ARSENIC DETECTION USING ZINC OXIDE MODIFIED WITH CURCUMIN

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF

MASTER OF TECHNOLOGY IN VLSI AND MICROELECTRONICS

THESIS SUBMITTED BY
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This is to certify that the thesis entitled "ARSENIC DETECTION USING ZINC OXIDE MODIFIED WITH CURCUMIN" has been carried out by **PRIYADARSHINI CHAKRABORTY (*University Registration No:* 154103** of **2020-2021**) under my guidance and supervision and be accepted in partial fulfillment of the requirement for awarding the degree of "**MASTER OF TECHNOLOGY IN VLSI AND MICROELECTRONICS**". The research results presented in this thesis have not been included in any other paper submitted for the award of any degree to any other Institute or University.

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The foregoing THESIS is hereby approved as a creditable study of an Engineering Subject carried out and presented in a manner of satisfactory to warrant its acceptance as a pre-requisite to the DEGREE for which it has been submitted. It is to be understood that by this approval, the undersigned do not necessarily endorse or approve any statement made, opinion expressed or conclusion drawn therein but approve the THESIS only for the purpose for which it has been submitted.

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DECLARATION OF ORIGINALITY AND COMPLIANCE OF ACADEMIC ETHICS

I hereby declare that this thesis contains literature survey and original research work done by the undersigned candidate, as a part of his degree of "**MASTER OF TECHNOLOGY IN VLSI AND MICROELECTRONICS".** All information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that as required by these rules and conduct, I have fully cited and referenced all materials and results that are not original to this work.

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ACKNOWLEDGEMENT

Firstly I would like to thank my Project mentor Dr Sayan Chatterjee for his constant help and support in designing this project. He has always cleared my doubts whenever necessary and guided me accordingly with invaluable suggestions.

I am also grateful to Professor Chandan Kuumar Ghosh of Nanotechnology Dept for his help and guidance.

I would like to extend my thanks to Mr Ashok Kumar Mondal, without whom this project could never have been a success.

Last but not the least, I'm indebted to all the members of the Nanotechnology laboratory and IC Centre, Jadavpur University for the constant help, support and encouragement.

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ABSTRACT

Arsenic is a highly toxic contaminant present in ground water. It is available in two forms, As(III) and As(V), the former being more toxic as compared to the later. It's toxic properties were well known in the past and it has been used asa poison since ancient times.Today, it is one of the leading causes of groundwater contamination.

In this thesis the major reason of arsenic toxicity has been studied along with its effect on human health, emphasizing on the distribution of contaminated groundwater across West Bengal and India. The methods of determining arsenic dissolved in water in recent times has been studied and summarised, comparing the different technologies used . Then,the thesis has mainly focused on developing a cheap, portable and easy to use technology for detection of arsenic in drinking water. For this purpose the use of simple aqueous phase chemistry method has been used to modify the surface of Zinc oxide using curcumin. When in contact with arsenic, the resultant sample shows strong fluorescence, thereby detecting arsenic. The physics behind the phenomenon has been studied in detail and an experiment has been performed to verify the results.

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CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

With the advancement of science and technology the world today has entered a new domain of nanotechnology today wherein hybrid substances are formed in order to enhance some typical characteristics of a particular compound and thereby use it for a specific purpose.This in turn imparts novel characteristics and functions to these substances.Arsenic, a metalloid,is often found dissolved in groundwater. It is highly poisonous and results in several severe health issues as discussed subsequently.

Toxicity of arsenic was known as early as 370 BCE. Hippocrates, then described it as abdominal colic in a miner of metals.Theophrastus of Erebus in the fourth century BCE and by Pliny the Elder in the first century BCE were also of the same opinion. Pedanius Dioscorides who authored the famous historical pharmacopeia *De Materia Medica* and a Greek physician pr the court of the infamous Roman Emperor Nero, described arsenic as a poison.[1]

Many people in rural areas directly drink water from ponds or wells without passing it through proper treatment channels. If this water has arsenic content then it proves to be fatal . Therefore it is the need of the hour to develop a proper arsenic detection technology that is low cost and can be readily made available to everyone.Here an attempt has been made to incorporate the functionalities of organic systems onto the surface of metal oxide nanoparticles.Likewise, here we have added curcumin to zinc oxide and used it to detect arsenic in drinking water.

1.2 THE HISTORY OF ARSENIC CONTAMINATION

Throughout history, humankind has encountered various environmental challenges that have left an indelible mark on societies. One such hidden menace is arsenic contamination, an insidious poison that has plagued civilizations for centuries. Arsenic, a naturally occurring element, possesses a dual nature. It has been lauded for its medicinal properties while simultaneously serving as a deadly toxin.

The Ancient Origins:

The history of arsenic contamination can be traced back to antiquity. Ancient civilizations, such as the Egyptians and Greeks, recognized arsenic's therapeutic potential in treating ailments like skin disorders and ulcers. However, they were oblivious to its hazardous effects when present in higher concentrations. The Egyptians' use of arsenic-based compounds in cosmetics, combined with their proximity to arsenic-rich geological formations, inadvertently exposed their population to chronic poisoning.[2]

The Toxic Renaissance:

The toxic Renaissance in Europe during the 15th and 16th centuries witnessed a surge in the use of arsenic compounds. [3]It became a popular choice for murderers and poisoners due to its tastelessness, odorlessness, and potent toxicity. Infamous historical figures like Lucrezia Borgia and Madame de Brinvilliers used arsenic to eliminate their victims discreetly. As the demand for arsenic increased, so did its production and distribution, inadvertently contributing to environmental contamination and subsequent health crises.[4][5]

Industrial Revolution and Beyond:

The advent of the Industrial Revolution in the 18th century saw a significant upsurge in arsenic contamination. Arsenic was employed extensively in industries such as glass manufacturing, dye production, and the preservation of wood and textiles. Factory workers, artisans, and communities residing near these industrial hotspots faced severe health risks due to occupational exposure and contamination of air, water, and soil. Tragically, arsenic-related ailments like skin lesions, respiratory problems, and cancers went unnoticed for years, perpetuating the cycle of suffering.[6]

The Tragedy of Arsenic in Water:

Perhaps the most notorious manifestation of arsenic contamination in modern history is the contamination of drinking water. In the late 20th century, it was discovered that vast regions across the world, including Bangladesh[7], West Bengal in India, and parts of Southeast Asia, [8]suffered from naturally occurring arsenic in groundwater. Unbeknownst to millions, their primary source of sustenance had become a silent killer. Chronic exposure to arsenic-laden water led to a multitude of health problems, including skin lesions, cancer, cardiovascular diseases, and developmental issues in children.[9]

Environmental Impact and Remediation Efforts:

Beyond its impact on human health, arsenic contamination also poses a significant threat to the environment. Industrial activities, mining operations, and agricultural practices have contaminated soil and water bodies, disrupting ecosystems and endangering flora and fauna. Recognizing the urgency of the issue, governments, scientific institutions, and NGOs have

undertaken various initiatives to mitigate arsenic contamination. These efforts include the development of arsenic removal technologies, public health interventions, and regulatory measures to limit exposure.

The history of arsenic contamination is a sobering reminder of the unforeseen consequences that can arise from humanity's interaction with the environment. From ancient civilizations' fascination with its medicinal properties to the Industrial Revolution's industrial abuse, arsenic's dual nature has exacted a heavy toll on human health and the planet. As we move forward, it is crucial to learn from history, strengthen regulations, promote sustainable practices, and prioritize the well-being of both present and future generations. Only through concerted efforts can we ensure that the unseen poison of arsenic contamination becomes a relic of the past

1.3 THE ARSENIC PROBLEM TODAY:

Arsenic, a metalloid with an atomic number of 33, exists in various oxidation states, mainly +3 or +5, known as arsenate (As III) and arsenite (As V), respectively. The toxicity of arsenic depends on its oxidation state, with As III being more toxic than As V. This is because As III can bind to thiol groups on proteins and enzymes and is excreted from the body at a slower rate. The World Health Organization recognizes the extreme toxicity of inorganic arsenic to humans, setting a maximum limit of 10 parts per billion (ppb) in water, and it also poses significant harm to marine life.

The primary reservoir of arsenic on Earth is the lithosphere, specifically the crust, which contains over two hundred types of minerals containing arsenic, including various sulfides. Arsenopyrite (FeAsS) and tennantite are examples of arsenic-containing minerals found in ore deposits. Additionally, sedimentary rocks such as coal and shale can have high concentrations of arsenic. Volcanic emissions play a role in transporting arsenic from the lithosphere to the atmosphere.

Soil is the second-largest global reservoir of arsenic. Under toxic conditions, arsenic exists in soils as arsenate (As III), which can bind to Fe(III) hydroxides. The speciation of arsenic in soil depends on factors such as soil pH. Acidic soils typically contain arsenate bound to aluminum and iron, while basic soils contain arsenate bound to calcium. The residence time of arsenic in soils varies depending on climate, ranging from 1,000 to 3,000 years in moderate climates.

Freshwater and groundwater generally contain less than 1 ppb of arsenic. The concentration of arsenic is pH-dependent, with acidic conditions mobilizing arsenic at pH levels below 5. Toxic seawater typically contains arsenate (As III) as arsenate, with an average concentration of 1.7 ppb.

Arsenic is naturally present in the biosphere, with the highest concentrations found in plant roots. Terrestrial plants can contain up to 200 parts per million (ppm) of arsenic. Water-dwelling

organisms like Annelida and Echinodermata have approximately 6-8 ppm of arsenic. Traces of arsenic are also found in the human body, with the highest concentrations found in the kidneys and liver, reaching up to approximately 1.5 ppm.

Human beings use arsenic in pesticides, wood preservatives, metal treatment, paint, and coal-based power plants. Anthropogenic residues and discharges from coal-based power plants, mining, and smelting can contaminate rivers, lakes, streams and soil. Anthropogenic As emissions originate mostly from steel and glass production, and forest and by grassland burning. In the atmosphere, As is mainly present in particulates such as dust, with a residence time of 7 to 10 days. [10]

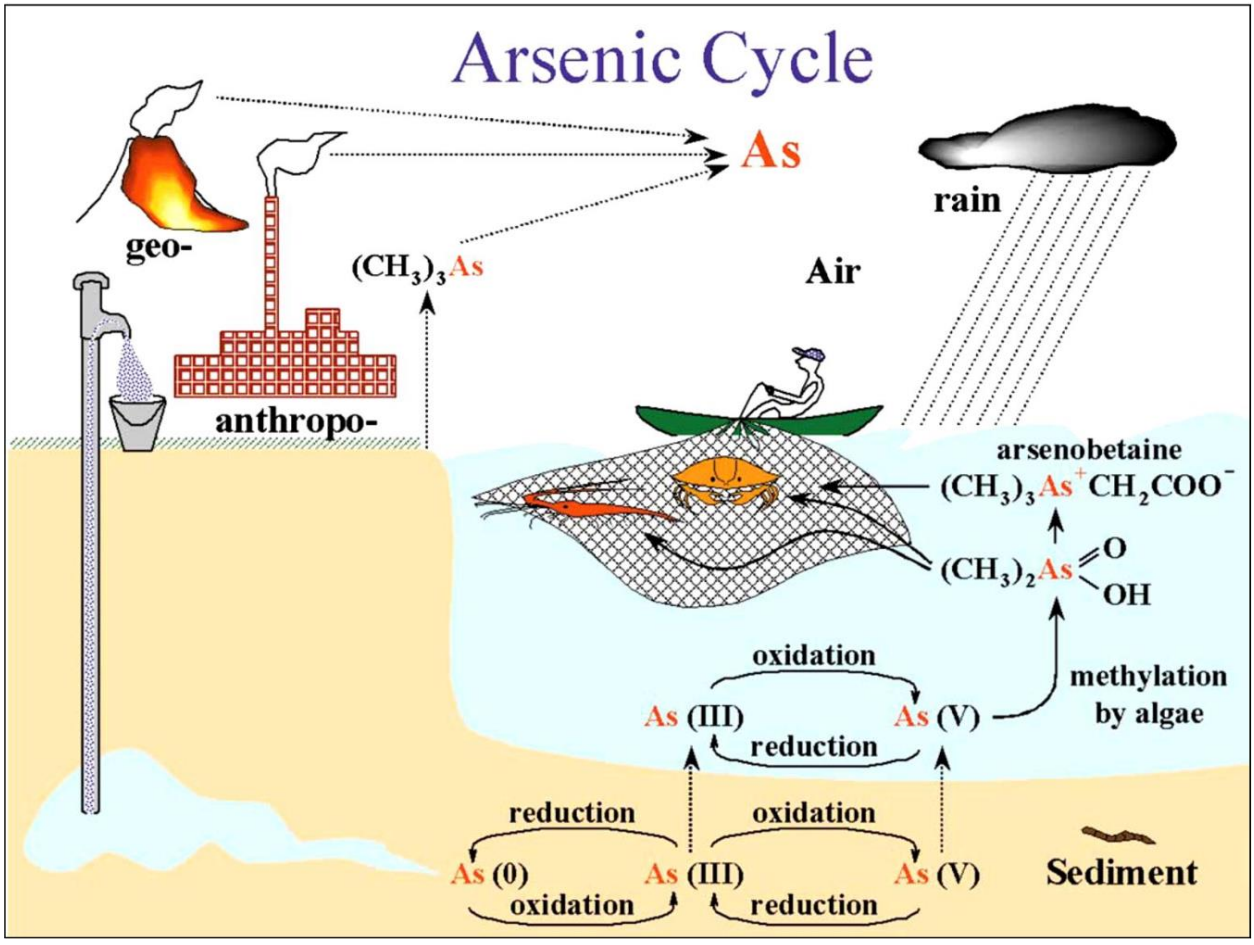


Fig 1.1: The arsenic cycle in nature [71]

Arsenic contamination in water often involves the presence of arsenous acid, arsenic acid, or their derivatives. These compounds are soluble forms of arsenic that can be found at close to neutral pH levels. They are typically extracted from the surrounding rocks near the aquifer.

Arsenic acid, for instance, tends to exist as ions such as [HAsO4]2− and [H2AsO4]− in neutral water, while arsenous acid remains non-ionized

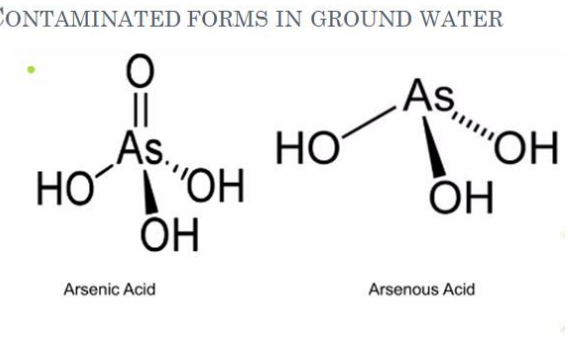


Fig 1.2: Arsenic forms in ground water[92]

Access to clean and safe drinking water is a significant challenge for more than 2.5 billion people worldwide who rely on groundwater as their primary source of water . This has become a major concern for human civilization. The presence of high concentrations of heavy metals, such as arsenic (As), in drinking water poses a potential threat to human health and raises significant health concerns

According to the World Health Organization (WHO), the recommended limit for arsenic in drinking water is 0.01 mg/l or 10 ppb [3]. The absolute lethal dose of arsenic for adults is estimated to be between 70 mg and 200 mg or 1 mg/kg/day.[11]

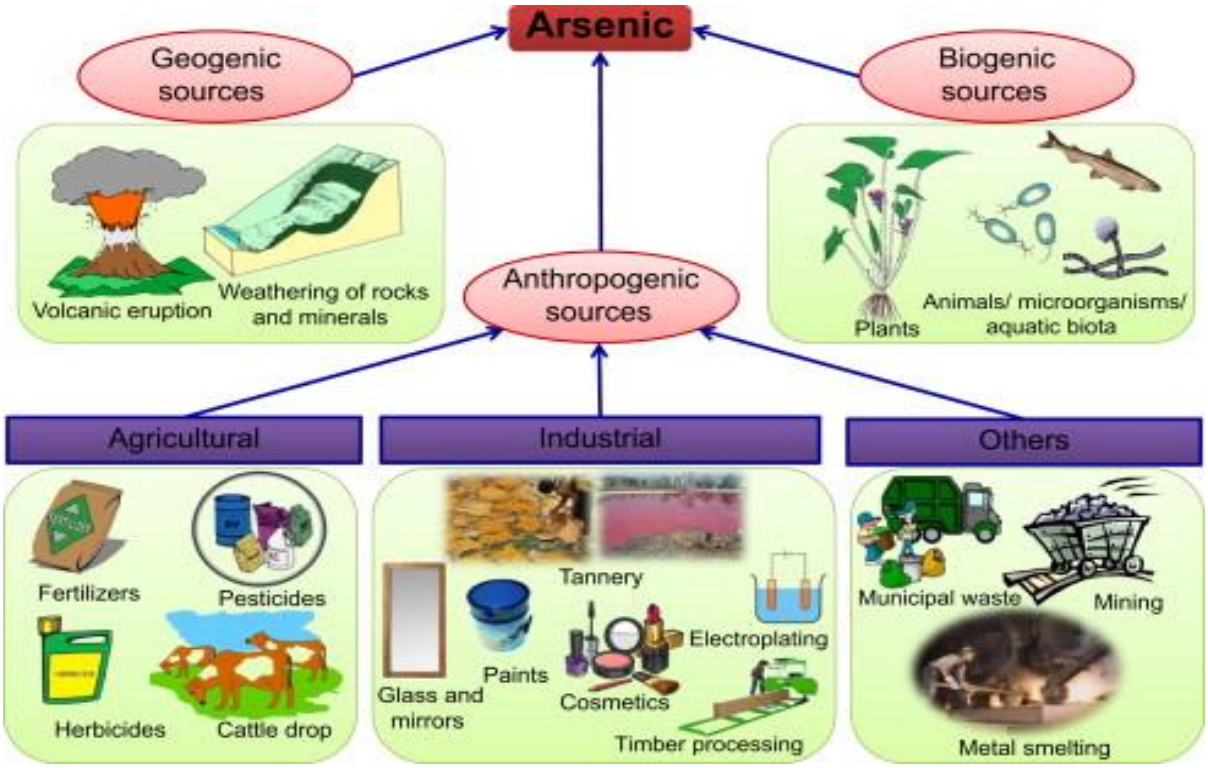


Fig 1.3: Sources of arsenic in groundwater [72]

In the past decade, there has been an increase in reports of newly affected regions and a significant rise in global arsenic contamination. Currently, it is estimated that around 108 countries worldwide have experienced groundwater contamination with arsenic concentrations exceeding the maximum permissible limit of 10 ppb. The highest number of affected countries are located in Asia (32) and Europe (31), followed by Africa (20), North America (11), South America (9), and Australia (4). Approximately 230 million people worldwide are at risk of arsenic poisoning, with 180 million in Asia alone. The most severely affected countries include Bangladesh, India, Pakistan, China, Nepal, Vietnam, Burma, Thailand, and Cambodia. In India, arsenic contamination has been reported in 20 states and 4 Union Territories.[12]

Studies evaluating the correlation between arsenic poisoning and aquifer type have shown that unconsolidated sedimentary aquifers, particularly those located within younger orogenic belts, are the most affected. Geogenic sources account for over 90% of arsenic pollution, with alluvial sediments being a primary source of groundwater contamination. The contamination is closely linked to plate tectonic processes, mountain building, erosion, and sedimentation. Prolonged consumption of arsenic-contaminated groundwater leads to severe health hazards such as skin diseases, lung and kidney cancer, bladder cancer, coronary heart disease, bronchiectasis, hyperkeratosis, and arsenicosis.

