Detection and Quantification of Arsenic in Contaminated Drinking Water Using Electronic Tongue

Sujeevan Kumar Agir

Department of Chemical Engineering
National Institute of Technology Rourkela

Detection and Quantification of Arsenic in Contaminated Drinking Water Using Electronic Tongue

Dissertation submitted in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy

in

Chemical Engineering

by

Sujeevan Kumar Agir

(Roll Number: 512CH6010)
based on research carried out
under the supervision of
Dr. Madhusree Kundu

January 2019

Department of Chemical Engineering

National Institute of Technology Rourkela

Department of Chemical Engineering
National Institute of Technology Rourkela

Dr. Madhusree Kundu
Professor

11th June, 2019

Supervisor’s Certificate

This is to certify that the work presented in the dissertation entitled "**Detection and Quantification of Arsenic in Contaminated Drinking Water Using Electronic Tongue"** submitted by **Sujeevan Kumar Agir,** Roll Number **512CH6010**, is a record of original research carried out by him under my supervision and guidance in partial fulfillment of the requirements of the degree of *Doctor of Philosophy* in *Chemical Engineering.* Neither the dissertation nor any part of it has been submitted earlier for any degree or diploma to any institute or university in India or abroad.

Date: **(MADHUSREE KUNDU)**

Dedication

I dedicate my dissertation to my mother Smt. Suguna Agir, my father Sri. Laxmaiah Agir, my wife Smt. Priya Darshini Kumari and my supervisor Prof. Madhusree Kundu without whom my successful pursuit of Ph.D. would be impossible.

Declaration of Originality

I, *Sujeevan Kumar Agir*, Roll Number *512CH6010* hereby declare that this dissertation entitled *Detection and Quantification of Arsenic in Contaminated Drinking Water Using Electronic Tongue* presents my original work carried out as a doctoral student of NIT Rourkela and, to the best of my knowledge, contains no material previously published or written by another person, nor any material presented by me for the award of any degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this dissertation have been duly acknowledged under the sections “References”. I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present dissertation.

June 11, 2019 **(SUJEEVAN KUMAR AGIR)**
NIT Rourkela

Acknowledgement

When we started to work on the project, many doubted the fate of the inter-disciplinary work undertaken by an electronics engineer in the department of chemical engineering. The reason I chose to work on this project was because of its social relevance. I am a person who believes every engineer should have productive output useful to the society and the project directly fit into something I would love to do.

When your passion is fueled with the blessings of ever-loving and “never-say-no” parents, support of an understanding and doting wife, best wishes from wonderful friends surrounded by you and the best guidance from your supervisor, then something great is bound to happen. I believe the same happened in my life.

I am very thankful to my friend Mr. J Bhaskara Rao who is responsible for tagging me to my supervisor Dr. Madhusree Kundu. I am very lucky to have worked under guidance of a passionate supervisor who, with unselfish dedication, invested a lot of time and personal money in getting the project done. Apart from the professional help, she imparted me high morale, never-give up attitude and never-compromising, stern work ethics, which I shall hold and follow for the rest of my life. The playful evenings I spent with cheerful Khushi are unforgettable.

Only with the support and coordination of many individuals, I could pull out the feat of reaching to a logical conclusion of my research. I miss my first friend at Ph.D., Late Ms. Deepthi Thirumalaraju who helped me a lot to settle in the new place when I moved in to this campus. It grieves me to know that she is not by my side as I complete my work.

My sincere thanks to Dr. Palash Kumar Kundu, Assoc. Prof., EEE Dept., Jadavpur University, a very honest human being and one of the finest researchers I met personally, for giving constant motivation and valuable inputs regarding my work.

I was blessed with abundance of wonderful friends Zefree Lazarus, Sureshkumar Ayyalusamy, Charan Kumar Ala, Mamatha, Venkatesh Pilli, Vinay Sagar Kommukuri, Tatinaidu Kella, Nidhi Panda, Visweswara Rao Samoju, Om Sahu, Anand Babu, Seshu Kumar Damerla, Mr. & Mrs. Sharath Chandra, Raju Moola and Gopi Krishna to name a few with whom I shared my highs and lows and are a big reason for my cheerful days at NITR. The endless debates on Friday nights to midnight birthday celebrations across Naga pond to daily evening tea breaks at sector-1 to relishing homemade delicacies from the house of Venkatesh Pilli to evening badminton plays to the dinner parties for every petty reason, I have had a handful of memorable events to cherish during my stay at NITR. The smiling faces of the security guards as I pass through the gates made me forget my day’s tiredness.

