has limited sensitivity (detection limit of 1 mg/L) and cannot be used under harsh experimental conditions. DNA, a target for oxidative damage by reactive oxygen species (ROS), was attached to the surface of a screen-printed carbon electrode. DNA damaged by arsenite, dimethylarsinic acid (DMAs (V)), phenylarsenate (PhAs(V)) and p-arsanilic acid (pASA(V)) was analyzed, and the DNA-based biosensor was higher for the aromatic arsenicals than for inorganic arsenic. However, there was no significant difference in the effect of individual organic arsenic compounds, so this sensor seems to lack selectivity. An advanced surface plasmon resonance-based DNA biosensor for As2O3 detection was developed using self-assembled monolayers for DNA immobilization. The surface-sensitive analytical technique of surface plasmon resonance (SPR) was applied to monitor the binding of double-stranded calf thymus deoxyribonucleic acid (dsCT-DNA) with As2O3. The surface of the gold electrode was modified with 1-ethyl-3-(-3-dimethylaminopropyl) carbodiimide (EDC)/N-hydroxysuccinimide (NHS) on hydroxyl-terminated (OH) terminal self-assembled monolayers of β-mercaptoethanol (MCE). The study had a very low detection limit and a minimum response time, and the dsCT-DNA/2-ME/Au electrode is not selective for As2O3 and can only be utilized for the initial screening of drinking water and wastewater (Mary Reynolds)[19]. In addition to DNA-based biosensors, a variety of proteins have been used for sensing arsenicals. As (III) is a thiophilic metalloid that forms strong coordinate bonds with sulfur thiolates in proteins. Trivalent arsenicals inhibit or activate enzymes by binding to cysteine thiolates. Most protein-based biosensors developed for As (III) or A s (V) are based on inhibition. An amperometric biosensor was developed to study the inhibition of acetylcholinesterase by As (III). The principle of the biosensor is based on the inhibitory effect of As (III) on the activity of acetylcholinesterase immobilized on a graphite electrode. In the presence of As (III), the levels of the thiocholine oxidation current were decreased proportionally to the As (III) concentration. The limitation is the action of As (III), as an acetylcholinesterase inhibitor is not specific. A number of other heavy metal ions, including Fe3+, Cd2+ and Cu2+, had a similar effect. Later, acid phosphatase (AcP)-polyphenol oxidase, arsenite oxidase, L-cysteine and acid phosphatase were each used for the construction of arsenic biosensors, but these also had limitations, such as a lack of specificity and low storage stability (Turdean)[20].

Chemo –sensors: Chemo-sensors are classified as follows:

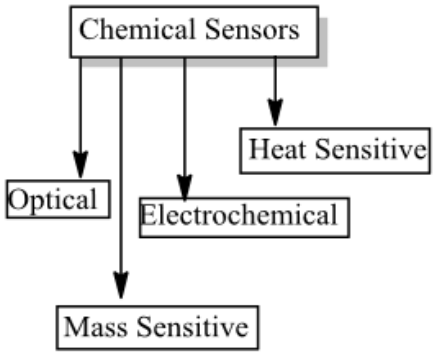

Figure 6:

Optical Chemical Sensors: An optical sensor device consists of the following components: (a) the recognition unit, where specific interaction and identification of the analyte takes place; (b) the transducer unit that converts the recognition process into a measurable optical signal; (c) an optical device (process unit) which consists of at least a light source and finally (d) a detector (in the simplest form a photodiode), which detects and converts the change of optical properties, after amplification of the primary signal, into a unit readout (Dorothee Grieshaber)[21]. The optical properties measured can be absorbance, reflectance, luminescence, light polarization, Raman and other Optical sensors have found many applications in various fields, including biomedical, clinical, and environmental monitoring and process controlling. They are an attractive analytical tool, whenever continues monitoring and real-time information is desired. They can track sources of contamination in an industrial process, follow the formation and movement of environmental pollutants and can raise the alarm when a toxic species exceed an expected level of exposure (Zhong)[22].