Due to the geogenic origin of arsenic in groundwater, the extent of pollution is complexly linked to the geometry and properties of the aquifer in a region. Remedial measures need to be designed based on the source minerals, climatological factors, and hydrogeological conditions specific to the region. The most concerning aspect is that the majority of the affected population in Asian countries belongs to the poor rural class, who often lack awareness about arsenic poisoning and appropriate treatment protocols [13]

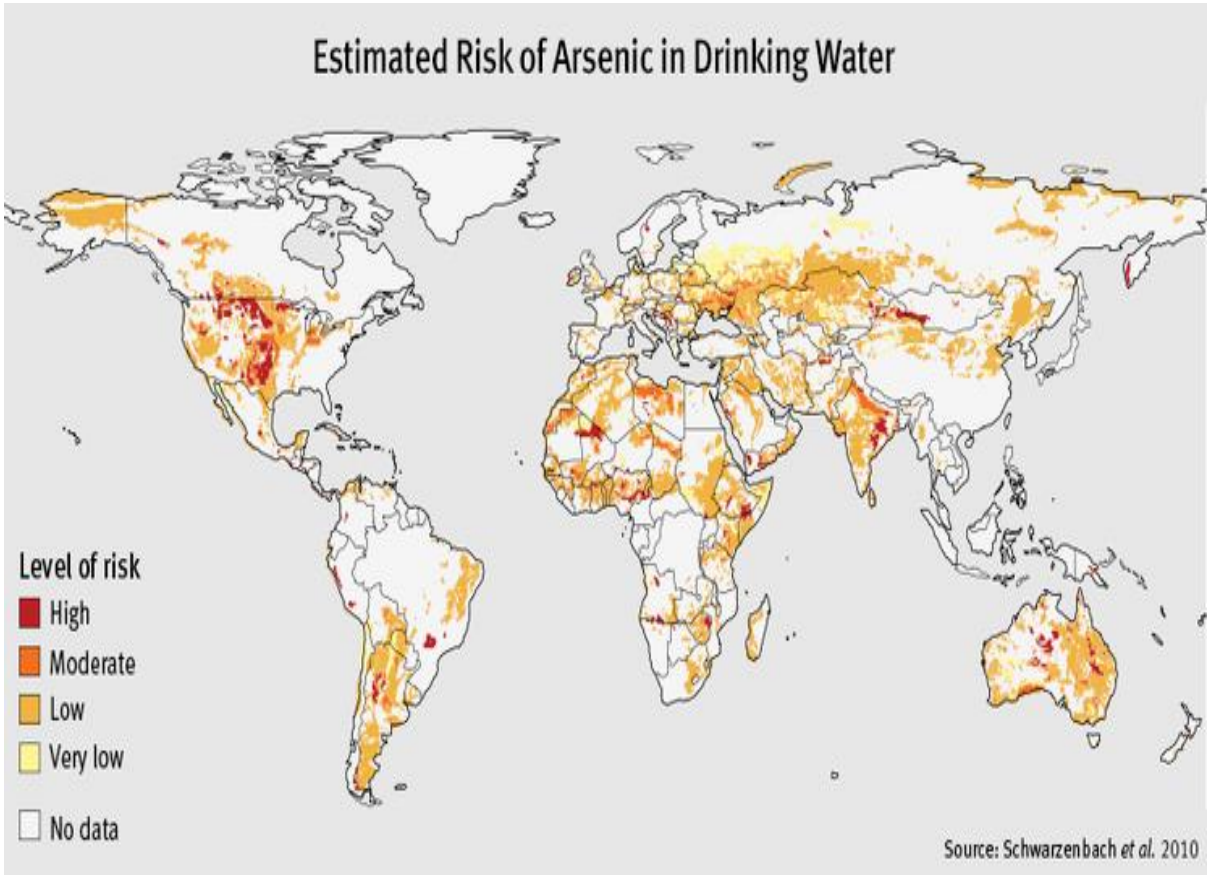


Fig 1.4: Arsenic risk areawise across the world [73]

A prolonged and chronic exposure to arsenic in humans through various sources such as drinking water, medications, occupational hazards, and environmental factors can affect multiple organ systems in the body. This exposure can result in various manifestations and diseases. Here are the different effects of chronic arsenic toxicity on the human body:

Skin and Systemic Manifestations:

Chronic arsenic toxicity can cause specific skin diseases such as pigmentation and keratosis. These conditions were observed in a population-based survey conducted in West Bengal, where individuals exposed to arsenic toxicity showed a higher prevalence of keratosis and pigmentation. The survey indicated that males exposed to arsenic through drinking water had two to three times more toxicity in terms of keratosis and pigmentation compared to females. Additionally, chronic arsenic toxicity can also produce systemic manifestations along with skin lesions.

Respiratory Disease:

Prolonged exposure to arsenic-contaminated drinking water can lead to non-malignant lung diseases. Individuals exposed to arsenic were found to have a higher incidence of chronic cough and chronic lung diseases compared to those who were unexposed.[14]

Gastrointestinal Disease:

Chronic arsenic toxicity can cause gastrointestinal issues such as dyspepsia (indigestion) and gastroenteritis. Dyspepsia is a common syndrome associated with chronic arsenic toxicity, while gastroenteritis can occur if the arsenic concentration in drinking water exceeds 50 mg/L.[15]

Diseases of the Nervous System:

Peripheral neuropathy, characterized by conditions like paresthesia (tingling, numbness), limb weakness, and others, can result from chronic exposure to arsenic through drinking water. In West Bengal, peripheral neuritis and other neural complications, including sleep disturbances, weakness, cognitive and memory impairment, have been reported in patients with chronic arsenic toxicity. Cerebrovascular diseases were also found to be more prevalent in individuals affected by chronic arsenic toxicity.[16]

Cardiovascular Disease:

Chronic arsenic toxicity can lead to peripheral vascular diseases such as Blackfoot disease (BFD), Raynaud's syndrome, and acrocyanosis. The prevalence of BFD was reported to be around 8.9% among individuals affected by arsenic. Arsenic contamination has also been associated with an increase in the prevalence of hypertension.[17]

Hematological Effects:

Both acute and chronic arsenic poisoning can result in hematological abnormalities, including anemia, leucopenia, and thrombocytopenia. In West Bengal, a significant percentage of anemia cases (around 50%) were attributed to exposure to arsenic-contaminated groundwater.[18]

Diabetes:

Cumulative arsenic exposure has been linked to an increased prevalence of diabetes mellitus in areas with arsenic-contaminated drinking water. However, no reports of diabetes mellitus caused by arsenic were found in areas of West Bengal. [19]

Arsenicosis and Cancer:

Exposure to arsenic, primarily through drinking water, can lead to severe carcinogenic effects. The most commonly affected areas include the skin, urinary bladder, and lungs. Skin cancer and internal cancers were detected in villages with arsenic-contaminated areas in West Bengal.[20]

Genotoxic Effects:

Prolonged exposure to arsenic through drinking water can result in genotoxic effects, including an increased rate of chromosomal aberrations and micronuclei formation in buccal and urothelial cells. In West Bengal, the frequencies of micronuclei formation were significantly higher in exposed individuals compared to unexposed individuals, particularly in peripheral lymphocytes, oral mucosa, and urothelial cells.[21]

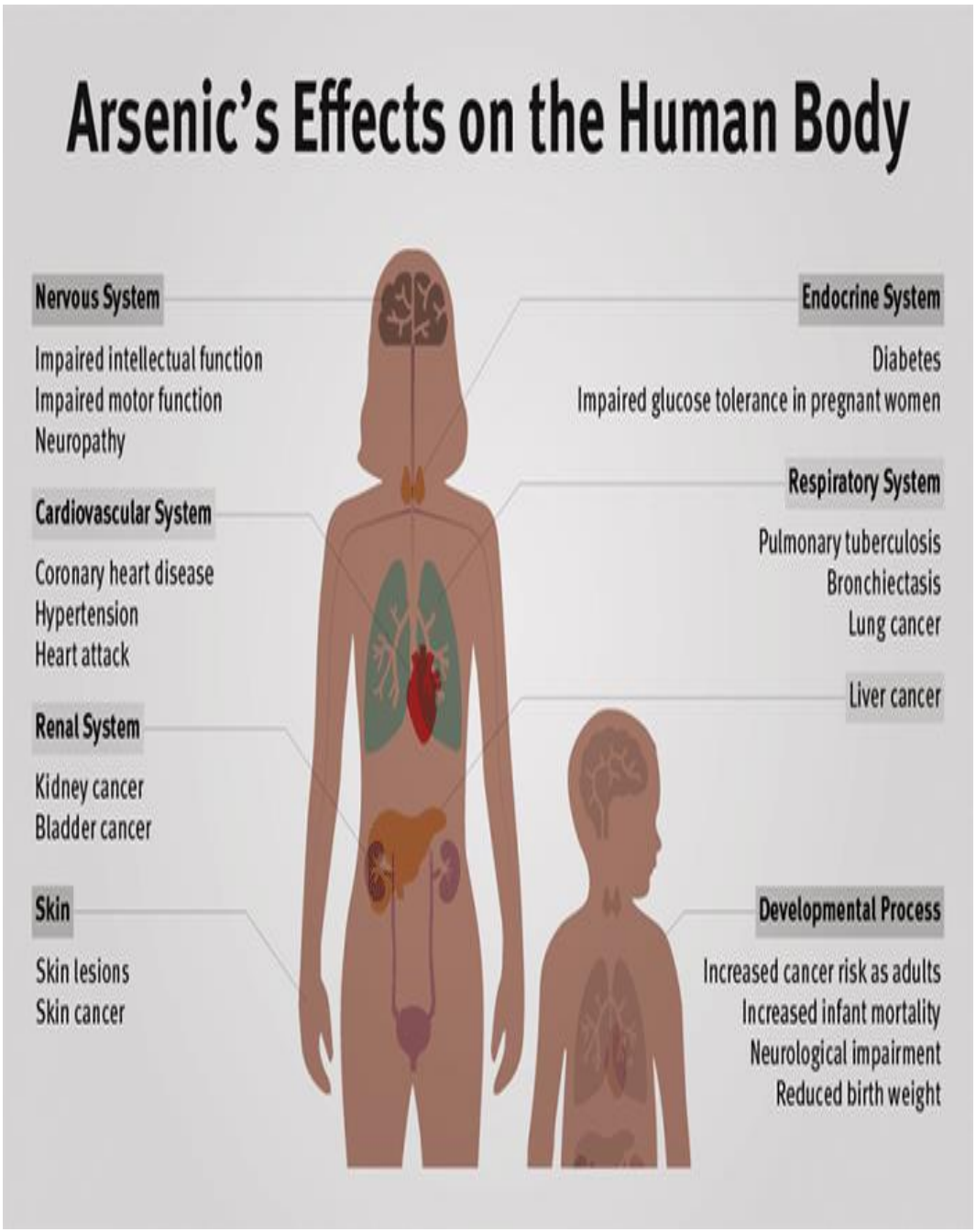


Fig 1.5: Arsenic's effect on human body[93]

The first instance of arsenic contamination in groundwater was documented in West Bengal, India, in 1978. This issue affected 79 blocks across eight districts, out of a total of 26 districts in the region, where the concentration of arsenic in groundwater exceeded 50µg/L. The districts that experienced the most severe contamination were Murshidabad, Maldah, Nadia, North and South 24 Parganas, Burdwan, Howrah, and Hooghly. Many of these districts contained multiple blocks with arsenic contamination ranging from 50% to 100%.[22]

Arsenic contamination poses a significant threat to public health globally. The affected regions face challenges in providing safe drinking water to their populations. Efforts to mitigate and remediate arsenic contamination require a combination of technological advancements, policy changes, and community involvement. Continued research, monitoring, and awareness are crucial to address this complex issue and safeguard the health and well-being of communities around the world.

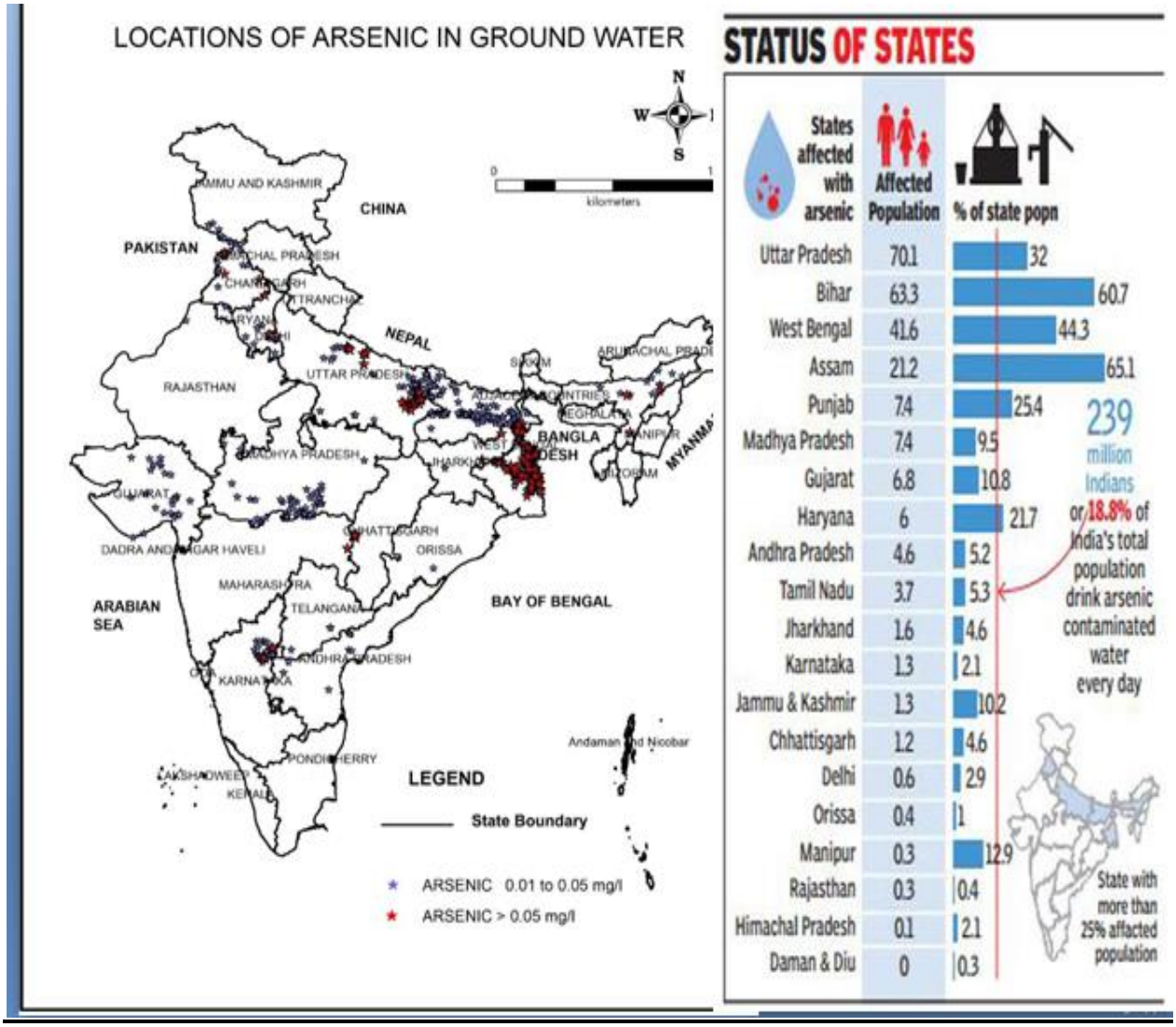


Fig 1.6: A representation of position of West Bengal among arsenic affected states[74]

1.4OBJECTIVE:

The aim of the project is to design a sensor that can efficiently detect arsenic in drinking water and is readily available to common man as a complete product.

CHAPTER 2

LITERATURE SURVEY

2.1 OVERVIEW

Arsenic contamination in water sources poses a significant threat to human health, making its detection and monitoring a matter of utmost importance. Over the past two decades, extensive research has been conducted to develop reliable and efficient methods for arsenic detection. This literature survey aims to provide an overview of the advancements in arsenic detection methods, highlighting the key developments and trends in the field.

In ancient days the following methods were used for arsenic detection:

- Garlic Odor: One of the earliest known methods of detecting arsenic involved the use of garlic. It was observed that when arsenic compounds were heated, they produced a garlic-like odor. This observation was made as early as the 4th century BCE by the Greek philosopher Theophrastus. While this method could indicate the presence of arsenic, it lacked specificity and could not quantify the amount of arsenic present.[81]
- Flypaper Test: In the 19th century, a simple test known as the flypaper test was developed for the detection of arsenic in food and drink. This method involved suspending flypaper strips over the food or drink suspected to be contaminated with arsenic. If arsenic was present, the flypaper would turn yellow or brown due to the reaction between arsenic and the sulfur present in the paper. Although this method was simple and inexpensive, it was not very sensitive and could not accurately quantify arsenic levels.
- Marsh Test: The Marsh test, developed by the British chemist James Marsh in 1836, was a significant advancement in arsenic detection during that time. This test involved generating arsine gas (AsH3) by reacting the sample containing arsenic with zinc and sulfuric acid. The gas was then ignited, and if arsenic was present, it would form a deposit of arsenic on a cold surface. This test allowed for the qualitative detection of arsenic, but it still did not provide precise quantification.[82]

It is important to note that these ancient methods were limited in their accuracy, sensitivity, and specificity compared to modern detection techniques. Over time, advancements in scientific understanding and technology have led to more sophisticated and reliable methods for arsenic detection, as mentioned in the previous response.

The conventional arsenic detection methods include colorimetric assays[83], atomic absorption spectrometry (AAS), and inductively coupled plasma mass spectrometry (ICP-MS)[84].