My special thanks to Dr. Archana Mallik, Asst. Prof., Metallurgy Dept., Sureshkumar, Jayarao Gorinta, Sivamani, Debalaxmi Pradhan, Namrata Jaiswal, Prince George, Gaurav, Ujjal Mandal, Praneeth, Rahul Purbia, Suresh Chaluvadi and Alok Ranjan for their timely help in lending me the apparatus when I fell short of and Ms. R Subhashini, Asst. Prof., EE Dept., Dr. D. P. Acharya, Assoc. Prof., ECE Dept., Dhiman Das and Sams Akhtar for doing necessary help required to get the PCB printed for experimentation. My sincere thanks to Mr. Ayas

Kanta Sahoo, Asst. Prof., ECE Dept. and Tarun Kumar for their guidance in helping me clear my course work. I am indebted to Mr. Kumar Prabhanjan Panigrahi, Asst. Registrar (Academic) and Mr. M N Anand Babu, Asst. Registrar (SRICCE) for their timely advices at various junctures of my Ph.D.

I am grateful to Dr. Abanti Sahoo (Chairman, DSC) for taking extra effort in expediting the process of filing the patent and Dr. Mukesh Gupta, Assoc.Prof., BME Dept., for guiding through the process. I am glad to be associated with Dr. Basudeb Munshi, DSC member, who practices a disciplined lifestyle. Dr. Munshi had been very understanding, cooperative and always gave proper advice in the hour of the need. I am thankful to DSC members Dr. H. B. Sahu and Dr. Arvind Kumar, for the productive scrutiny and advice throughout the Ph.D. programme. I also thank Department of Science & Technology, Government of India, for partially funding our research work under Water Technology Initiative scheme.

I am glad I was part of Thirdeye, photography club of NITR and Cinematics, movie-making club of NITR. These experiences made me close to many friends and helped me learn more about shooting still and motion pictures. Special thanks to my lab mates, Seshu Kumar Damerla, Shubhashis Adak and Sayantani Sikder for the good times we had together.

I am greatly indebted to Sri. K. S. Ravi Kumar, Chairman, Jayaprakash Narayan College of Engineering, Mahabubnagar for financially supporting me during my research. I am lucky to have friends like Kedarinath Kandikonda, Kiran Kumar Burugu, Shravan Kumar Madireddi, Nagendra Kumar Perabattula, Mohammad Yasin, Sivaram Subramani and Murali Pullari who I can turn to when my going gets tough and I always find a solution.

Lastly, but most importantly, I am always thankful to my parents and my siblings – Vijay Kumar Agir & Srilaxmi Kandikonda who extend their unconditional support to every effort I put in, to my wife for agreeing and supporting me in my decision to leave a lucrative job of software engineer and pursue research and to my extended family Prashanthi, Kedarinath Kandikonda, Hansini, Suhaas, Shiva Rani, Aruna Rani, Vijaya, Tanisha, Sneha, Lakshmi Gupta and Soniya Rani.

Sujeevan Kumar Agir

Abstract

Arsenic poisoning is a serious challenge faced by many countries, which is caused by ingestion through drinking water. Lack of rapid analysis methods/tools is a reason for millions of people unaware about of the arsenic content, consume water from aquifers affected with arsenic contamination. A novel hardware-software combination (electronic tongue) has been developed that is economic, easy to use and highly portable and can be deployed for on-site analysis of water samples. The e-tongue makes use of anodic stripping voltammetry for arsenic detection and it was tested across a varying range of arsenic concentrations ranging from 5 ppb to 250 ppb. Copper interference studies also proved the proposed solution is unaffected by presence of copper in the sample being analysed for detection and estimation of arsenic. Further field samples collected from various sites in the 24 paraganas district of West Bengal state were analyzed and the results were validated with those produced by AAS. The proposed solution has a great potential for large-scale deployment to enable mass analysis of aquifers in the areas affected by arsenic contamination

Keywords**:** arsenic, arsenic poisoning, potentiostat, arsenic detection, e-tongue, electronic tongue, anodic stripping voltammetry

Table of Contents

List of Figures

List of Tables

1 INTRODUCTION

Water is life. Safe drinking water is every individual's basic need for survival. 97% of the planet's water is present in the form of oceans. While 3% of earth's water is fresh water, more than two-thirds of it is present in frozen form in Antarctica and Greenland, which is not accessible to humans for consumption. Most of the drinking water needs are fulfilled by ground water, which caters to agricultural and industrial requirements as well. Such a scarce, critical resource suffers from various contaminations, which includes manmade pollution caused by agricultural and industrial practices. These contaminated waters cause adverse health effects upon consumption. Arsenic contamination or "arsenic poisoning" of drinking water is one such serious problem that is daunting many countries. Arsenic is a carcinogenic heavy metal and the problem is aggravated because it is naturally abundant in geological deposits and seeps into drinking water when they both make contact. Millions across the globe have already been adversely affected by arsenic poisoning. The main challenge is to detect the presence of arsenic beyond safe limits and mark the aquifers accordingly. The present analytical techniques suffer from various limitations and major setback is that they are all laboratory based. With millions of tube wells in operation, which provide drinking water, it is impractical to analyze or monitor arsenic levels using lab-based techniques. This research is an attempt to provide an economic, portable, safe, easy-to-use, reliable analytical instrument for quantification of arsenic that can be taken to the site in arsenic-prone areas for rapid analysis.