Sensors based on chromophores: The majority of heavy metal ion sensors are based on the use of an indicator dye which undergoes a binding reaction with the ions. This reaction is accompanied by a change in the absorbance or fluorescence of such chelates. In other words, an indicator acts as a transducer for the chemical species that cannot be determined directly by optical means. Many indicators cannot be used in optical sensors because of unfavorable analytical wavelengths, poor photos tability, low molar absorptivity or the need for additional reagents. Most of them bind with the metal ion irreversibly or only at low or high pH so they cannot be used for continuous sensing at near neutral pH. Upon binding with the metal ion, most

indicators undergo a change in color, with one band appearing asAnother disappears, rather than an intensity change of one single band (ÖTER)[23].

Sensors based on fluorophores: In contrast to chromogenic reagents, fluorescent indicators are of the on/off type in that only one of the species (the complexed or the noncomplexed) is fluorescent. Fluorescent indicators frequently provide improved sensitivity (which is important in miniature sensors) and also selectivity because it is unlikely that an interfering species would have the same absorbance and emission as the analyte complex. Fluorimetry (and luminescence spectrometry in a wider sense) also offers a broad variety of spectroscopic techniques including the measurement of life time, polarization and energy transfer. An important group of indicators is based on quenching of luminescence by heavy metals and transition metals. In the case of static quenching, the quencher interacts with the fluorophore in its ground state. In dynamic (collisional) quenching, the interaction between the metal ion (quencher) and the fluorophore occurs in the excited state only and leads to a reduction in both the emission intensity and the decay time. The photophysical process of dynamic quenching is fully reversible, that is, the indicator is not consumed. Hence, the quenching efficiencies of many transition metals, in particular Fe(III), Co(II) and Ni(II), are thought to be due to their numerous unpaired spins(Zhong)[24].

Electrochemical Sensors: Electrochemical sensors with rapid and highly sensitive detection capabilities of various bio/chemical species are in great demand in many areas of science. Developing easy -to-use electrochemical sensors for detecting the concentration and activities of the various species therefore become very important. Hand-held electrochemical devices with accuracy and sensitivity similar to that of bench-top analyzers have already been developed for certain applications. Although still at basic research stage, many new applications are yet to be discovered. Improved modern fabrication techniques play a major role in developing these miniaturized devices (D. R. Thévenot)[25].

Currently Available Field Assays to Measure Arsenic

Colorimetric Test Kits: Field kits have been used extensively to test for arsenic in groundwater, and in many cases, it is the only assay applied. The current baseline methodology involves a variety of technologies that are all variations of the "Gutzeit" method. These assays have been applied almost exclusively to water samples, although they may be applied to testing solid waste and soil, using either an acidic extraction or an acidic oxidation digestion of the sample. The "Gutzeit" method and its variants involve treating the water sample with a reducing agent that transforms the arsenic compounds present in the water into arsenic trihydride (arsine gas). This separates the arsenic from the sample. The arsenic trihydride diffuses out of the sample where it is exposed to a paper impregnated with mercuric bromide. The reaction with the paper produces a highly colored compound. The concentration of the arsenic can be approximated using a calibrated color scale. This test method is inexpensive, and minimally trained personnel can readily perform it and read the results in the field. However, sulfur, selenium, and tellurium compounds have the potential of interfering with this assay. Organoarsenic species, such as monomethylarsonate and dimethylarsinate, cannot be directly detected using this assay. Although these compounds are transformed into CH3AsH2 and (CH3)2AsH in the presence of reducing agents like sodium borohydride, it is not clear if these compounds react with the mercuric bromide in the test strip. One of the most dramatic cases of a population at risk from naturally occurring arsenic in groundwater exists in Bangladesh and Eastern India where millions of people are affected. The enormous scale of the arsenic problem in one of the world's largest populations at risk brought full-scale public concern and international aid to find a remedy for the problem. display problems affecting the accuracy and reproducibility of the available field test kits occurred. All of the test kits rely on the Gutzeit method that generates highly toxic arsine gas (Melamed)[26].