However the novel techniques and emerging technologies that offer improved sensitivity, selectivity, and ease of use. Some of the notable methods to be covered include:

- Electrochemical Sensors[: Discussing the development of electrochemical sensors based on various transducers, such as screen-printed electrodes, nanomaterial-modified electrodes, and field-effect transistors.[85]
- Optical Techniques: Highlighting the use of spectroscopic methods, such as surface-enhanced Raman spectroscopy (SERS), fluorescence spectroscopy, and colorimetric sensors based on gold nanoparticles.[86]
- Biosensors: Exploring the integration of biological components, such as enzymes, antibodies[87], and DNA probes[88], for selective and sensitive arsenic detection.
- Nanomaterial-Based Sensors: Discussing the utilization of nanomaterials, such as graphene, carbon nanotubes, metal-organic frameworks (MOFs), and quantum dots[89], in developing highly efficient arsenic sensors.
- Microfluidic Systems: Describing the advancements in microfluidic-based platforms for arsenic detection, including lab-on-a-chip devices and paper-based sensors.

The efforts made so far has been discussed in details in the following chapter.

2.2 RECENTLY PUBLISHED WORKS ON ARSENIC DETECTION METHODS:

In 2006 [23]JayrajBehari et.al presented a method for accurately quantifying the total arsenic content in water samples . The technique involved utilizing a vapor generation assembly (VGA) in conjunction with an atomic absorption spectroscopy (AAS) system.The vapor generation assembly, a crucial component of the setup, was attached to the AAS system. It comprised two distinct channels: an acid channel and a reduction channel. The acid channel was filled with a highly concentrated hydrochloric acid (HCl) solution, specifically 10 M HCl. On the other hand, the reduction channel was filled with sodium borohydride (NaBH4).The purpose of the acid channel was twofold. Firstly, it served to acidify the water sample being analyzed. This acidification process facilitated the release of arsenic in the form of arsine gas (AsH3). The liberated arsine gas then passed through the vapor generation assembly for subsequent analysis. Secondly, the acid channel prevented any interference from other elements that might be present in the water sample, thereby enhancing the specificity of the arsenic analysis.The reduction channel, filled with sodium borohydride, played a crucial role in the vapor generation assembly. It facilitated the conversion of the arsine gas generated in the acid channel into a more stable and detectable form. Sodium borohydride acted as a reducing agent, transforming the arsine gas into

compounds like arsine-methanol or arsine-hydride complexes. These complexes were amenable to analysis using atomic absorption spectroscopy.By utilizing the vapor generation assembly attached to the AAS system, Behari and Prakash aimed to provide a reliable and sensitive method for determining the total arsenic content in water samples. The paper likely detailed the experimental procedure, including sample preparation, calibration techniques, and the analysis of both standard reference materials and real water samples. The authors may have also discussed the validation of the method, its limitations, and potential applications.

In 2007 J. Michon[24] employed the Graphite Furnace Atomic Absorption Spectrometry (GFAAS) technique to detect arsenic in drinking water samples. This method offered several advantages, including its rapidity and a low limit of detection.The GFAAS technique involves using a graphite furnace as the atomizer in the atomic absorption spectrometer. This furnace allows for the precise control of temperature, enabling the analysis of trace elements such as arsenic.[25] By optimizing the GFAAS method, the researchers aimed to achieve accurate and sensitive determination of total inorganic arsenic in drinking water.The paper likely detailed the optimization steps undertaken to enhance the method's performance. These optimizations could include the selection of appropriate analytical parameters such as the heating program, atomization temperature, and the use of chemical modifiers. By fine-tuning these parameters, the researchers sought to improve the sensitivity, precision, and accuracy of arsenic detection.The researchers reported a limit of detection of approximately 0.26 μg As l^{-1} for a sample volume of 16 μl, corresponding to 4.2 pg As. This low limit of detection indicated the method's sensitivity in identifying even trace amounts of arsenic in drinking water.The paper may have also discussed the validation of the method by analyzing real drinking water samples and comparing the results with other established techniques. Additionally, the researchers might have addressed the applicability and limitations of the optimized GFAAS method for total inorganic arsenic determination.

In 2007 Ademola Idewu et al [26] employed the gas-phase chemiluminescence method to detect and separate organic and inorganic arsenic species. The study focused on utilizing liquid chromatography in combination with gas-phase chemiluminescence detection for arsenic speciation analysis.The gas-phase chemiluminescence method utilized in the study allowed for sensitive detection of arsenic species. The liquid chromatography technique facilitated the separation of different arsenic species based on their chemical properties, allowing for accurate quantification and identification.To further enhance the analysis, the separated arsenic species were subjected to a UV photo-oxidation reactor. This reactor played a crucial role in decomposing the species by converting them into arsenate (As(V)). Arsenate is a commonly studied and well-characterized form of arsenic, making it suitable for subsequent analysis and quantification.The paper likely discussed the experimental setup and conditions used for liquid chromatographic arsenic speciation. This may have included details about the chromatographic column, mobile phase composition, gradient elution, and detection parameters specific to the gas-phase chemiluminescence technique.The results obtained from the analysis of arsenic

species, both organic and inorganic, were likely presented, demonstrating the capability of the method to distinguish between different forms of arsenic. The researchers may have also compared their findings with other established techniques or validated their method using reference standards or real samples.

In 2009 Silvia Sanllorente-Méndez[27] investigated the application of platinum-modified screen-printed carbon electrodes for the electrochemical detection of arsenic. The researchers aimed to develop a reliable and sensitive method for the determination of arsenic(III).The study focused on modifying the surface of screen-printed carbon electrodes with platinum nanoparticles. The modified electrodes were characterized using scanning electron microscopy (SEM) to examine the morphology and structure of the electrode surfaces after modification.The researchers found that the platinum-modified electrodes exhibited good precision and accuracy for the electrochemical detection of arsenic(III). Importantly, no interference from copper(II) was observed during the determination, even in the presence of copper(II) ions.However, it was noted that the electroinactive form of arsenic, arsenic(V), needed to be reduced to arsenic(III) prior to determination. This reduction step was achieved by treating the sample with sodium thiosulfate, which converted arsenic(V) to arsenic(III) for subsequent electrochemical detection.The detection limit for arsenic(III) using the platinum nanoparticle-modified screen-printed carbon electrodes was determined to be approximately 5.68 μg L^{-1}. This low detection limit demonstrated the sensitivity of the method in quantifying arsenic(III) in samples.The researchers also evaluated the accuracy of the method by analyzing both real samples and spiked tap water samples. The results likely indicated that the developed method provided accurate determination of arsenic(III) concentrations.

In E. Diesel et al[28] proposed a method for detecting arsenic in groundwater, both in field settings and laboratory environments. The approach involved utilizing bacteria-based bioassays, which relied on genetically modified strains of Escherichia coli, Bacillus subtilis, Staphylococcus aureus, and Rhodopseudomonas palustris as biosensor-reporter strains.The biosensor-reporter strains of bacteria were designed to respond to the presence of arsenic in the water samples. When exposed to arsenic, these genetically modified bacteria produced a specific reporter protein. The amount or activity of this reporter protein could be measured within the bioassay, providing a quantitative indication of the arsenic concentration in the tested water samples.The proposed method allowed for the detection of arsenic in both field and laboratory settings. It offered a potentially rapid and sensitive approach to assess the presence of arsenic in natural waters, such as groundwater. By utilizing different genetically modified bacterial strains, the researchers aimed to enhance the specificity and versatility of the bioassay for arsenic detection.The paper likely provided details on the development and optimization of the bacteria-based bioassays. This might have included information on the genetic modification of the bacterial strains, selection of suitable reporter proteins, and the experimental conditions for conducting the bioassays.The efficacy of the proposed method was likely evaluated through validation experiments using water samples with known arsenic concentrations. The sensitivity,

accuracy, and reliability of the bioassay results would have been assessed and compared to established techniques for arsenic detection..

In 2010 Haydon Baros[29] utilized total deflection X-ray fluorescence (TXRF) methods for the determination of arsenic in water samples. However, in order to implement this method, a prior separation and pre-concentration procedure was necessary.The researchers employed an alumina-based separation and pre-concentration technique. The water samples containing arsenic were subjected to this procedure, which involved the use of alumina as an adsorbent material. The arsenic species were adsorbed onto the alumina, facilitating their concentration and separation from the sample matrix.Quantification of arsenic was performed using the Al-Kα and Co-Kα lines as internal standards. The prepared samples, containing the adsorbed arsenic species on the alumina matrix, were compared to a calibration curve constructed using aqueous standards. During the analysis, parameters such as temperature, pH, and time were controlled to ensure accurate quantification.After the quantification step, the alumina was separated from the sample matrix using centrifugation. The separated alumina was then washed with de-ionized water to remove any impurities or interfering substances. Subsequently, the cleaned alumina was directly analyzed using total reflection X-ray fluorescence on a sample holder.The pre-concentration factor achieved with the alumina-based method was approximately 100, indicating a substantial enrichment of the arsenic species. The detection limit of the method was determined to be 0.7 μg/L, indicating its sensitivity in detecting low levels of arsenic in water samples.
The percentage of recovery for arsenic(III) was found to be 98%, while for arsenic(V) it was determined to be 95%. These values indicate the efficiency of the separation and pre-concentration procedure in retaining and quantifying the arsenic species accurately.

In 2014 X. Savarinithu et al. [30]focused on the implementation of electrochemical sensors for the rapid and on-site detection of arsenic in drinking water in arsenic-contaminated areas of West Bengal, India. The electrochemical sensor they developed utilized a three-electrode system consisting of carbon, silver, and silver/silver-chloride electrodes, which were integrated with a handheld electrochemical analyzer. This design offered advantages such as enhanced portability and minimized instrumentation requirements.Two different types of electrochemical analyzers were used in conjunction with the sensor: a bench-top CHI730D electrochemical analyzer for laboratory testing and a portable CheapStat electrochemical analyzer for field testing. The electrochemical detection methods employed were cyclic voltammetry (CV) and anodic stripping voltammetry (ASV).For cyclic voltammetry, current values were measured within a potential range of -0.5 to 0.6 V, a scan rate of 100 mV/s, and a sample interval of 1 mV. Anodic stripping voltammetry involved fixing the potential at -0.5 V for one minute, followed by a potential sweep from -0.5 to 0.6 V at a scan rate of 100 mV/s and a sample interval of 1 mV. As a control, a scan was conducted using 0.1 M HNO3. Then, an arsenic-contaminated sample in 0.1 M HNO3 was deposited over the sample zone, and CV/ASV scans were obtained to detect the

presence of arsenic.To validate the sensing mechanism quantitatively, anodic stripping voltammetry was performed using the three-electrode system and the bench-top electrochemical analyzer. The carbon counter electrode (CHI 104), silver working electrode (CHI 103), and silver/silver-chloride reference electrode (CHI 111) were used for arsenic detection. In the absence of arsenic, no significant current peak was observed near the stripping potential. However, when the sample was spiked with increasing amounts of arsenic and ASV measurements were carried out, noticeable changes in the current response were observed. Each spike contained approximately 100 µg of arsenic, and the presence of 100 µg of arsenic resulted in a robust observation of 2.2 µA in the signal. As the researchers increased the arsenic concentration through serial additions, increasing currents were observed.

In theyear 2014, Rong He et al in their paper "Facile synthesis of pentacle gold–copper alloy nanocrystals and their plasmonic and catalytic properties"studied the catalytic properties of gold-copper alloy nanocrystals and tried to analyse how it can be subsequently used for arsenic detection.[31]

In 2014 B. Liu[32] presented a method using magnetic beads to adsorb fluorescently-labeled oligonucleotides through the phosphate backbone, resulting in fluorescence quenching. However, in the presence of arsenate, the adsorbed oligonucleotides were displaced due to the higher affinity of arsenate, leading to increased fluorescence. This approach served as a biosensor for the detection of arsenate in samples.The magnetic beads used in this study had the ability to selectively adsorb the fluorescently-labeled oligonucleotides via interactions with the phosphate backbone. This adsorption process resulted in the quenching of the fluorescence emitted by the oligonucleotides. However, when arsenate was present in the sample, it exhibited a higher affinity for the magnetic beads compared to the oligonucleotides. As a result, the arsenate displaced the oligonucleotides from the surface of the magnetic beads, leading to the recovery of fluorescence signal.By measuring the fluorescence intensity before and after the introduction of the arsenate-containing sample, the researchers were able to determine the presence and concentration of arsenate. The biosensor demonstrated a low limit of detection, reaching as low as 300 nM for arsenate.

In 2015 P Devi et al [33] demonstrated novel carbon manganese oxide nanocomposite for electrochemical detection of arsenic.Here reduced grapheme oxide/manganese oxide nanocomposite for electrochemical detection of arsenic was performed based on electrochemical reduction method, characterized by optical, structural and electrical properties.

In 2016 Ruma Gupta et al [34] demonstrated the use of metallic ruthenium nanoparticles formed on glassy carbon electrodes for the highly sensitive detection of arsenite at ultratrace concentrations in aqueous matrices.The researchers achieved the formation of ruthenium nanoparticles on glassy carbon electrodes by applying an electron deposition potential of approximately 0.75 V. These nanoparticles possessed an arsenite-selective surface and a conducting core, making them well-suited for the design of a highly sensitive and reproducible

detection system for arsenite.Electrochemical impedance spectroscopy was conducted on the arsenite-loaded RuNPs/GC electrode, revealing a linear increase in the charge transfer resistance as the concentration of As(III) increased. This impedance-based method allowed for the determination of arsenite concentration within a few minutes.The detection limit achieved by this method was 0.1 parts per billion (ppb), indicating its high sensitivity. Additionally, the reproducibility of the measurements was reported to be 5.4%.

In 2016 paper Ali A. Ensafi [34] presented a method using aptamers to induce the aggregation of cationic cysteamine-stabilized CdTe/ZnS core/shell quantum dots, resulting in fluorescence quenching. However, in the presence of arsenic(III) (As(III)), the aptamer formed a complex with As(III), preventing the aggregation of the quantum dots. As a result, the fluorescence intensity of the quantum dots was enhanced upon de-aggregation, which depended on the concentration of As(III).The researchers utilized cationic cysteamine-stabilized CdTe/ZnS core/shell quantum dots, which exhibited fluorescence emission. By introducing an aptamer specific to As(III), the researchers were able to induce the aggregation of the quantum dots through the binding between the aptamer and the quantum dots, resulting in fluorescence quenching.However, in the presence of As(III), the aptamer formed a complex with As(III) ions. This complex formation prevented the interaction between the aptamer and the quantum dots, leading to the de-aggregation of the quantum dots. Consequently, the fluorescence intensity of the quantum dots was enhanced, and the degree of enhancement depended on the concentration of As(III) present in the sample.This method provided a simple and sensitive approach for the ultrasensitive detection of As(III) based on the fluorescence response of the quantum dots. The fluorescence intensity could be correlated with the concentration of As(III) in the sample, allowing for the quantification of As(III) at low levels.

In 2016, Song L et al[35] presented a novel optical biosensor for arsenic (III) detection based on the Surface-enhanced Raman scattering (SERS) technique. The biosensor utilized a combination of a specific trivalent arsenic aptamer and Raman-labeled Au@Ag core-shell nanoparticles.The biosensor employed Au@Ag core-shell nanoparticles as the SERS substrate, which exhibited strong surface-enhanced Raman scattering signals. The aptamer, specifically designed to bind to trivalent arsenic (III), was immobilized on the surface of the nanoparticles. In the presence of arsenic (III), the aptamer formed a complex with the target analyte, leading to a change in the SERS signal of the nanoparticles.By analyzing the SERS spectra, the concentration of arsenic (III) in the sample could be determined. The biosensor showed a detection range of 0.1 parts per billion (ppb) to 0.5 ppb, indicating its high sensitivity for arsenic (III) detection.This biosensor based on Au@Ag core–shell nanoparticles and SERS detection provided a promising approach for the sensitive and selective detection of arsenic (III) in aqueous samples..

In 2017 C Gao et al[36] introduced a novel method for detecting arsenic in drinking water. Their approach utilized square wave anodic stripping voltammetry and did not rely on noble metals. By combining the high adsorptivity of Fe3O4 microspheres towards As(III) and the advantages of room temperature ionic liquid (RTIL), the researchers developed a modified

screen-printed carbon electrode (SPCE) called the Fe3O4-RTIL composite. This composite demonstrated superior electrochemical performance compared to conventional noble metal-based electrodes.

In 2018 G Bhanjana[37] presented a method for detecting arsenic(III) based on cyclic voltammetry. The researchers utilized a regular lead pencil as the working electrode, which was modified with tin oxide (SnO_2) nanoneedles. These nanoneedles, synthesized using a chemical precipitation method, exhibited sizes ranging from 60 to 80 nm and were characterized in terms of their elemental, topological, morphological, and structural features. The resulting sensor demonstrated a detection limit of 10 ppb, with a linear range of 50-500 ppb and an ultrasensitivity of 28.13 $\mu A\ cm^{-2}\ ppb^{-1}$.

In 2018, Zeng et al.[38] developed a highly sensitive fluorescence-based detector for the detection of arsenic(III). The detector employed an amplification strategy utilizing sequential signal amplification in the presence of analytes. The key component of the detector was a specific As(III)-aptamer, which acted as a biorecognition element. When the analyte was present, the blocking DNA was released, initiating a cascading signal process.To facilitate the amplification process, DNA recycling with the cooperation of Exo III was performed. Exo III acted as a bio-cutter, enabling the introduction of many mg-dependent DNAzymes into the assay system. Through magnetic separation, DNAzymes with multiple turnover numbers were isolated and employed to catalyze the sequential cleavage of fluorophore-quencher-functionalized substrate strands. This resulted in a highly amplified fluorescence signal for the detection of the analyte.The combined action of Exo III and DNAzyme synergistically amplified the signal, leading to an exceptionally low detection limit of 0.016 ppb. This demonstrated the remarkable sensitivity of the fluorescent biosensor developed in this study.

In 2018, Pola-López L et al [39] developed a bacterial biosensor using a genetically modified bacterium called POLA (ABP). The biosensor was constructed using three genetic modules, including a promoter, reporter gene, and gene expression amplifier. The basis of this method involved utilizing a genetically modified bacterium derived from the IGEM 2012 series, specifically the Bio parts of Escherichia coli MG1655k12.The biosensor operated by measuring fluorescence as a response to the presence of arsenite. The fluorescence generated by the optical biosensor exhibited a linear response concerning both the time taken and the concentration of arsenite. The concentration range of arsenite tested in the study ranged from 5 to 140 ppb.By utilizing this bacterial biosensor, researchers were able to detect and quantify the presence of arsenite based on the fluorescence response of the genetically modified bacterium POLA (ABP). This approach provided a novel and potentially effective method for arsenite detection and monitoring.