Portable X-ray Fluorescence: Portable X-ray fluorescence has recently been accepted as a field technique to measure arsenic in dry solid samples, such as soil and dried sludge. A current draft EPA test method, SW-846 6200, has reportedly performed with an interference free detection limit of 40 mg/kg (40 ppm) in quartz sand. The main interferents listed in this method were variations in particle size, moisture, and lead co-contamination. Environmental samples are irradiated with high-energy photons (x-rays when generated by an electronic device or gamma rays when generated from a radioisotope). For arsenic detection, a sealed Cd109 radioisotope source is used. After the sample is irradiated, the sample atom may absorb the photon, dislodging an electron from the inner shell of the atom. In this process, known as the photoelectric effect, the resulting vacancy is filled by an electron that cascades in from outer electron shells. This rearrangement of electrons results in emission of x-rays characteristic of each atom, termed x-ray fluorescence (XRF). This combination uses a specific energy photon for the photoelectric effect while precisely measuring the energy of the XRF photon emitted by the sample to allow for an accurate identification of the elements in a sample. In field investigations, EPA often requires a fixed laboratory analysis of duplicates to verify the performance of the field technology. Typically,

verification is performed using acid digestion followed by any of the accepted analytical methods, such as GFAA, ICP, or HGAAS. However, caution should be applied when comparing the results from these two techniques. XRF measures the bulk concentration of arsenic in the solid sample, while acid extractions are limited to the arsenic that can be removed from a sample using any of a number of standardized extraction (Dittrich, Tachikawa and Manz)[27].

X-ray Fluorescence (XRF): X-ray fluorescence is a promising technology for detecting arsenic in the field. It is one of the few techniques that can directly measure arsenic in soil without requiring aqueous soil extractions. Improvements continue on the initial application of this field technology. A portable XRF instrument was used for an in situ analysis of arsenic from an arsenic-contaminated abandoned industrial site. The extent of contamination of the abandoned buildings at the site measured down to and compared to laboratory analyses. Isolated building materials, debris, as well as unidentified deposits found at the site were examined for arsenic. This gave a better understanding of the potential reuse of the site as well as the proper disposal of the building debris. XRF instrument was portable, field-ready (i.e., battery-powered for up to 8 hours), and weighed less than 20 pounds. A radioactive Cd source was used to irradiate samples. Each device was able to measure a MDL ~100 mg/kg of arsenic in soil (100 ppm) with an average of □□□□□ drift. Drift is defined as the variation of an instrument to measure a known quantity of arsenic after a period of time, usually corrected by frequent calibration of the instrument. XRF field units have improved the software and thus the signal, calibration, and ability to convert x-ray intensities to concentration. Also, radioactive isotopes are beginning to be replaced with miniature x-ray tubes. This change offers the possibility for greater power and analyses of different wavelengths, as well as increased federal regulatory relief because it eliminates the use of radioactive materials. XRF has shown strong sensitivity and utility for direct measurement of arsenic in other field applications, the potential exists for XRF in combination with a cone penetrometer to measure arsenic under conditions where interference from lead would not be a problem (Melamed)[28].