In 2018, Sunderarajan[40] proposed a system presented in the paper was based on nanotechnology and utilized Anodic Stripping Voltammetry (ASV) for the detection of arsenic (III). The design aimed to fabricate a more sensitive arsenic sensor using Electro-Chemical Stripping Voltammetry.The method offered several advantages, including speed and portability. Voltammetric stripping methods provided a rapid, cost-effective, and reliable means of measurement, even at lower levels of concentration. The arsenic concentration in water using nanotechnology-ASV was determined by varying electro-deposition parameters such as deposition time and concentration of nanoparticles. The deposition time was directly related to the mean size of the nanoparticles, which, in turn, was proportional to the strength of the analyte being tested.ASV is a specific procedure that determines the strength of an analyte by electro-depositing it and then stripping it through sweeping anode potential. This paper employed two types of electrodes: a conventional glassy carbon electrode and a screen-printed electrode as the sensing system for arsenic. Various films, such as mercury, bismuth, gold nanoparticles, etc., were coated on these electrode surfaces and utilized for arsenic sensing. The performance of the sensor was calibrated using a standard As(III) solution, and varying concentrations of As(III) were analyzed using a suitable background electrolyte.Pre-concentration of As(III) was carried out at suitable deposition potentials ranging between -0.3 and -0.7 Volt vs. Mercury Mercurous Sulfate (MMS). Subsequently, an anodic sweep was applied to the electrode from 0.619V to -0.481V vs. MMS. The peak of arsenic stripping was expected to occur around 0.3V vs. MMS. The peak current was then correlated with the ionic strength of arsenic in the sample, and a calibration plot was generated. This calibration plot allowed for the estimation of the concentration of an unknown quantity of As in a given solution.

In 2019 X Jia et al [41] developed an arsenic whole-cell biosensor (WCB) using Escherichia coli DH5α with a positive feedback amplifier. The incorporation of the positive feedback amplifier significantly enhanced the sensitivity of the WCB, improving it by approximately one order of magnitude compared to a WCB without positive feedback. This improvement was demonstrated when evaluating the WCB using a half-saturation concentration of As(III).The introduction of positive feedback resulted in a lower minimum detection limit for As(III), reducing it by one order of magnitude to 0.1 μM. This detection limit was lower than the arsenic level standard set by the World Health Organization for drinking water, which is 0.01 mg/liter or 0.13 μM. The enhanced sensitivity and lowered detection limit of the WCB with positive feedback provided a more effective and specific biosensor for the detection of arsenic.

In 2019 Maria G. Trachiote et al[42] developed a method to prepare gold nanoparticles by utilizing direct metal to substrate electric discharge at ambient conditions. The process involved applying a voltage of 1.2 kV between the source metal (gold) and low-cost graphite screen-printed electrodes (SPEs).The researchers successfully generated sparked nanoparticles through an evaporation-condensation process. To compare the results, they conducted experiments using both pure gold (Au) and a eutectic Au/Si (97/3 wt%) alloy. The modified sparked AuNP-SPE and eAuNP-SPE samples were characterized using scanning electron microscopy, cyclic

voltammetry, and electrochemical impedance spectroscopy (EIS).The researchers demonstrated that the modified sparked gold nanoparticle screen-printed electrodes exhibited a linear response in the detection of arsenic over a concentration range of 0.5 to 12 ppb. This innovative approach provided a low-cost and efficient method for the determination of arsenic at sub-parts per billion (ppb) levels using screen-printed sensors.

In 2020, Q. Tang[43] aimed to measure trace amounts of Arsenic(III) using the Au-PANI-Fe-CNFs composite as a sensing platform.The composite was constructed by forming a polyaniline (PANI) nanosheet array on electrospun Fe-containing carbon nanofibers (Fe-CNFs) substrate, followed by self-deposition of gold nanoparticles (AuNPs). This composite exhibited excellent electrochemical performance for the detection of Arsenic(III) in water.The uniform deposition of Au nanoparticles on the PANI nanosheet surface enhanced the electrochemical properties of PANI. The particle size of the Au nanoparticles was approximately 20 ± 6 nm. Additionally, the presence of Fe in the CNFs facilitated the growth of PANI nanosheets and improved the adsorption of As(III) during the sensing process.The results demonstrated a wide linear range of detection from 5 to 400 ppb and high sensitivity, with a detection limit of 0.5 ppb. This research provided valuable insights into the development of a sensing platform for the accurate detection of trace amounts of Arsenic(III) using the Au-PANI-Fe-CNFs composite.

In 2020, Tia Agustiany et al [44] focused on the electrodeposition method for arsenic detection.The electrode was prepared by wet chemical seeding and underwent thermal annealing before and after the electrodeposition process. The surface topography and composition of elements were analyzed through scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS).To evaluate the electrochemical behavior of the modified diamond, cyclic voltammetry was performed specifically for arsenic (III). Under optimal conditions, which involved a phosphate buffer solution at pH 3 and a scan rate of 50 mV/s, the modified diamond electrode exhibited a linear calibration curve in the concentration range of 1–100 μM, with a detection limit of 4.64 μM.Furthermore, the modified electrode demonstrated excellent stability and repeatability, with relative standard deviations of 2.6% and less than 0.4%, respectively. The results indicated a proper linearity and sensitivity for the measurement of arsenic (III) and arsenic (III)-contaminated water. The study highlighted the potential of the stable iridium-modified boron-doped diamond electrode as a reliable tool for electrochemical detection of arsenic (III).

In 2020, T.T. Lew, Minkyung Park et al [45]introduced a novel approach called Plant Nanobionic Sensors for real-time arsenic detection. This method utilized the natural ability of wild-type plants to extract and pre-concentrate arsenic from the underground environment. By engineering plant nanobionic sensors, the researchers embedded near-infrared fluorescent nanosensors within plant tissues to enable sensitive and selective detection of arsenite.The optical nanosensors were strategically designed to access and monitor the internal dynamics of arsenic absorbed by the plants through their roots. This integration of optical nanosensors with living plants transformed the plants into self-powered autosampling devices capable of detecting

arsenic in their environment.The effectiveness of this approach was demonstrated using three different plant species as nanobionic sensors for arsenite detection. Through experiments and validation of a kinetic model, the researchers found that the nanobionic sensors could detect arsenic levels as low as 0.6 ppb after 7 days and 0.2 ppb after 14 days.This innovative technique of leveraging the natural abilities of plants, combined with the integration of optical nanosensors, showcased the potential of plant nanobionic sensors for real-time and non-destructive arsenic detection in the environment.

In 2021, Shalini Thakkar et al [46] focused on the current state of nano-enabled methods for arsenic detection and emphasized the strategic fabrication of nanostructures and the modulation of nanomaterial chemistry as a means to enhance the understanding and development of novel nano-enabled solutions for arsenic contamination.The paper provided a comprehensive overview of the various nano-enabled approaches that have been employed for arsenic detection in water. These approaches harness the unique properties and characteristics of nanomaterials to enhance the sensitivity, selectivity, and efficiency of arsenic sensing. By utilizing nanomaterials, such as nanoparticles, nanowires, nanotubes, and nanocomposites, researchers have been able to develop highly sensitive and reliable sensors for arsenic detection.The authors highlighted the importance of understanding the fabrication techniques and strategies involved in creating nanostructures for arsenic sensing. They discussed the synthesis methods, surface functionalization, and sensor architectures that have been utilized to optimize the performance of nano-enabled sensors. Additionally, the modulation of nanomaterial chemistry, including surface modifications and functionalization with specific receptors or recognition elements, was explored as a means to enhance the selectivity and specificity of arsenic detection.Overall, the paper provided a comprehensive overview of the current advancements in nano-enabled sensors for arsenic detection in water. It emphasized the importance of strategic fabrication of nanostructures and the modulation of nanomaterial chemistry to drive innovation and develop novel solutions for combating arsenic contamination..

In 2021, Haradhan Kolya[47] focused on the use of gold, silver, and metal oxide nanoparticles for the colorimetric detection of arsenic.The paper discussed the utilization of gold nanoparticles modified with lauryl sulfate for the detection of arsenic (III) through a colorimetric sensing approach. The modification of gold nanoparticles allowed for the enhancement of their sensing capabilities. The interaction between the gold nanoparticles and arsenic (III) led to changes in the localized surface plasmonic resonance (LSPR), resulting in observable color changes that could be detected visually or using spectrophotometric techniques.The authors reported a limit of detection (LOD) of 2 ppb for the colorimetric sensing of arsenic (III) using the gold-modified lauryl sulfate nanoparticles. This indicates that the developed method is capable of detecting arsenic (III) at very low concentrations. The colorimetric approach offers the advantage of being simple, cost-effective, and easily interpretable, making it suitable for rapid on-site detection of arsenic in various samples.Furthermore, the paper discussed other metal-based nanoparticles, such as silver and metal oxides, that have been explored for colorimetric arsenic detection. The

unique properties of these nanoparticles, such as their plasmonic and catalytic activities, have been leveraged to develop sensitive and selective colorimetric sensing platforms.Overall, the paper highlighted the recent advances in colorimetric detection of arsenic using metal-based nanoparticles, specifically focusing on gold, silver, and metal oxide nanoparticles. The utilization of these nanoparticles offers promising opportunities for the development of sensitive, rapid, and cost-effective arsenic sensing methods.

In 2022, Natasha D. Reich et al [48] conducted a study aimed at developing a practical method for the colorimetric determination of dissolved inorganic arsenic in water samples. Their research focused on utilizing a silver coordination polymer as the sensing material.The researchers demonstrated that by using a crystalline polymer framework, they could effectively stabilize silver(I) ions. This stabilization was crucial as it significantly reduced both the photosensitivity and water solubility of the silver ions. Despite these modifications, the polymer framework retained sufficient reactivity to detect arsenic in water samples at low parts per billion (ppb) levels.To assess the effectiveness of their method, the researchers fabricated test strips using the silver-based polymer. These test strips were designed for field tests of groundwater under real-world operating conditions. The results showed that the test strips exhibited performance comparable to commercially available mercury-based test strips, highlighting their practicality and competitiveness.In addition to the colorimetric analysis, the researchers also employed spectroscopic methods to investigate the reaction products formed during the detection process. By examining the spectroscopic data, they aimed to gain a better understanding of the sensing mechanism involved in the interaction between the silver-based polymer and dissolved inorganic arsenic.Overall, the study by Reich et al. in 2022 presented a practical method for the colorimetric determination of dissolved inorganic arsenic in water samples. The use of a silver coordination polymer as the sensing material, along with the stabilization of silver(I) ions within a crystalline polymer framework, allowed for effective and sensitive detection of arsenic at low ppb levels. The research demonstrated the potential of these silver-based test strips for field testing of groundwater and highlighted their performance on par with existing commercial options. The spectroscopic analysis provided valuable insights into the underlying sensing mechanism, contributing to a better understanding of the detection process.

In 2022, Hongai Ge[49] developed a portable and simple method for the selective determination of As(III) using the surface-enhanced Raman scattering (SERS) signal of As(III)–O vibration. This method relied on the synergistic effect of nanoparticle aggregation and analyte adsorption analysis.The experimental results demonstrated that the ligands of HH@Ag nanoparticles were replaced by phosphate ions, leading to enhanced adsorption of As(III) on the surface of HH@Ag nanoparticles. To further improve the detection capability of the system for arsenic contamination, phosphate was introduced as an agglomerating agent in the system.The developed method exhibited excellent selectivity for As(III) detection. It showed a linear relationship between concentrations ranging from 5×10^{-8} M to 0.8×10^{-6} M, with a detection limit as low as 1.8×10^{-9} M. Moreover, when tested with actual water samples, the

method successfully detected As(III), demonstrating its practical applicability.Overall, the portable method developed by Ge and In in 2022 provided a reliable and selective approach for the determination of As(III) levels. By leveraging the SERS signal of As(III)–O vibration and utilizing nanoparticle aggregation and analyte adsorption analysis, the method demonstrated good sensitivity, selectivity, and successful detection of As(III) in water samples.

In 2022, Shalvi[50] provided a comprehensive review of various advanced approaches for detecting arsenic at low concentrations. The focus of the review was on the utilization of nanomaterials in two prominent detection methods: colorimetric and electrochemical techniques.The authors discussed the recent advancements in nanomaterial-based sensors for arsenic detection and highlighted their key features, including sensitivity, selectivity, stability, repeatability, and the lower limit of detection. Nanomaterials have shown great potential in enhancing the performance of arsenic sensors due to their unique properties and high surface-to-volume ratio.Colorimetric methods rely on changes in color or optical properties of nanomaterials upon interaction with arsenic ions. The review discussed various nanomaterials used in colorimetric sensing, such as gold nanoparticles, silver nanoparticles, metal-organic frameworks, and quantum dots. The sensitivity and selectivity of these sensors were evaluated, and their performance in detecting trace levels of arsenic was examined.Electrochemical methods, on the other hand, exploit the electrochemical properties of nanomaterials for arsenic detection. The authors discussed the use of nanomaterials, including carbon-based materials, metal oxides, and metal nanoparticles, as sensing elements in electrochemical sensors. The advantages of electrochemical methods, such as rapid response, high sensitivity, and real-time monitoring, were emphasized.Overall, the review provided a comprehensive overview of the recent advances in nanomaterial-based approaches for detecting arsenic at trace levels. It highlighted the significance of nanomaterials in improving the sensitivity and selectivity of arsenic sensors. The discussion on sensor properties and performance parameters helps researchers and practitioners understand the capabilities and limitations of different nanomaterial-based detection techniques for arsenic.

2.3 SUMMARY:

Method	Year	Researchers	Key Techniques/Instruments	Advantages
Vapor Generation Assembly (VGA) and AAS	2006	Jayraj Behari et al	VGA, AAS	Accurate quantification of total arsenic content, enhanced specificity, reliable and sensitive method
Graphite Furnace Atomic Absorption Spectrometry	2007	J Michon et al	GFAAS	Rapid, low limit of detection, precise control of temperature, accurate and sensitive determination of total inorganic arsenic in drinking water
Gas-phase Chemiluminescence Method	2007	Ademola Idewu et al	Liquid chromatography, gas-phase chemiluminescence	Sensitive detection and separation of organic and inorganic arsenic species, accurate quantification and identification
Platinum-modified Screen-printed Carbon Electrodes	2009	Silvia Sanllorente-Méndez et al	Electrochemical detection, platinum nanoparticles, sodium thiosulfate	Reliable and sensitive method for arsenic(III) determination, low detection limit, accurate analysis of real samples and

				spiked tap water samples
Bacteria-based Bioassays	2009	E Diesel et al	Genetically modified bacterial strains, biosensor-reporter strains	Rapid and sensitive detection, potential for on-site testing, specificity and versatility through different bacterial strains
Total Deflection X-ray Fluorescence (TXRF)	2010	Haydon Baros et al	Alumina-based separation and pre-concentration	Determination of arsenic in water samples, substantial enrichment, sensitive and accurate quantification
Electrochemical Systems	2014	Savarinithu et al	Three-electrode system, carbon, silver, and silver/silver-chloride electrodes	Rapid on-site detection, portable and minimizes instrumentation requirements, cyclic voltammetry and anodic stripping voltammetry methods
Catalytic Properties of Gold-Copper Alloy Nanocrystals	2014	Rong He et al		Studying the potential for arsenic detection based on the catalytic properties of nanocrystals
Adsorption of oligonucleotides on magnetic beads	2014	B Liu et al	Magnetic beads fluorescence quenching	Studying the potential for arsenic

				detection
Electrochemical detection using carbon manganese oxide nanocomposite	2015	P Devi	Reduced graphene oxide/manganese oxide nanocomposite	Studying the potential for arsenic detection
Metallic ruthenium nanoparticles on electrodes	2016	Ruma Gupta et al	Ruthenium nanoparticles on glassy carbon electrodes	Studying the potential for arsenic detection
Aptamer-induced quantum dot fluorescence response	2016	Ali. A. Ensafi et al	Aptamer-induced quantum dot aggregation and de-aggregation	Studying the potential for arsenic detection
Surface-enhanced Raman scattering (SERS)	2016	Song L et al	Trivalent arsenic aptamer + Raman-labeled Au@Ag core-shell nanoparticles	Studying the potential for arsenic detection based on SERS technique
Square wave anodic stripping voltammetry	2017	C Gao et al	Fe3O4 microspheres + room temperature ionic liquid (RTIL)	Studying the potential for arsenic detection
Cyclic voltammetry with tin oxide nanoneedles	2018	G Bhanjana et al	Regular lead pencil + tin oxide nanoneedles	Studying the potential for arsenic detection upto 10 ppb
Fluorescence-based detector with amplification	2018	Zeng et al	As(III)-aptamer + Exo III + DNAzymes	Studying the potential for arsenic detection based on As(III)-aptamer + Exo III + DNAzymes
Genetically modified bacterial biosensor	2018	Pola Lopez L et al	Genetically modified bacterium POLA (ABP)	Studying the potential for arsenic detection based on V

Nanotechnology-based Anodic Stripping Voltammetry	2018	Sunderarajan	Various films on glassy carbon or screen-printed electrodes	Studying the potential for arsenic detection based on nanotechnology
Arsenic Whole-Cell Biosensor (WCB) with Positive Feedback Amplifier	2019	X. Jia et al	Whole Cell Biosensor	Positive feedback amplifier improved sensitivity by approximately one order of magnitude compared to WCB without positive feedback. Lowered detection limit for As(III) to
Direct Metal to Substrate Electric Discharge for Gold Nanoparticles	2020	Maria G. Trachiote et al [42]	Gold nanoparticles	Generated gold nanoparticles through evaporation-condensation process. Screen-printed sensors exhibited linear response in arsenic detection (0.5 to 12 ppb).
Au-PANI-Fe-CNFs Composite Sensing Platform	2020	Q tang	Au-PANI-Fe-CNFs Composite Sensing Platform	Composite exhibited excellent electrochemical performance for detecting Arsenic(III). Wide linear range of detection (5 to 400 ppb) and detection limit

				of 0.5 ppb.
Electrodeposition Method	2020	Tia Augustany et al	Diamond electrode	Modified diamond electrode exhibited linear calibration curve for arsenic (III) detection (1-100 μM) with a detection limit of 4.64 μM. Excellent stability and repeatability
Plant Nanobionic Sensors for Arsenic Detection	2021	.T. Lew, Minkyung Park	Plant based sensors	Engineered plant nanobionic sensors embedded with near-infrared fluorescent nanosensors for real-time arsenic detection. Detected arsenic levels as low as 0.2 ppb after
Nano enabled sensors	2021	Shalini thakkar		Review of nano-enabled approaches for arsenic detection in water. Nanomaterials enhance sensitivity, selectivity, and efficiency of sensors. Emphasis on fabrication techniques and modulation of

				nanomaterial chemistry.
Colorimetric Detection of Arsenic using Metal Nanoparticles	2022	Haradhan Koyla et al	Gold nanoparticles	Utilized gold nanoparticles and other metal-based nanoparticles for colorimetric arsenic detection. Limit of detection of 2 ppb using gold-modified nanoparticles. Simple, cost-effective, and easily interpretable approach.
Surface-enhanced Raman scattering (SERS)	2022	Hongai Ge et al	SERS	Portable method utilizing SERS signal of As(III)–O vibration. Synergistic effect of nanoparticle aggregation and analyte adsorption analysis. Selective detection of As(III) with a low detection limit of 1.8 × 10^−9 M.
Nanomaterial-Based Sensors for Arsenic Detection	2022	Shalvi et al	Gold and silvernanoparticles	Review of nanomaterial-based sensors in colorimetric and electrochemical techniques. Nanomaterials enhance sensitivity,

				selectivity, and stability. Gold nanoparticles, silver nanoparticles, metal-organic frameworks, and quantum dots used in colorimetric sensing. Various nanomaterials used in electrochemical sensors. Advantages of electrochemical methods discussed

2.4 CONCLUSION:-

In the above survey we came across various studies performed for detection of arsenic in drinking water .Several studies have focused on studying the potential for arsenic detection using different materials and techniques. These include the catalytic properties of Gold-Copper Alloy Nanocrystals (2014), adsorption of oligonucleotides on magnetic beads (2014), electrochemical detection using carbon manganese oxide nanocomposites (2015), metallic ruthenium nanoparticles on electrodes (2016), aptamer-induced quantum dot fluorescence response (2016), surface-enhanced Raman scattering (SERS) techniques (2016 and 2022), and many more.