Anodic Stripping Voltammetry (ASV): Electrochemical assays for the detection of arsenic have demonstrated promise for detecting arsenic in the field. These methods work best for liquid samples, such as groundwater. Solid samples must be digested or extracted before testing. ASV is capable of measuring from 0.1 to 300 µg/L of free (i.e., not adsorbed or bound to any other species in solution) arsenic. Although not designed specifically for field use, commercially available versions of the laboratory equipment for this method may be readily transported and used in the field. Anodic stripping voltammetry provides an alternative analytical technique for measuring dissolved arsenic in drinking water. The ASV method is equally sensitive for As (III) and As (V) and is suitable for measuring low levels of arsenic. This method uses anodic stripping to quantify free dissolved arsenic [as As (III) and/or As (V) ions] at a potential of +145 mV with respect to the saturated calomel electrode from a conditioned gold-plated electrode. The analysis by ASV involves three major steps. First, a glassy carbon electrode (GCE) is prepared by plating a thin film of gold onto the electrode, which is then conditioned. The samples are made acidic and rendered conductive by adding hydrochloric acid. The electrode is placed in the sample solution, and a fraction of the dissolved arsenic is reduced onto the electrode surface. The arsenic removed from solution forms a layer of arsenic on the gold electrode that is subsequently oxidized off. A careful measurement of the amount of electrical current required to remove (or strip) the arsenic oxidatively (an anodic process) gives a quantitative measure of the amount of material that was removed from solution. The arsenic concentration in the sample is determined by comparing the electrochemical response from the sample to external standards. Dissolved antimony and bismuth are positive interferences. Dissolved cooper at concentrations greater than 100 times the arsenic concentration is also an interferent (Turdean)[29].

Electrophoresis Techniques: Capillary electrophoresis is a technique that can only extract and separate ions species from an environmental matrix; it cannot detect or measure the concentration of these species. However, when combined with a sensitive detection technique, it has potential as an analytical technique. Often this technique, which is combined with instruments, such as ICP-MS, is used for arsenic speciation in the laboratory. EPA Methodassays the following inorganic anions: fluoride, bromide, chloride, nitrite, nitrate, ortho-phosphate, and sulfate in aqueous matrices using capillary ion electrophoresis with absorption spectroscopy. In some cases, the anion can be directly measured by its absorbance spectrum; in other cases, indirect detection is required. In indirect absorbance detection, a strongly absorbing species is placed in the buffer. As the anion of interest migrates down the capillary, it displaces the buffer, changing the absorption spectrum for that region of the capillary and allowing the anion to be detected and quantified. An UV-light absorbing electrolyte is placed in a 75 µm diameter fused silica capillary. Voltage is applied through the capillary causing electrolyte and anions to migrate towards the anode and through the

capillary's UV detector window. Anions are separated based upon differential rates of migration in the electrical field directly related to the local ion concentration (H.Tsai)[30]. Capillary electrophoresis has been used to detect arsenic by direct absorbance of the arsenic species with detection limits in the ppm range, which is several orders of magnitude above the required sensitivity levels. However, with indirect UV, detection limits below 1 ppb have been achieved. The technology has been applied successfully to arsenic spiked water samples and soil extracts.

Laser Induced Breakdown Spectroscopy (LIBS) for the Detection of Arsenic: Laser-induced breakdown spectroscopy can determine the elemental composition of aerosols, liquids, gases, and solids qualitatively and quantitatively in real time with a single laser pulse. A high-powered, pulsed laser beam is focused directly into the targeted sample to form a small laser-induced breakdown, called a laser spark. The resulting high-temperature plasma is sufficient to vaporize, atomize, and electronically excite a small amount of the sample matter. The electrons within these atoms gain energy, and subsequently emit light at characteristic wavelengths as the plasma cools and the electrons relax to their original condition (i.e., ground state). This process, which is known as atomic emission, forms the basis of LIBS as an analytical technique. The resulting emissions frequency spectrum is a fingerprint of the elemental composition of the sample but not its speciation. After calibration, the intensity of each peak in the spectrum can be used to quantify elemental concentrations (Jokerst, Emory and Henry)[31].

Microcantilever Sensors: Recently, a new set of environmental sensors has been developed from Atomic Force Microscopy (AFM) technologies, permitting atomic and molecular scale resolution of surfaces. These sensors use the micrometer scale cantilever (microcantilever) or springboard that is fabricated for AFM. These miniature cantilevers are coated with a "detector film" that interacts with the desired species. When the desired species adsorbs onto this film, it causes one of several changes: surface stress, a temperature change, or increased mass. These surface changes all result in the microcantilever deforming (bending). Although this deformation can be measured in several ways, laser reflection is the standard method. These sensors all demonstrated excellent sensitivity, capable of ppb detection limits, and high selectivity. It may be possible to design a coating capable of selectively binding arsenic. Preliminary results from this technology indicate excellent potential for developing a highly specific, highly sensitive arsenic sensor (Manju Phadke)[32].

Surface Enhanced Raman Spectroscopy: Surface Enhanced Raman Spectroscopy (SERS) is a powerful tool for classifying unknown chemicals by their vibrational spectra. A molecule is adsorbed onto a specially prepared metal surface (usuallysilver), and laser light is reflected off the adsorbed molecule. The change in wavelength of the scattered light is dependent on the vibrational spectrum of a target molecule and is an indication of its structure. The Raman spectrum can uniquely "fingerprint" the desired molecular species, and with computer assistance, it can specifically identify and quantify a single chemical species in a large sampling environment (Turdean)[33]. Raman spectroscopy identifies and quantitates the concentration of molecules by carefully measuring the wavelength and intensity of the laser light scattering. Researchers developed a sensor that uses cationic-coated silver particles as substrates to detect perchlorate, chromate, dichromate, and cyanide anions. The coating attracts the anions to the SERS substrate where they are identified and quantified by their characteristic Raman scattering. The investigators were able to detect chromate anions to levels of 60 ppb. If SERS technology demonstrates similar sensitivity and selectivity for detecting arsenic compounds in environmental field studies, it can be developed into a possible field portable detection system (Mary Reynolds)[34].

Challenges and opportunities for microfluids: Microfluidics is an emerging field which focuses on the development of miniaturized, integrated lab-on-a-chip (LOC) devices. In the past 25 years, there has been a surge of interest in the field as researchers miniaturize traditional macro-scale processes to micro-dimensions, and explore new aspects of science previously unseen from a macro-scale vantage point. This technology has been used by studies in a range of applications, from clinical medicine and microbiology, to electronics and the oil industry. In comparison to their macro-scale counterparts, microfluidic processes have the following advantages: faster reaction times and better process-control; reduced waste generation and reagent consumption; system compactness and parallelization; and reduced cost and disposability. The inherent portability of microfluidics, coupled with the successful employment of LOC devices in other fields, readily lends this technology for the development of practical arsenic sensors (Zhong)[35].

Towards Better Arsenic Detection in Water

The Ideal Arsenic Sensor: While extensive research has been invested towards portable arsenic detection, current field techniques lack the robustness and reliability required to accurately declare a water source as being 'safe' or 'unsafe'. To be successfully used for mass

monitoring of water drinkability, an ideal arsenic sensor must meet five essential criteria:

1. The arsenic sensor must be sensitive and selective: Although the provisional MCL in most developing nations is 50 µg/L, it is desirable to have the ability to measure down to the WHO limit of 10 µg/L. It is important to quantitatively measure a range of arsenic concentrations to determine the extent of contamination. Moreover, since arsenic is a trace contaminant of water, most other potentially interfering species would be present in high excess. Therefore, the sensor must be selective to arsenic. Also, it is desirable to be able to differentiate the various species of arsenic, as the form in which it is present dictates its bioavailability and toxicity.
2. The arsenic assay must proceed quickly and yield reproducible results: Millions of tube-wells need to be tested in regions such as Bangladesh; achieving this in practice requires an assay that can be performed in high throughput. Because most wells will be tested only once before being painted green or red, it is imperative that all sensors produce reliable and reproducible results.
3. The arsenic kit must be fully portable and robust enough for field use: Preferably, the entire assay should be physically performed at the source location. Not only will this eliminate the need for complex sample labelling and handling, but more importantly it will increase local awareness about the monitoring process. For reliable use in the field, the sensor and all associated reagents/components must be robust enough to withstand harsh ambient conditions.
4. The arsenic detection process must reduce health and environmental risks: The purpose of arsenic monitoring is to mitigate the development of arsenicosis and arsenic-related cancers within a population. Chemical processes in the analysis should reduce the risks of exposure by technicians and convert arsenic species to less toxic forms. Also, the testing of millions of tube-wells will generate a large volume of chemical waste; the toxicity of these waste-products should be minimized such that they do not further poison the surrounding environment.
5. The arsenic monitoring plan must be affordable and easy to implement for the local population. Current field kits average less than 1 USD per test. This is a good target price for products designed for the developing world. To be affordably implemented, the ideal field sensor should be simple enough to be directly used by the well owners themselves, or local technicians, with only very minimal training (H.Tsai)[36].