In recent years, nanotechnology has played a significant role in the development of arsenic detection methods. Nanomaterials such as gold and silver nanoparticles have been used in colorimetric and electrochemical techniques, enhancing sensitivity, selectivity, and efficiency of sensors. These nanomaterials, along with metal-organic frameworks and quantum dots, have shown promising results in colorimetric sensing, while various nanomaterials have been employed in electrochemical sensors.

Overall, the comparative study of these methods and technologies reveals the continuous efforts to improve arsenic detection by enhancing sensitivity, selectivity, detection limits, and practicality. While each method has its advantages and limitations, the research highlights the potential of various approaches to tackle the critical issue of arsenic contamination in water, providing valuable insights for further developments in this field.

CHAPTER 3

DETECTION THEORY

3.1 ARSENIC PROPERTIES:

At the atomic level, arsenic consists of a nucleus containing 33 protons and typically 42 neutrons (although the number of neutrons may vary in different isotopes of arsenic). Electrons orbit the nucleus in various energy levels or electron shells. In the case of arsenic, these shells are filled in the following manner: 2 electrons in the 1s shell, 2 electrons in the 2s shell, 6 electrons in the 2p shell, 2 electrons in the 3s shell, 6 electrons in the 3p shell, and 3 electrons in the 3d shell.

When it comes to the crystalline structure of arsenic, it has different allotropes, meaning it can exist in multiple forms with different arrangements of atoms in a solid state. The most stable form of arsenic at room temperature is gray arsenic, which has a rhombohedral crystal structure. In this structure, arsenic atoms are arranged in layers, with each layer consisting of a hexagonal arrangement of atoms. The layers are held together by weak van der Waals forces.

Arsenic exhibits three allotropic forms: black, yellow, and gray. In its stable state, it forms a silver-grey, brittle crystalline solid. It tarnishes rapidly upon contact with air and at high temperatures, producing a white cloud of arsenic trioxide. The metallic form of arsenic is somewhat brittle and becomes tarnished when oxidized to arsenic trioxide. The non-metallic form is less reactive but readily dissolves when heated with strong oxidizing acids and alkalis. Here are the chemical properties of arsenic:

- Allotropy: Arsenic exists in multiple allotropic forms, including black, yellow, and gray.
- Appearance: In its stable state, arsenic appears as a silver-grey, brittle crystalline solid.
- Reactivity with air: Arsenic tarnishes rapidly when exposed to air, forming a white cloud of arsenic trioxide.
- Reactivity with high temperatures: At high temperatures, arsenic readily oxidizes, producing arsenic trioxide.
- Metallic properties: The metallic form of arsenic is somewhat brittle and prone to tarnishing when oxidized.
- Non-metallic properties: The non-metallic form of arsenic is less reactive but easily dissolves when heated with strong oxidizing acids and alkalis..

The chemical properties of arsenic are summarized in the below table:

Group	15	Melting point	Sublimes at 616°C, 1141°F, 889 K
Period	4	Boiling point	Sublimes at 616°C, 1141°F, 889 K
Block	p	Density (g cm-3)	5.75
Atomic number	33	Relative atomic mass	74.922
State at 20°C	Solid	Key isotopes	^{75}As
Electron configuration	[Ar] $3d^{10}4s^24p^3$	CAS number	7440-38-2
ChemSpider ID	4514330	ChemSpider is a free chemical structure database	

Fig3.1: Chemical properties of arsenic[75]

Numerous substances have been used for arsenic detection. To increase the sensitivity and accuracy of analysis, the arsenic-bearing species is often isolated from its matrix and concentrated. The principal preconcentration procedures used are coprecipitation, liquid–liquid extraction, and volatilization.[51]

While pentavalent arsenic is detected with ferric hydroxide, hydroxides of cerium and zincornium [52][53], thionalide can effectively collect arsenic from seawater.[47]Trivalent arsenic can be detected and extracted using mixtures of ketone and carbon tetrachloride.[54]Arsenic can also be separated from its matrix by volatilization, as arsine (boiling point, −55 C) or a substituted arsine. The necessary reduction can be effected by using zinc and acid in the presence of stannous chloride or potassium iodide.[49]

The other methods implemented for detection are paper chromatography, electrophoresis, volatilization [55] or conversion to the corresponding arsine [50] or iodide[51] gas chromatography. A specific compound is identified by its retention characteristics, sometimes in combination with a specific detector for arsenic

Here we have alterted zinc oxide with curcumin and used it for arsenic detection. Zn(cur)O which is weakly fluorescent becomes strongly fluorescent when subjected to arsenic.

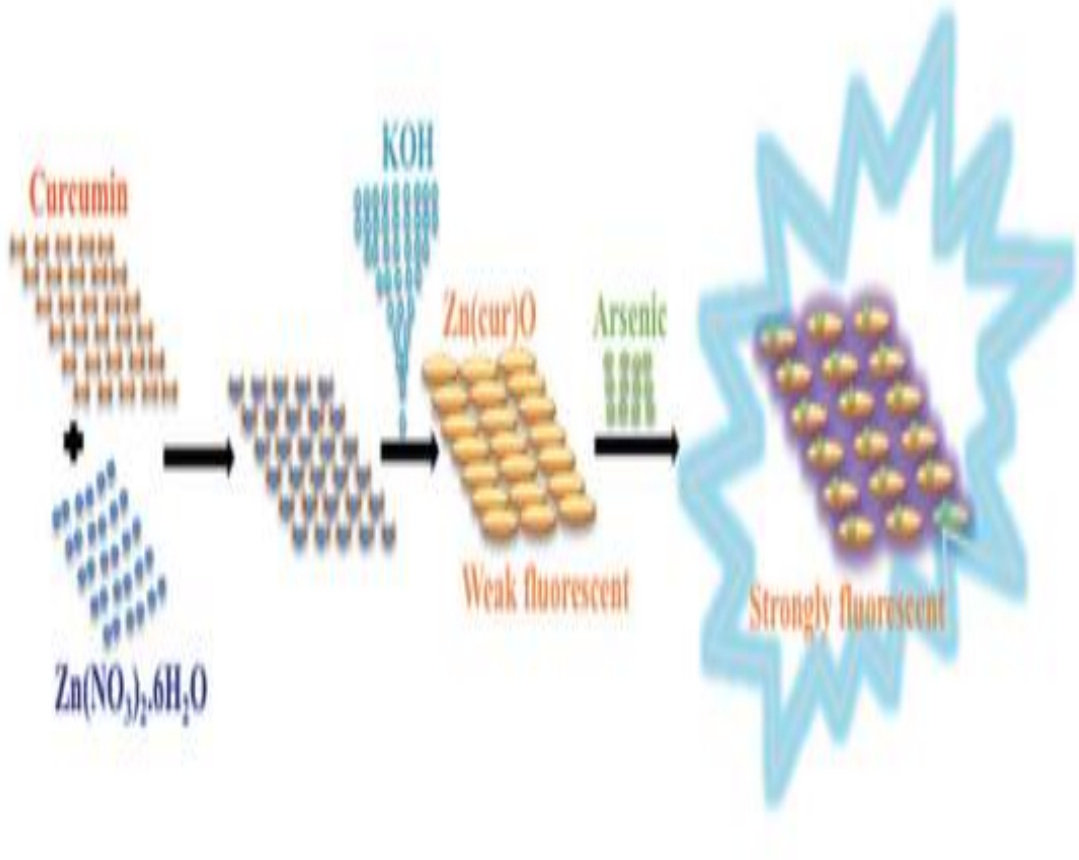


Fig 3.2: The action of arsenic on Zinc Curcumin Oxide[76]

3.2 AN ANALYSIS OF PREVIOUS METHODS USED FOR ARSENIC DETECTION

The conventional arsenic detection methods include colorimetric assays, atomic absorption spectrometry (AAS), and inductively coupled plasma mass spectrometry (ICP-MS).

1. Colorimetric Methods: Colorimetric methods are widely used for the detection and quantification of various substances, including arsenic. These methods utilize the phenomenon of color changes that occur as a result of specific chemical reactions between reagents and the analyte of interest—in this case, arsenic ions.

- Silver diethyldithiocarbamate (Ag-DDTC) and silver diethylarsinate (Ag-DEAA) are examples of reagents commonly employed in colorimetric tests for arsenic detection.
  Ag-DDTC is a reagent that forms a colored complex with arsenic ions. When Ag-DDTC is added to a solution containing arsenic, a chemical reaction takes place, resulting in the formation of a reddish-brown precipitate. The intensity of the color change is directly proportional to the concentration of arsenic present in the sample. This colorimetric reaction allows for qualitative and quantitative analysis of arsenic.

Silver Diethylarsinate (Ag-DEAA):

Ag-DEAA is another reagent used in colorimetric tests for arsenic detection. It reacts specifically with arsenic ions to form a colored compound. In the presence of arsenic, Ag-DEAA undergoes a reaction that leads to the development of a yellow color. The intensity of the yellow color is indicative of the concentration of arsenic in the sample.

Both Ag-DDTC and Ag-DEAA have been extensively used in various colorimetric assays for arsenic detection. These tests are relatively simple and cost-effective, making them suitable for rapid screening of arsenic contamination in water, soil, or other environmental samples. However, it is important to note that colorimetric methods alone may not provide highly accurate quantitative results, and they are often used as initial screening tools. For precise measurements, more sophisticated techniques such as atomic absorption spectroscopy or inductively coupled plasma mass spectrometry are typically employed.

It's worth mentioning that there are other colorimetric reagents and methods available for arsenic detection as well. The selection of a particular reagent or method depends on factors such as sensitivity, selectivity, ease of use, and the specific requirements of the analysis. Researchers continuously explore and develop new colorimetric approaches to enhance arsenic detection capabilities..[65][66]

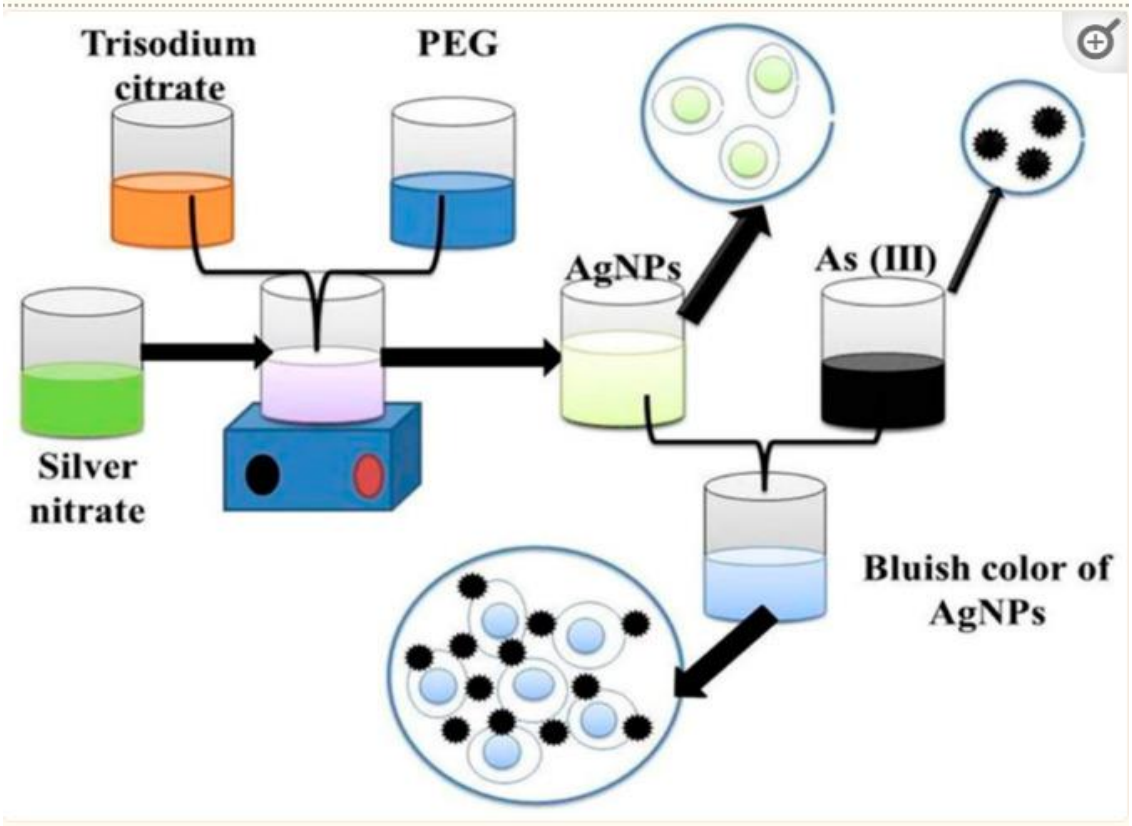


Fig 3.3:An example of colorimetric arsenic detection method[77]

2. Atomic Absorption Spectroscopy (AAS): AAS is an analytical technique used to measure the concentration of specific elements in a sample. It works based on the absorption of light by the atoms of the target element. AAS was widely used for arsenic detection in groundwater. The sample is typically atomized and then exposed to a light source of specific wavelength to measure the absorption.[66]
   Atomic Absorption Spectroscopy (AAS) is a widely used analytical technique for the detection and quantification of various elements, including arsenic. It is based on the principle of absorption of light by atoms in the ground state, specifically the absorption of light at characteristic wavelengths by the target element.

   Here are the details and elaboration on how AAS is applied for arsenic detection:

   Instrumentation:
   A typical AAS instrument consists of the following components:
   Light source: A hollow cathode lamp that emits light at the specific wavelength corresponding to the absorption line of the target element. In the case of arsenic, the wavelength commonly used is 193.7 nm.

Sample introduction system: It includes a nebulizer, which converts the liquid sample into an aerosol, and a spray chamber, where the aerosol is mixed with a carrier gas (usually an inert gas like argon) to form a sample vapor.

Atomizer: AAS utilizes different types of atomizers, such as flame, graphite furnace, or hydride generation systems, depending on the sample matrix and the desired sensitivity.
Monochromator: A device that selects the specific wavelength of light emitted by the hollow cathode lamp.

Detector: Usually a photomultiplier tube (PMT) or a solid-state detector that measures the intensity of the transmitted or absorbed light.

Principle of Operation:
In AAS, the sample is atomized and introduced into a flame or another atomization system. The hollow cathode lamp emits light at the characteristic wavelength for arsenic (193.7 nm), which is directed through the atomized sample. As the light passes through the sample, the arsenic atoms absorb radiation at the specific wavelength, resulting in a reduction in the transmitted light intensity.

Calibration and Analysis:
To determine the concentration of arsenic in a sample, a calibration curve is constructed. This is done by measuring the absorbance or the decrease in light intensity at the characteristic wavelength of arsenic for a series of standard solutions with known arsenic concentrations. The relationship between the absorbance and the concentration is linear, allowing for the quantification of unknown samples based on their absorbance values.

Sensitivity and Limit of Detection:
AAS is known for its high sensitivity, capable of detecting trace levels of arsenic in various matrices. The limit of detection (LOD) depends on factors such as the instrument's specifications, the sample introduction system, and the sample matrix. Typically, AAS can achieve LODs in the range of parts per billion (ppb) to parts per trillion (ppt) for arsenic.

Advantages and Limitations:
Advantages of AAS for arsenic detection include its high sensitivity, wide dynamic range, and relatively straightforward operation. It can analyze a large number of samples in a short period, making it suitable for routine analysis. However, AAS requires access to specialized equipment, and sample preparation steps may be required to remove interferences. Additionally, AAS provides elemental analysis only and does not provide information about the chemical form or speciation of arsenic present in the sample. [67]

3. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS): ICP-MS is a highly sensitive and accurate analytical technique used for the detection and quantification of elements in a sample. It combines the capabilities of inductively coupled plasma (ICP) as an ionization source with mass spectrometry for element identification and quantification. ICP-MS has been commonly used for analyzing trace amounts of arsenic in groundwater.[68]

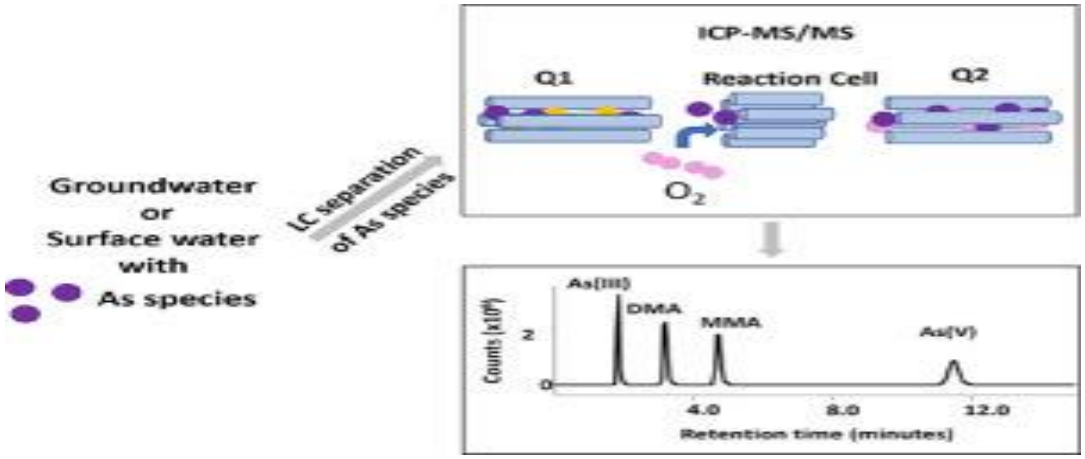


Fig 3.4: Representation of ICP-MS[78]

Here are the details of how ICP-MS is applied for arsenic detection:

Sample Preparation:
Sample preparation is a crucial step in ICP-MS analysis. It involves various techniques such as digestion, extraction, and filtration to ensure that the arsenic in the sample is in a suitable form for measurement. Solid samples are typically digested using acids to dissolve the analyte, while liquid samples may require minimal preparation before analysis.