The Merits of Microfluidics: The field of microfluidics is characterised by the manipulation of small volumes of fluids, typically on the sub-millilitre scale. Relative to their macro-scale counterparts, microfluidic processes have the advantages of faster reaction times and better process-control; reduced waste generation and reagent consumption; system compactness and parallelization; and reduced cost and disposability (Mary Reynolds)[37]. When compared to traditional analytical techniques, microfluidic processes are known for their general advantages associated with their smaller size. This smaller size is accompanied by many virtues such as portability, enhanced resolution, better process integration, and risk mitigation. Miniaturization allows smaller reaction volumes and diffusion distances, and therefore faster reaction times. In addition, such systems are capable of both high speed and high throughput processes. This quality is quite advantageous, because in many applications, information is of little value unless it can be generated quickly. Miniaturization also reduces costs. Smaller devices have lower material and waste disposal costs. This reduces the environmental footprint of the analysis. Faster reactions also have lower opportunity costs and personnel costs (Pumera, Merkoçi and Alegret)[38]. The potential portability of microfluidics coupled with the successful employment of LOC devices in other fields readily lends this technology for the development of the ideal arsenic sensor. Several groups are currently exploring the use of microfluidics for the detection of arsenic and other heavy metals.

Future Trends: Microfluidic devices are yet to be made highly portable, reliable, sensitive and capable for onsite analysis for heavy metals. The major limitations are the inability to analyze metal speciation and the lack of demonstrated success in real environmental water samples, among others. None of the devices were able to provide speciation information, which is critical for environmental monitoring because the same heavy metal ions with different oxidation status might exhibit distinct toxicity and mobility. Only one approach illustrated the feasibility for the detection of AsV in the presence of both As V and As III. However, the real challenges come from complex compositions of real environmental samples (e.g. sea water, surface water, tap water) that may be high in alkalinity, salinity, turbidity or other metal ions that could cause significant interferences (H.Tsai)[39]. One future trend involving microfluidic devices for heavy metal detection is the integration of nano-materials to improve the sensitivity. Devices will be made either simple for rapid and economic testing, or fully integrated to be robust enough, potentially to replace traditional

analytical instruments or for monitoring water quality remotely and autonomously. In addition, there are other approaches to improve selectivity and sensitivity, such as the use of a masking agent to hide interfering ions, or improving electrode materials (Jokerst, Emory and Henry)[40].

Integration of nano-materials: The use of nano-materials to enhance selectivity, sensitivity, and reproducibility plays a crucial role in the future development of a sensitive heavy metal sensing device. Nano – material based sensors, such as inorganic quantum dots (QDs). plasmonic sensors, and composite sensors (e.g. QD–DNA-GNP) exhibit excellent performance for heavy metal ion sensing. As the detection in those sensors is optical based, they are of high compatibility with optical microfluidic devices that share similar design. Integration of novel nano-materials into a 3D paper-based microfluidic device. In this device, fluorescent carbon nanocrystals (CNCs) were used to provide ECL signals while silica nanoparticles were employed for immobilization of CNCs onto the paper based device to yield a high loading and thus to enhance signal intensity and sensitivity. Besides, the Ruthenium – GNPs (Ru@GNPs) used for the detection of PbII in parallel could be easily incorporated into a nucleotide -based sensor while exhibiting ECL behavior. The combination of the nucleotide -based biosensor with the nano-material provided sensitive recognition of the target metal ions as well as high signal intensity. LODs of 2.1 and 40 ppt for detection of Pb II and Hg II, respectively, were achieved, which are considerably lower than the ppb level of LODs provided by conventional analytical methods (ManjuPhadke)[39].

Application of paper-based device: The development of paper based microfluidic devices is a major breakthrough compared to conventional microfluidic devices for three main reasons: extremely low cost; ease of fabrication patterning by simple cutting and wax printing; and compatible to many bio/chemical assays, including electrochemical, colorimetric, immunoassay and enzyme-based assays. Many researchers have taken advantage of the high compatibility of paper based devices for environmental monitoring, especially for water quality monitoring, Successful integration of an electrochemical sensor onto a paper-baseddevice. In this device, layers of different types of paper were stacked vertically to create a microfluidic channel used for sample loading, and to define the detection zone where electrodes were located Anodic stripping analysis was performed for the detection of PbII and a low LOD was achieved on this device (Chowdury). Besides the aforementioned advantages, there are many other important features of paper-based devices that lead the future trend of simple and accessible microfluidic platforms. One important feature is that operation of paper-based devices does not require external energy for solution transportation or mixing. In addition, several paper layers can be stacked in a certain format to perform assays in 3-dimensional patterns. which enables paper -based devices to be used for more complex assays, such as detection of multiple analytes in parallel. Moreover, coupling a paper-based device with a commercialized reader (e.g. personal glucose meters) provided another approach for rapid and low-cost detection, because the glucose meters are readily available and easy to operate. Yet the one major obstacle of coupling such glucose meters has been the limited number of detectable targets (usually glucose only) (Pumera, Merkoçi and Alegret)[41].

Micro -Total Analysis Systems: A fully integrated system, or so-called micro-total analysis systems (μTASs), is considered to be the ultimate goal for environmental analysis, as well as for other types of analysis such as in medical fields. Such a device may contain several elements to separate and concentrate a target of interest (especially for heavy metal ions in trace levels) so as to achieve high sensitivity. Integration of sample preparation techniques such as solid-phase extraction (SPE) and capillary electrophoresis (CE) can not only improve the sensitivity for trace heavy metal detection but also minimize the impact of interference, as the target is separated from the bulk solution and/or concentrated. A trend of designing μTASs is to combine a microfluidic device with telecommunication technologies to enable the use of such devices in remote areas, and the major benefit, among others, is allowing μTASs to be more accessible to non-experts for sophisticated analysis. The idea of using a mobile phone for imaging of the colorimetric results from paper -based microfluidic device and for transmitting the data wirelessly to the lab where the analysis would be performed. combined cell-phone and satellite communication technologies for performing enzyme-linked immunosorbent assays (ELISA), allowing analysis or monitoring in resource-limited areas with laboratory-level accuracy (Dittrich, Tachikawa and Manz).

CONCLUSION

Arsenic contamination is a very seios problem in the world. Most of the laboratory can detect arsenic levels well below the WHO limit. These are highly expensive and require centralized facility. So these cannot be used for mass monitoring applications. Portable Gutzeit-method based arsenic test strips are also less sensitive, risky and less sensitivity and reliability required for a human-health risk determination. For development of an ideal arsenic sensor as per the global need of arsenic

monitoring, the sensor should have good sensitivity and selectivity, speed and reproducibility, portability and robustness, health and environmental safety, and affordability and ease of use. Many researchers are working on the development of alternate arsenic sensors using colorimetric, electrochemical, biological, electrophoretic, surface sensing, spectroscopic and paper-based methods. Advantages of the integration of microfluidic technology is point-of-care-type device development; increased portability, faster reactions, higher throughput, increased reliability, reduced cost, reduced health and environmental impacts, and easier handling. Future of portable microfluidic arsenic detection is quite bright. Once an integrated LOC is developed for arsenic analysis, all that is required is to click together the necessary auxiliary modules and the ideal portable arsenic sensor.

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