ICP-MS Instrumentation:

ICP-MS consists of several key components:
Sample introduction system: It includes a nebulizer, which converts the liquid sample into a fine aerosol, and an argon gas flow that carries the aerosol into the plasma torch.
Inductively coupled plasma (ICP) torch: It generates a high-temperature plasma by ionizing the argon gas using radiofrequency energy. The plasma reaches temperatures of approximately 10,000 Kelvin and atomizes the sample, converting the analytes into ions.
Mass spectrometer: The ions produced in the plasma are introduced into the mass spectrometer. ICP-MS typically uses quadrupole or sector field mass analyzers, which

separate ions based on their mass-to-charge ratio (m/z). The mass spectrometer measures the abundance of specific arsenic isotopes and calculates their concentration in the sample.

Detector: A detector, such as an electron multiplier, measures the ion currents, allowing for the quantification of the analyte.

Arsenic Detection and Quantification:
In ICP-MS, arsenic is detected and quantified based on its mass-to-charge ratio (m/z). Arsenic exists in several isotopic forms, including ^75As, ^74As, ^73As, and ^72As, but ^75As is the most commonly used isotope for detection. By monitoring the intensity of the ^75As ion signal, the concentration of arsenic in the sample can be determined.

Calibration and Analysis:
To determine the concentration of arsenic in a sample, a calibration curve is constructed using standard solutions with known arsenic concentrations. The standard solutions are analyzed under the same conditions as the sample, and the relationship between the signal intensity and the concentration is established. Unknown samples can then be quantified by comparing their signal intensities to the calibration curve.

Sensitivity and Limit of Detection:
ICP-MS offers exceptional sensitivity for arsenic detection, capable of detecting trace levels of arsenic in various sample matrices. The limit of detection (LOD) for arsenic in ICP-MS analysis is typically in the sub-parts per billion (ppb) or even parts per trillion (ppt) range, depending on instrument capabilities and sample preparation techniques.

Advantages and Limitations:
ICP-MS is highly regarded for its sensitivity, wide dynamic range, and multi-element capabilities. It can simultaneously detect and quantify multiple elements, making it efficient for analyzing complex samples. However, ICP-MS is a complex and expensive technique that requires skilled operators and sophisticated instrumentation. It may also require extensive sample preparation and quality control measures to ensure accurate results.

4. Ion Chromatography (IC):IC is a separation technique that utilizes the differences in the retention and elution times of ions in a chromatographic column. It can be used for the analysis of various ions, including arsenic. IC coupled with various detection methods, such as UV-Vis spectroscopy or conductivity, has been employed for arsenic detection in groundwater.[69]

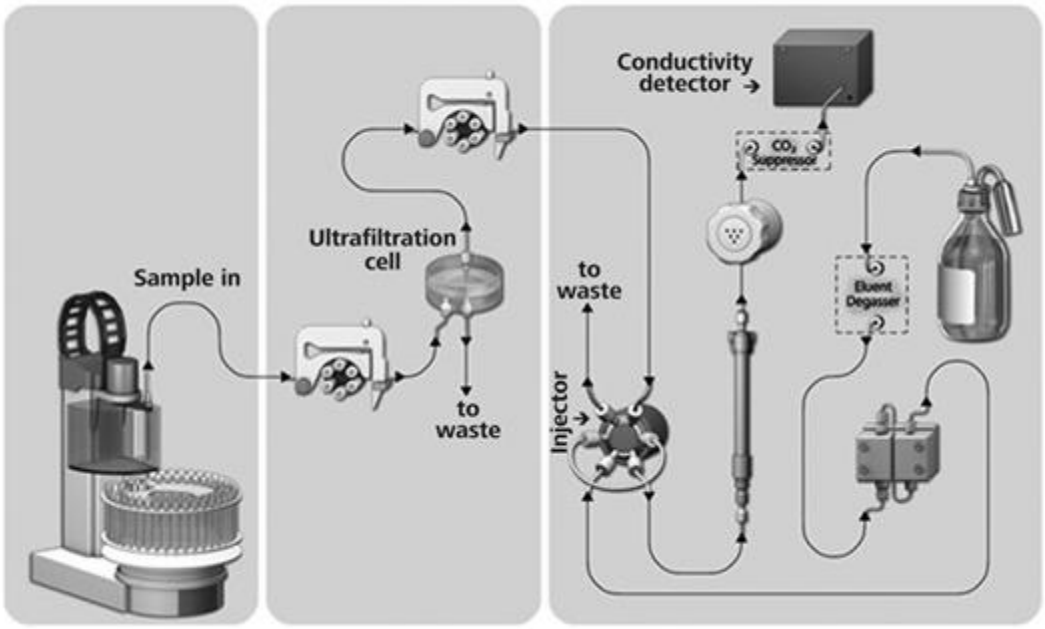


Fig 3.5:Setup for ion chromatography[79]

Sample preparation for arsenic detection using ion chromatography typically involves extracting arsenic ions from the sample matrix. This may include processes such as sample filtration, dilution, and sometimes sample pretreatment steps like complexation or oxidation/reduction reactions to convert the arsenic species into a detectable form. The aim is to ensure that the arsenic ions are in a suitable form for analysis.

Ion Chromatography Instrumentation:
An ion chromatography system consists of several essential components:

Pump: Provides a constant flow of mobile phase through the chromatographic column.
Injection system: Introduces the prepared sample into the chromatographic system.
Chromatographic column: Specialized columns with ion-exchange resins or other stationary phases designed to separate ions based on their affinity for the stationary phase.
Detector: Various detectors can be used in IC for arsenic detection, including conductivity detectors, UV-Vis detectors, and mass spectrometers (IC-MS). For arsenic detection, conductivity detectors and IC-MS are commonly employed due to their selectivity and sensitivity.
Arsenic Detection and Quantification:
In IC, arsenic ions are separated based on their ionic interactions with the stationary phase of the chromatographic column. Arsenic species, such as arsenate (As(V)) and arsenite (As(III)), can be separated and detected individually or simultaneously,

depending on the analytical setup. The choice of column and eluent composition plays a crucial role in achieving efficient separation.
Conductivity Detection: Conductivity detectors are commonly used in IC for arsenic detection. As arsenic ions elute from the column, they pass through a conductivity cell. Arsenic ions, being charged, can conduct electricity, and changes in conductivity are measured and recorded. The peak area or height corresponds to the concentration of arsenic ions in the sample.

Mass Spectrometry Detection: In some cases, IC is coupled with mass spectrometry (IC-MS) for highly sensitive and selective arsenic detection. The eluted arsenic ions are ionized and then detected and quantified based on their mass-to-charge ratio (m/z) using a mass spectrometer. IC-MS allows for the identification and quantification of specific arsenic species, providing valuable information about arsenic speciation.

Calibration and Analysis:
To determine the concentration of arsenic in a sample, a calibration curve is constructed using standard solutions with known arsenic concentrations. The standard solutions are analyzed under the same chromatographic conditions as the sample. The relationship between the peak area or height and the concentration is established, allowing for the quantification of unknown samples.

Sensitivity and Limit of Detection:
The sensitivity of arsenic detection using ion chromatography depends on factors such as the specific ion chromatography setup, column choice, and detector sensitivity. IC can achieve low detection limits for arsenic, typically in the range of parts per billion (ppb) to parts per trillion (ppt), depending on the specific method used.

Advantages and Limitations:
Ion chromatography offers several advantages for arsenic detection, including excellent selectivity for ionic species and the ability to separate various arsenic species. It is a versatile technique that can be applied to different sample matrices, such as water, soil, food, and biological samples. However, IC may require specialized columns, detectors, and consumables

5. Field Test Kits: In areas lacking laboratory facilities, field test kits have been used for preliminary screening of arsenic in groundwater. These kits often involve colorimetric methods, where a test strip or reagent is exposed to the water sample, and the resulting color change is compared against a color chart to estimate the arsenic concentration.[70]

Fig 3.6: Field test kits[80]

However the novel techniques and emerging technologies that offer improved sensitivity, selectivity, and ease of use. Some of the notable methods to be covered include:

- Electrochemical Sensors: Discussing the development of electrochemical sensors based on various transducers, such as screen-printed electrodes, nanomaterial-modified electrodes, and field-effect transistors.
- Optical Techniques: Highlighting the use of spectroscopic methods, such as surface-enhanced Raman spectroscopy (SERS), fluorescence spectroscopy, and colorimetric sensors based on gold nanoparticles.
- Biosensors: Exploring the integration of biological components, such as enzymes, antibodies, and DNA probes, for selective and sensitive arsenic detection.
- Nanomaterial-Based Sensors: Discussing the utilization of nanomaterials, such as graphene, carbon nanotubes, metal-organic frameworks (MOFs), and quantum dots, in developing highly efficient arsenic sensors.
- Microfluidic Systems: Describing the advancements in microfluidic-based platforms for arsenic detection, including lab-on-a-chip devices and paper-based sensors.

3.3PROPERTIES OF ZINC OXIDE AND CURCUMIN:

In the crystal structure of zinc oxide, each zinc ion (Zn2+) is surrounded by four oxygen ions (O2-) in a tetrahedral arrangement. Similarly, each oxygen ion is coordinated to four zinc ions,

resulting in a tetrahedral arrangement of oxygen ions. This arrangement gives rise to the hexagonal symmetry of the crystal structure.

The wurtzite structure can be visualized as a repeating unit cell, which consists of two interpenetrating triangular lattices. One lattice corresponds to the zinc ions, while the other lattice represents the oxygen ions. The unit cell has six atoms in total, with the zinc ions occupying half of the tetrahedral sites and the oxygen ions occupying the other half.

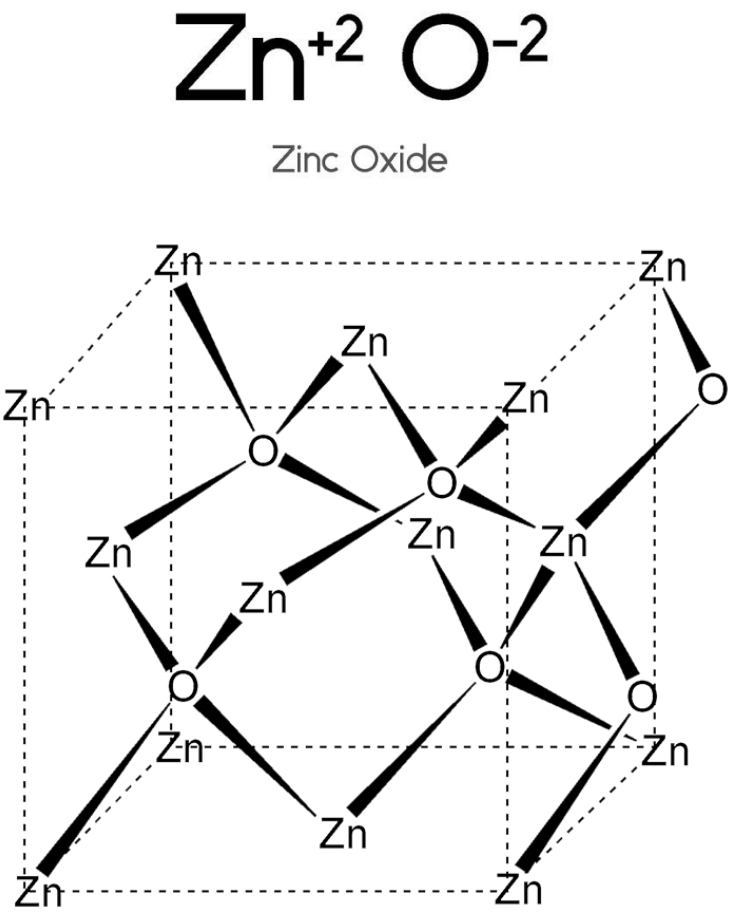


Fig 3.7: Structure of zinc oxide [90]

ZnO acts as a good adsorbent. However it also has has its own limitations. Zinc oxide (ZnO) is often used as an absorbent due to its unique properties and structure. Here is a detailed analysis of why zinc oxide is considered a good absorbent:

- High surface area: Zinc oxide can be prepared in various forms, including nanoparticles, which exhibit a high surface area-to-volume ratio. This high surface area provides more sites for adsorption, enabling zinc oxide to absorb a larger amount of substances.

- Adsorption capacity: Zinc oxide possesses strong adsorption capabilities, particularly for organic molecules and certain gases. It can attract and retain these substances on its

surface through various mechanisms, such as van der Waals forces, hydrogen bonding, and electrostatic interactions.

- Porous structure: Zinc oxide can be synthesized with a porous structure, allowing for the absorption of gases and liquids into its interconnected network of pores. The pores provide additional surface area and facilitate the diffusion of molecules, enhancing the absorption process.

- Chemical reactivity: Zinc oxide has inherent chemical reactivity, making it capable of interacting with different substances. It can form chemical bonds or complexes with various molecules, facilitating their absorption. For example, zinc oxide can react with acidic gases like sulfur dioxide (SO2) to form stable compounds, thereby removing these pollutants from the environment.

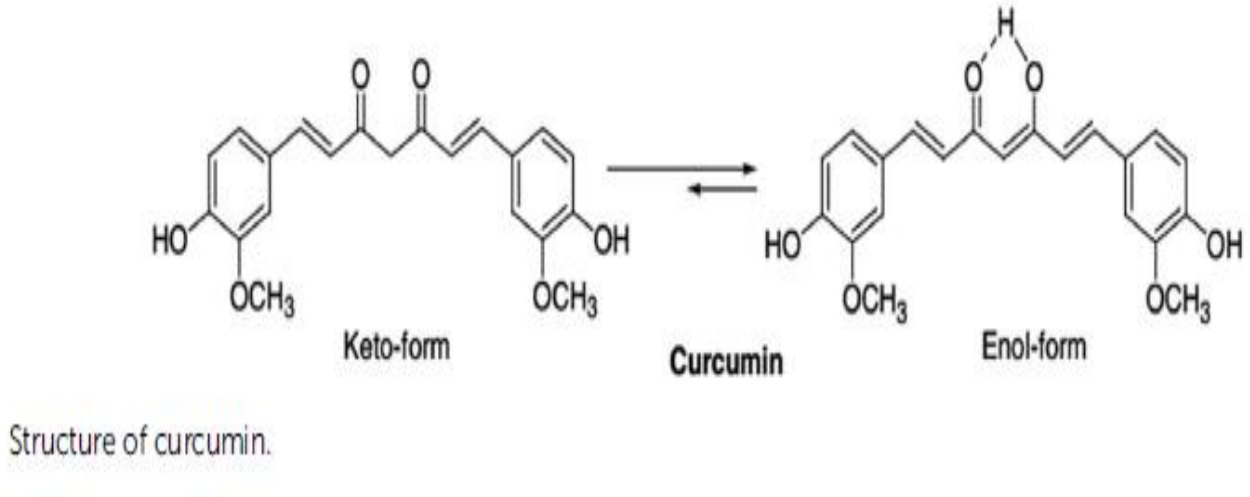
- Photocatalytic properties: Zinc oxide exhibits photocatalytic activity, meaning it can absorb photons of light and generate electron-hole pairs, which can participate in various chemical reactions. This property makes zinc oxide an excellent absorbent for pollutants and organic compounds that can undergo degradation or transformation upon exposure to light.

- Wide applicability: Zinc oxide is versatile and can be used as an absorbent in various applications. It is employed in wastewater treatment processes, air purification systems, personal care products, sunscreen formulations, and even as a component in certain medical dressings and bandages.

- Stability and regeneration: Zinc oxide is relatively stable and can withstand harsh conditions, including high temperatures. After absorbing substances, it can often be regenerated by releasing or desorbing the absorbed molecules, allowing for multiple cycles of absorption and reuse.[56][57]

It is worth noting that the effectiveness of zinc oxide as an absorbent can vary depending on factors such as the specific form and morphology of the material, the nature of the substance being absorbed, and the operating conditions. Therefore, optimizing these parameters is crucial for maximizing the absorbent properties of zinc oxide in various applications.Hence it has been doped with organic system , i. e compound curcumin so as to influenceadsorption and luminescence properties of ZnO[58]

Curcumin accounts as the major component in the curcuminoid complexes and wellknown for its pharmaceutical applications and medicinal potential in therapy of many diseases such as, cancer, cardiovascular disease, and rheumatoid arthritis.[59]



Structure of curcumin.

Fig 3.8: Structure of Curcumin [91]

Curcumin has very exciting photophysical and fuorescence properties.. Fluorescence is the emission of light by a substance after it absorbs light of a specific wavelength.The fluorescent properties of curcumin are due to its chemical structure. Curcumin is a polyphenolic compound composed of several aromatic rings connected by carbon-carbon double bonds. This structure allows curcumin to absorb light in the ultraviolet (UV) and visible regions of the electromagnetic spectrum.

When curcumin absorbs light, electrons within the molecule get excited to higher energy levels. These excited electrons are unstable and quickly return to their ground state by releasing the excess energy in the form of light. This emitted light has a longer wavelength than the absorbed light, typically in the visible range, which gives curcumin its fluorescent properties.[60]

The exact mechanism of curcumin fluorescence is not fully understood, but it is believed to involve intramolecular charge transfer and the formation of excited-state complexes. These processes contribute to the unique fluorescence characteristics of curcumin.[61]It's worth noting that the fluorescent properties of curcumin can be influenced by various factors, including pH, solvent polarity, and the presence of other molecules. These factors can alter the emission wavelength and intensity of curcumin fluorescence, making it a versatile tool for various applications in research and diagnostics.[62]Overall, the fluorescent properties of curcumin are a result of its chemical structure and the interactions that occur when it absorbs and emits light, allowing it to exhibit fluorescence.It also forms a Zn–curcumin complex by reacting with zinc salt.Curcumin has also been used to prepare ZnO–curcumin composites which has been used for detection purposes here.

3.4 THE PHYSICS BEHIND THE FLUORESCENCE OF ZINC-CURCUMIN-OXIDE IN CONTACT WITH ARSENIC:

When in contact with arsenic the zinc curcumin oxide binds to it and shows photoluminescence in the form of fluorescence.

$$ZnO + C_{21}H_{20}O_6 \rightarrow Zn(cur)O \qquad \text{Eqn[I]}$$

Actually the zinc-curcumin-oxide nanostructure hqas the morphology of a grain like wurtzite hexagonal crystal. The defects of ZnO which are visible luminescence centres get filled by doping it with curcumin. This causes prolonging of electron hole recombination thereby resulting in quenching of visible luminescence and enhancing the exciton emission of zinc oxide, rendering it weakly fluorescent.

In contact with arsenic it binds with it and becomes strongly fluorescent.

3.5 DETECTION LIMITS:

Actually the best results is expected to have been obtained in an wavelength of 200- 500 nm as demonstrated in the graph below as zinc curcumin oxide shows maximum fluorescence in that range.

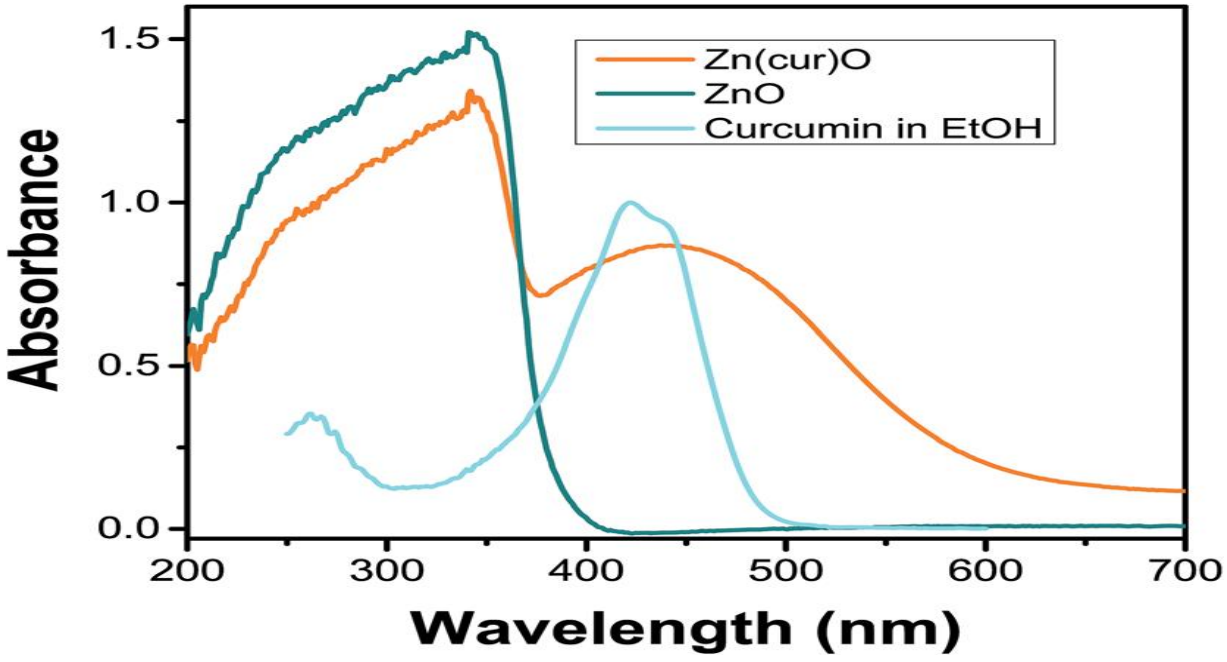


Fig 3.9: Graphical representation of range of detection [64]

CHAPTER 4

EXPERIMENTAL ANALYSIS

4.1:MATERIALS REQUIRED:

1 .Zinc nitrate Hexahydrate

2 .Potassium Hydroxide

3: Curcumin

4.Acetone

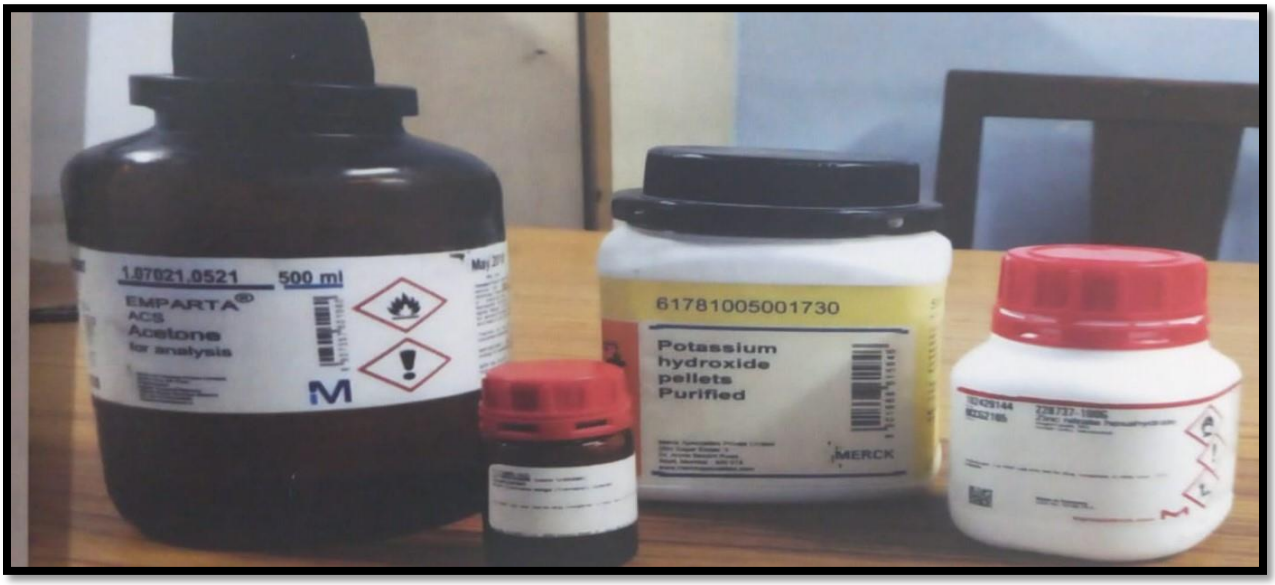


Fig 4.1: Materials used

4.2 DETAILED ANALYSIS OF MATERIALS USED:

1 .Zinc nitrate Hexahydrate:

Zinc nitrate, with the chemical formula $Zn(NO3)_2$, is an inorganic compound. It is a transparent, crystalline salt that readily absorbs moisture from the atmosphere, making it highly deliquescent. Typically, it occurs as a hexahydrate, Zn(NO3)2•6H2O, and is soluble in water as well as alcohol. Its molecular weight is approximately 297.49.

This compound is primarily employed in the synthesis of coordination polymers and serves as a foundational material in the production of zinc oxide-based nanowires. Additionally, it functions as a mordant in dyeing processes and contributes to the creation of a novel microporous zinc phosphate that utilizes organic templates. This microporous zinc phosphate exhibits catalytic properties and has various applications related to microporosity.

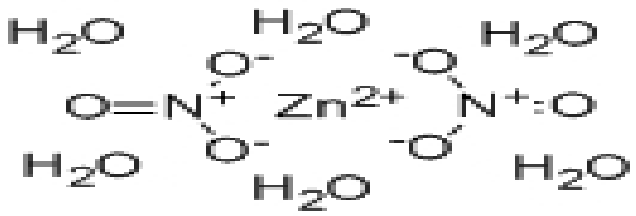


Fig 4.2: Chemical structure of zinc nitrate hexahydrate

Some of its key chemical properties:

- Molecular weight: The molar mass of zinc nitrate hexahydrate is approximately 297.49 g/mol.
- Physical appearance: It is a colorless crystalline solid that is commonly found in the form of white or transparent crystals.
- Solubility: Zinc nitrate hexahydrate is highly soluble in water. It readily dissolves in water to form an aqueous solution.
- Hygroscopicity: It is hygroscopic, meaning it has a tendency to absorb moisture from the surrounding environment.
- Decomposition: Upon heating, zinc nitrate hexahydrate decomposes to release nitrogen dioxide (NO_2), oxygen (O_2), and water (H_2O). The decomposition occurs around 40-50°C (104-122°F).
- Oxidizing properties: Zinc nitrate hexahydrate is considered an oxidizing agent. It can react with reducing agents and potentially cause combustion or explosive reactions.
- pH: When dissolved in water, the resulting solution is acidic due to the presence of nitrate ions, which can contribute to the production of hydrogen ions (H+).
- Reactivity: It can react with various substances, such as alkalis, metal hydroxides, carbonates, and bicarbonates, forming different zinc compounds and releasing nitrate ions.
- Zinc nitrate hexahydrate finds applications in various fields, including the synthesis of other zinc compounds, as a mordant in dyeing and printing textiles, in the production of catalysts, and as a corrosion inhibitor.

Fig 4.3: Zinc nitrate hexahydrate

2 .Potassium Hydroxide:

Potassium hydroxide (KOH) is an inorganic compound with the chemical formula KOH and is commonly referred to as caustic potash. It is classified as a strong base, along with sodium hydroxide (NaOH). This compound finds extensive use in various industries due to its caustic nature and high reactivity with acids. KOH serves as a crucial precursor for the production of soft and liquid soaps, as well as many potassium-containing chemicals utilized in diverse fields. It exists as a white solid with significant corrosive properties

The properties of KOH can be summarised as follows:

- Physical state: Potassium hydroxide is a white, odorless solid at room temperature. It is highly hygroscopic, meaning it readily absorbs moisture from the air, forming a slippery liquid.
- Solubility: Potassium hydroxide is highly soluble in water. It forms a strongly alkaline solution known as potassium hydroxide solution or potassium hydrate.
- Corrosive nature: Potassium hydroxide is a strong base and a highly corrosive substance. It reacts exothermically with acids and can cause severe burns if it comes into contact with the skin or eyes. Precautions should be taken when handling it.
- Alkalinity: Potassium hydroxide is a powerful alkali. Its aqueous solution has a high pH and can neutralize acidic substances. It is often used as a pH adjuster in various industries.

- Chemical reactivity: Potassium hydroxide is a versatile compound that participates in various chemical reactions. It reacts with acids to form salts and water, and it reacts with carbon dioxide to form potassium carbonate.
- Use as an electrolyte: Potassium hydroxide is commonly used as an electrolyte in alkaline batteries, including certain types of rechargeable batteries such as nickel-metal hydride (NiMH) batteries.
- Industrial applications: Potassium hydroxide has several industrial applications. It is used in the production of detergents, soaps, and other cleaning agents. It is also employed in the manufacturing of potassium salts, dyes, and pharmaceuticals. Additionally, it is utilized in industries such as food processing, oil refining, and chemical synthesis.

It is important to handle potassium hydroxide with care due to its corrosive nature. Proper protective equipment should be used when working with this compound, and it should be stored securely to prevent accidental exposure.

Fig 4.3: Potassium Hydroxide Pellets

3: Curcumin:

Curcumin is a bright yellow chemical produced by plants of the Curcuma longa species. It is the principal curcuminoid content of turmeric (Curcuma longa), a member of the ginger family, Zingiberaceae. It is commonly sold as a herbal supplement and used as an ingredient in cosmetics, food flavoring, and food coloring.

Chemically, curcumin is a diarylheptanoid and belongs to the group of curcuminoids, which are phenolic pigments responsible for the yellow color of turmeric.While curcumin has been extensively studied in laboratory and clinical research, no confirmed medical uses have been established thus far. Its instability and poor bioavailability make it challenging to study, and it is unlikely to lead to significant advancements in drug development [52].

Curcumin finds its most common applications as an ingredient in dietary supplements and cosmetics. It is also used as a flavoring agent in turmeric-flavored beverages in South and Southeast Asia and as a coloring agent in foods like curry powders, mustards, butters, and cheeses. In the European Union, it is assigned the E number E 100 as a food additive for orange-yellow coloring. Additionally, the U.S. FDA has approved its use as a food coloring in the United States [53].

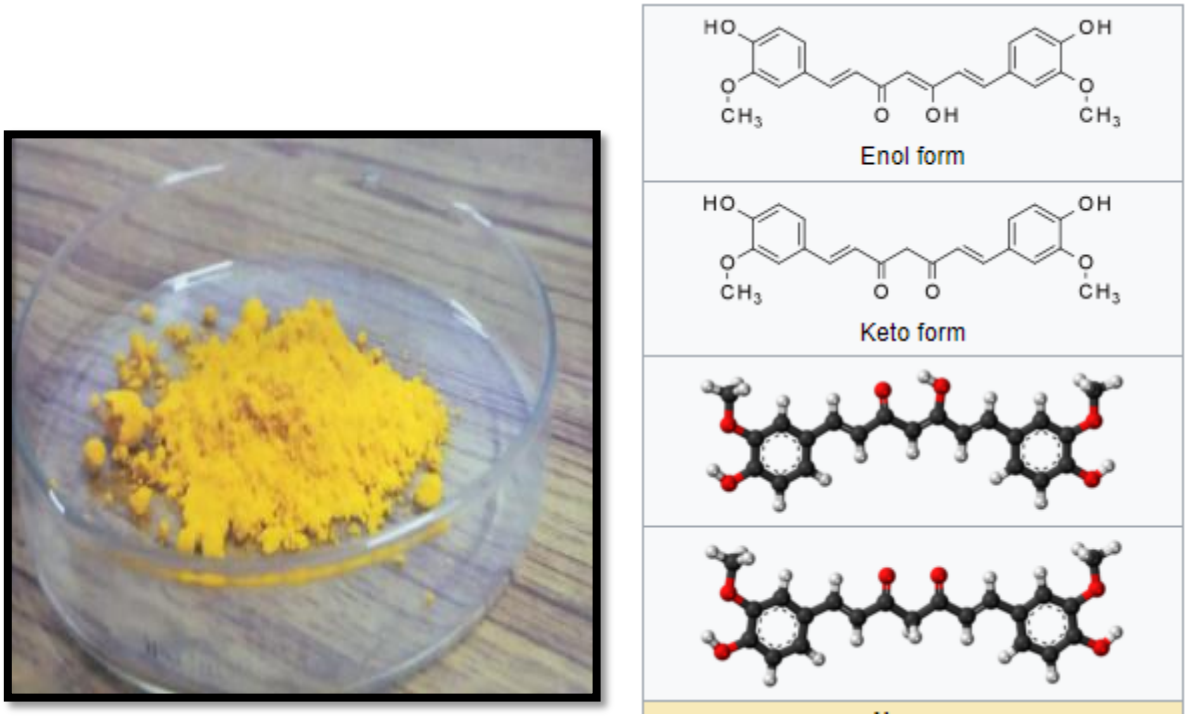


Fig 4.4: Curcumin

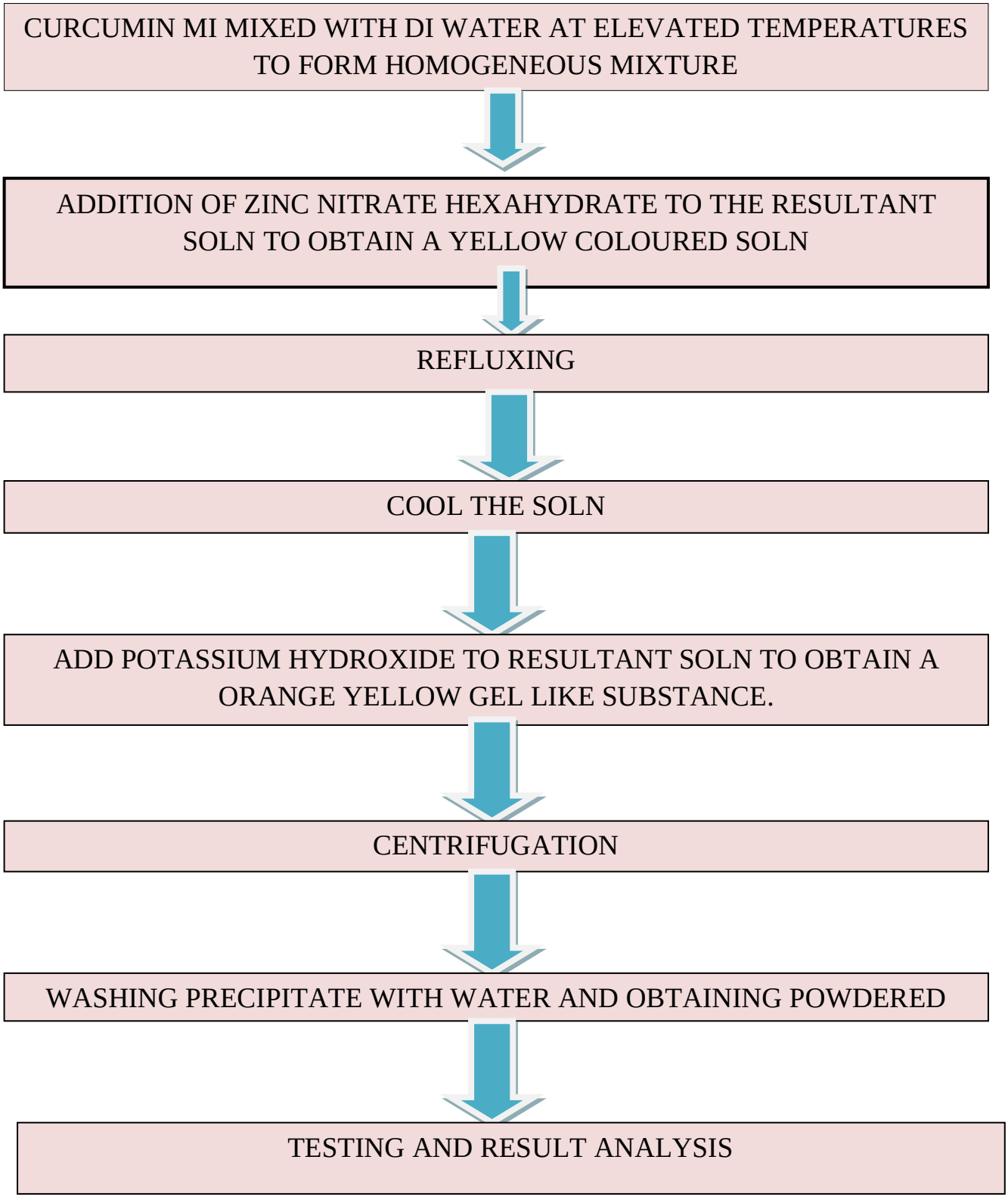
4. Acetone:

Acetone, also known as 2-propanone or dimethyl ketone, is an organic compound represented by the formula (CH3)2CO. It is the simplest and smallest ketone molecule, containing a carbonyl group (>C=O). Acetone is a colorless, highly volatile, and flammable liquid with a distinctive pungent odor. It is widely used as an organic solvent in various industries, households, and laboratories. In 2010, approximately 6.7 million tonnes of acetone were produced worldwide, primarily for its applications as a solvent and for the production of methyl methacrylate and bisphenol A, both of which are important precursors in the manufacturing of plastics. Acetone is also commonly utilized as a building block in organic chemistry.

Due to its miscibility with water, acetone is often employed as a solvent in household products such as nail polish remover and paint thinner. Notably, it has been granted volatile organic compound (VOC)-exempt status in the United States. Acetone is naturally produced and eliminated from the human body through normal metabolic processes. It is normally present in the blood and urine of individuals. However, individuals with diabetic ketoacidosis tend to produce larger amounts of acetone. Additionally, ketogenic diets, which elevate ketone bodies (including acetone, β-hydroxybutyric acid, and acetoacetic acid) in the bloodstream, are utilized to manage epileptic seizures in children with refractory epilepsy.

Fig 4.5: Acetone

4.3 FLOWCHART



4.4 PROCESS FLOW:

STEP 1:

A solution was prepared by taking 2.0 mg of curcumin in 50 mL of double distilled water (close to neutral pH) at 80–90 C.

It was made to rotate using a magnetic stirrer until the solution became comoletely homogenous.

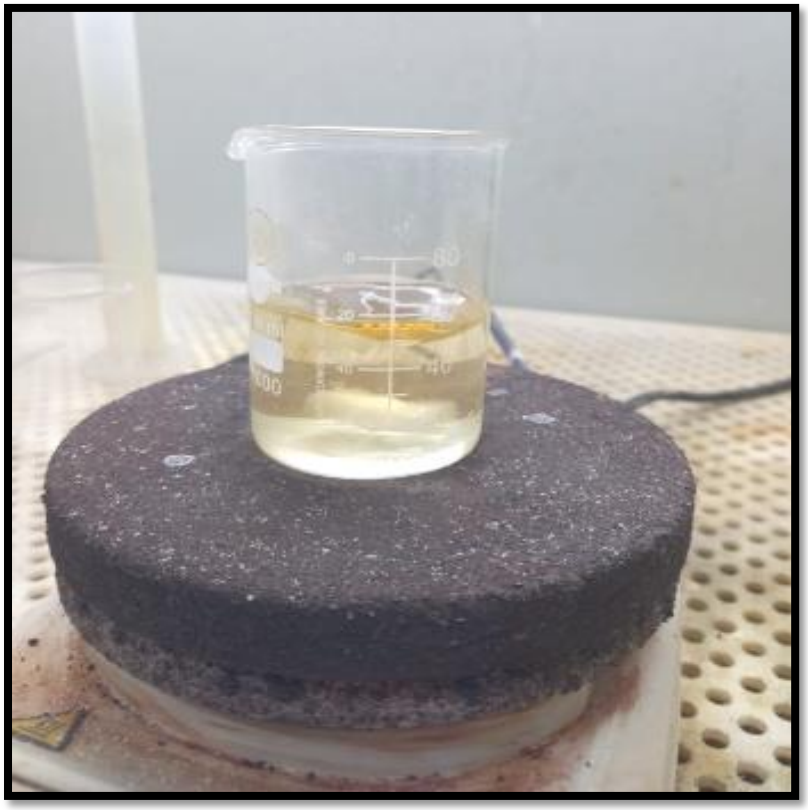


Fig 4.6: Preparation of above mentioned solution

STEP 2:

50 mL of 0.1 M Zn(NO3)2 solution prepared in double distilled water and was added to the solution.

CALCULATION INVOLVED:

SR NO	ELEMENT	MOLECULER WEIGHT (in g)
1	Hydrogen	1.00784
2	Oxygen	15.999
3	Nitrogen	14.0067
4	Zinc	65.38

Hence molecular weight of Zinc nitrate hexahydrate = [65.38+(14.0067*2)+(15.999*3*2)+(6*1.00784*2)+(15.99986)g

= 297.475g

=297.5g approx

Now 1 mole or 1000ml of Zinc nitrate hexahydrate =297.5g

Hence 1 mole 1ml of Zinc nitrate hexahydrate=297.5/1000 g

Hence 1 mole 50ml of Zinc nitrate hexahydrate=297.5/1000*50 g

Hence 0.1 mole 50ml of Zinc nitrate hexahydrate=(297.5/1000*50*0.1) g

= 1.4875g

= 1.5 g approx

Therefore here we have used 1.5 g of Zinc nitrate hexahydrate

STEP 3:

The resultant yellowish solution was refluxed for 1 hour at 85–90 C.

Since a condenser was unavailable, we covered the beaker containining the solution with a petri dish and filled it with ice cold water, changing it from time to time once it got hot.

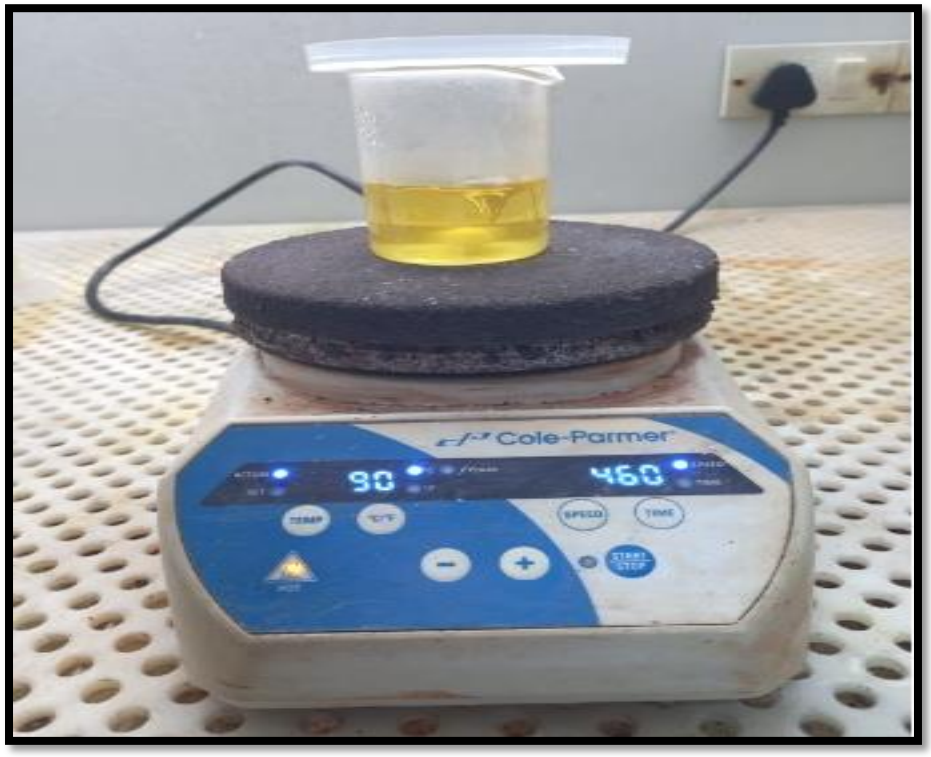


Fig 4.7: Representation of above mentioned step

STEP 4:

The solution was cooled down and 5 mL of 0.2 M KOH was added slowly at 4 C.

After that an orange yellow gel-like suspension was observed.

CALCULATION INVOLVED:

SR NO	ELEMENT	MOLECULER WEIGHT (in g)
1	Hydrogen	1.00784
2	Oxygen	15.999
3	Potassium	39.0983

Hence molecular weight of Potassium hydroxide = [39.0983+1.00784+15.999]g

= 56.105g

=56 g approx

Now 1 mole or 1000ml of Potassium hydroxide=56g

Hence 1 mole 1ml of Potassium hydroxide =56/1000 g

Hence 1 mole 5ml of Potassium hydroxide =56/1000*5 g

Hence 0.2 mole 5ml of Potassium hydroxide =(56/1000*5*0.2) = 0.056g

This being an extremely meagre amount we have used 20ml 0f 0.2mole(KOH) or 1.12g of KOH instead

Fig 4.8: Representation of orange yellow gel formed

STEP 5:

The solution was centrifuged at 2000 rpm and the precipitate was washed with water till no more yellow color was observed in the supernatant. The process was repeated thrice.

Acetone washes were necessary to remove any unanchored curcumin after which the final wash was with water.

STEP 6:

The precipitate Zn(cur)O was vacuum dried at room temperature by placing it in a dessicator

Fig 4.9: The precipitate being vaccuum dried in a dessicator

A white powdery substance was obtained.

Fig 4.10: White powdery substance obtained

It was stored in a vial for future use.

Fig 4.11: Representation of powder formed and stored in vial

4.5 RESULT:

A variety of samples were prepared and the effect of the obtained sample on each was observed as follows:

Fig 4.12: Arrangement for testing

CASE 1:

Arsenic trioxide (0.5mg) was mixed in 25 ml propanol and heated. The clear liquid thus obtained was subjected to 0.5g of the sample

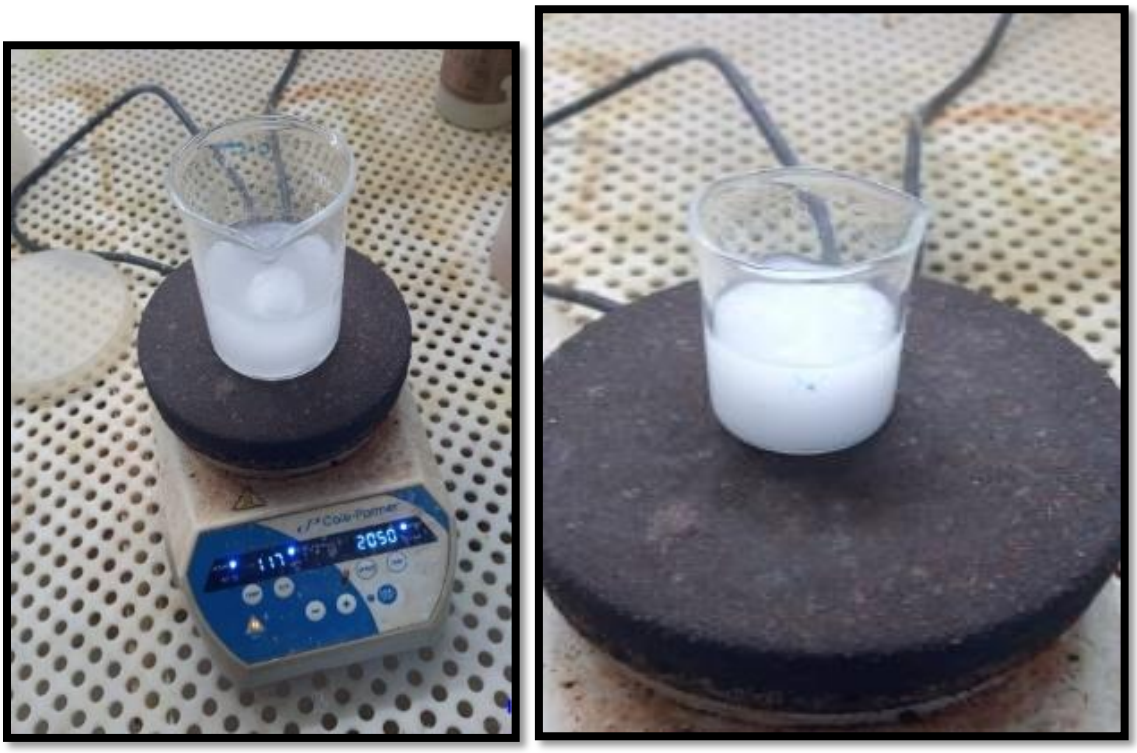


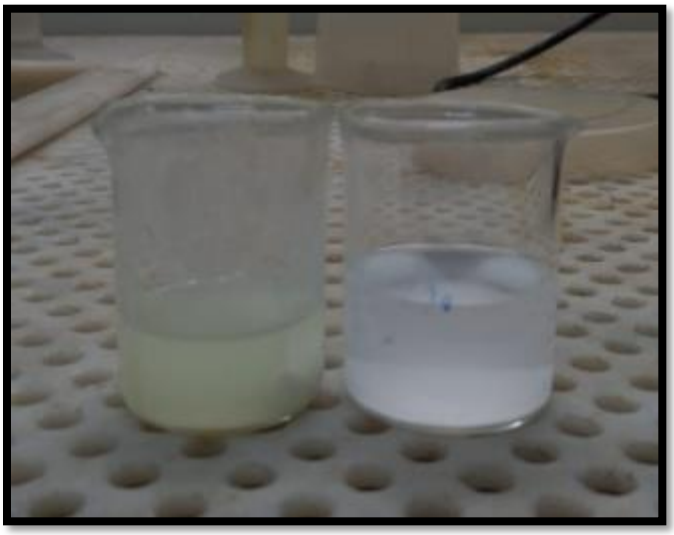
Fig 4.13: Initial stage Final form

A white colloidal mixture was obtained as a result. This is evident from the above figure.

CASE 2:

The sample(1g) was added to natural arsenic containing pond water.On heating the sample with a magnetic stirrer a white coloid was seen with a pale greenish hue at the bottom which fi finally on rest formed a colloid like solution with pale greenish hue in white.

Fig 4.14: Water before mixing sample final result



Natural water vs propanol(result on adding sample**)**

CASE 3:

Arsenic trioxde was added to a a solution 50ml DI water and 25ml water. Rsenic trioxide was barely soluble in water and formed smal globules.

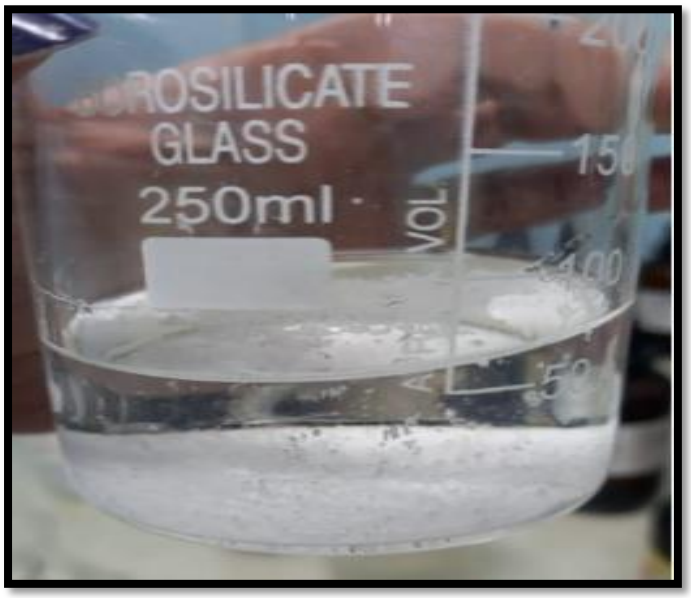


Fig 4.16: arsenic trioxide forming globules in water

CASE 4:

The sample (1g) was added to extreme high concentration of arsenic containing water. It showed a faint green colour.

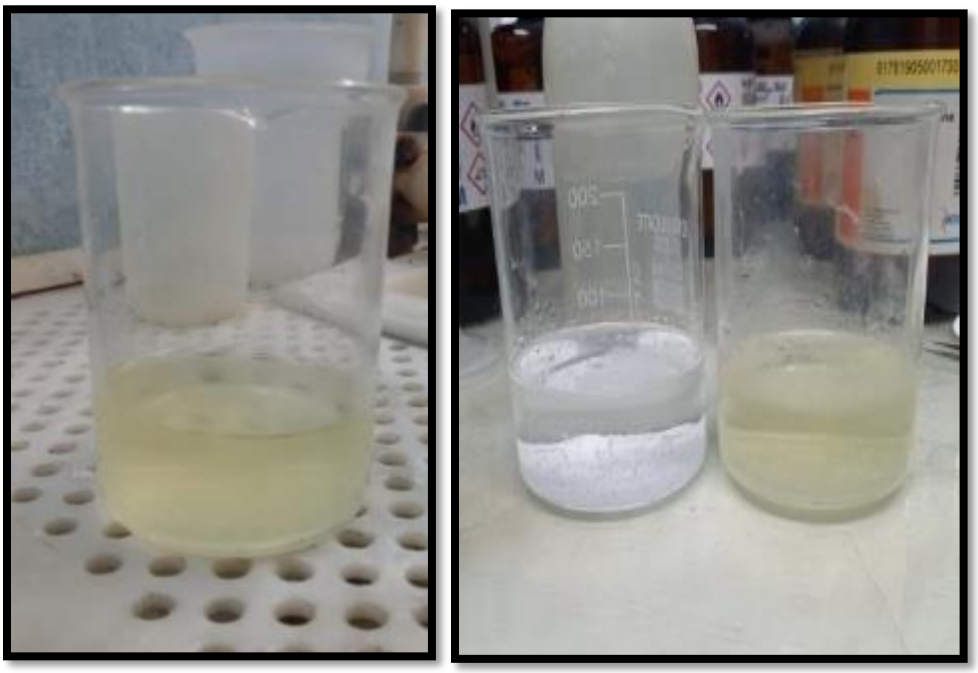


Fig 4.17: DI water vs arsenic contaminated water with sample added

4..6 DISCUSSION

The results were varied and did not exactly match with the estimated outcome. While the theory proposed a strong fluorescent characteristic in the water , the results demostrated only a faint green hue in the same.

Nevertheless the obtained sample showed a colour change in arsenic containing water and hence can be used for detection of arsenic in water.

CHAPTER 5

CONCLUSION AND FUTURE SCOPES

5.1CONCLUSION:

In this thesis a discussion has been made on the toxicity of arsenic and why is it fatal for consumption. The arsenic issue is one of the major problem of present day world. We have also discussed the arsenic contamination around the globe with special emphasis onWest Vengal and India.

While numerous ways of arsenic detection has been researched in the past, we have heremade an attempt to modify nanomaterials and develop a method that detects arsenic easily and can be easily made available to every household.

Likewise a discussion was made on why Zinc oxide was chosen and modified with curcumin and how it rendered the resultant sample to be fluorescent. Experiments were then performed after manufacturing the sample on propanol and arsenic containing water and varied results results were obtained.

Though only a weak colour change was obtained, yet it helped in the detection of arsenic. We believe that this shall in time prove to be beneficial for detection of arsenic in drinking water and help humanity in avoiding the risk of consuming arsenic contaminated ground water.

5.2 FUTURE SCOPES:

The present results have the following future scopes for improvement

- The obtained sample can further be incorporated on a non reactive insulating material like glass or alumina to form a sensor. For this the sample has to be mixed with some kind of neutral paste offering adhesive properties. The sensitivity and reactivity of the sensor are subject to experimental analysis.
- Likewise a sensor shall be obtained which can be used permanently by every household for detection of arsenic in water.

In general future scopes for arsenic detection may involve advancements in the following areas:

- Miniaturization and portability: There is a growing interest in developing portable and field-deployable arsenic detection devices that can be used in resource-limited settings or for on-site testing. Advancements in microfluidics, nanotechnology, and sensor

integration may contribute to the development of compact and user-friendly detection platforms.

- Selectivity and sensitivity: Improving the selectivity and sensitivity of arsenic detection methods remains a key focus. Researchers are exploring novel materials, such as nanomaterials and molecularly imprinted polymers, which can enhance the specificity and detection limits of arsenic sensors.
- Real-time monitoring: Real-time monitoring systems that can provide continuous data on arsenic levels in water sources or industrial settings are of great interest. Integrating arsenic detection technologies with wireless communication and data analysis platforms could enable real-time monitoring and early warning systems for arsenic contamination.

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