This chapter outlines the severity of arsenic problem, discusses the present established analytical techniques for detection of arsenic, sets objective and scope of the work and explains how the rest of the report is organized.

1.1 The Arsenic Problem

In the wake of first case of "arsenic-poisoning" in 1983, the world has learnt a shocking fact that around 140 million people across the globe consume drinking water contaminated with unacceptable amounts of arsenic. Arsenic is naturally available in terms of geological deposits in ground water and artificially added by industrial/agricultural practices and it made its way into human food chain through drinking water. Countries that are significantly affected with arsenic contamination of ground water are Argentina, Bangladesh, Chile, China, India, Mexico, Taiwan, Thailand and the United States. Bangladesh is the worst-struck nation with 30 to 60% of its population at the risk of consuming arsenic contaminated water. Long term ingestion of water contaminated with arsenic would lead to adverse health effects ranging from skin lesions to bladder, skin and lung cancers [1,2]. The provisional guideline value set by World Health Organization (WHO) for arsenic in drinking water is 10 µg/L. As(III) and As(V) are the most wide spread forms of arsenic of which As(III) is as much as 50 times more toxic than As (V) [3,4].

The report submitted by a team of researchers after an extensive survey across Ganga-Meghna-Brahmaputra plain inhabited by a population of more than 500 million, after analyzing water samples from 220,000 tube wells conveyed various alarming facts. Ground water contamination was tested in 64 districts of Bangladesh and of them, people from 51 districts (inhabited by a population of more than 130 million) were found to be consuming water containing arsenic more than 50µg/L, which is 5 times higher than the safe limit set by WHO. Out of the analyzed water samples from 140,150 tube-wells in the state of West Bengal, India, 23.8% of them were containing more than 50 µg/L of arsenic, 3.3% of the samples had arsenic concentrations more than 300 µg/L while 48.1% of them had concentrations above 10 µg/L. Similar results were found from analysis of water samples collected from Bihar, India where 17.75% of the samples contained more than 50 µg/L and 4.55% of the samples contained more than 300 µg/L of arsenic [5]. Unaware of these details, millions of people living in the Ganga-Meghna-Brahmaputra plain are at the risk of arsenic poisoning. Such a huge threat prevails because of lack of analytical equipment that could rapidly and accurately analyze water samples in bulk and quantify the amount of arsenic present.

1.2 Arsenic Analytical Methods Proposed by WHO

WHO, in their guidelines for drinking water quality, have proposed silver diethyldithiocarbamate spectrophotometric method, graphite furnace atomic absorption spectroscopy (GF-AAS), hydride generation atomic absorption spectroscopy (HG – AAS) and inductively coupled plasma - mass spectrometer (ICP-MS) for detection of arsenic upto as low as 1 µg/L [1,4]. These methods are discussed briefly in the following subsections.

1.2.1 Atomic Absorption Based Techniques

These techniques are based on AAS, which has three major components:

i. An emitter of light of specific wavelength
ii. A light detector that has knowledge of the wavelengths corresponding to various energy levels of analyte atoms
iii. An atomizer placed in between emitter and detector which volatilizes the analyte

As the analyte atoms come in contact with the light emitted by the emitter, the electrons of the analyte atom absorb energy from the incident light and moves to higher energy state. The energy absorbed by the electron corresponds to a particular wavelength, which is a characteristic of the analyte. Eventually, the detector will receive light with part of it attenuated. This attenuated light is basis to determine the concentration of analyte because it is proportional to the quantity of the analyte present in the sample. Figure 1.1 represents a schematic of an AAS [4,6]. Based on the nature of the atomizer, AAS techniques are categorized into various techniques.

The GF-AAS technique involves an open-ended graphite tube, which is placed in the path of the light from the emitter. The graphite tube is used as the atomizer, which is heated to as much as 3000°C which volatilizes the analyte. This method is faster than the conventional flame-based AAS and has got higher sensitivity than the former. The detection limits with GF-AAS can go as low as 1 µg/L of arsenic in the sample. The graphite tube method is more efficient atomizer than the flame-based AAS. Though GF-AAS can detect lower

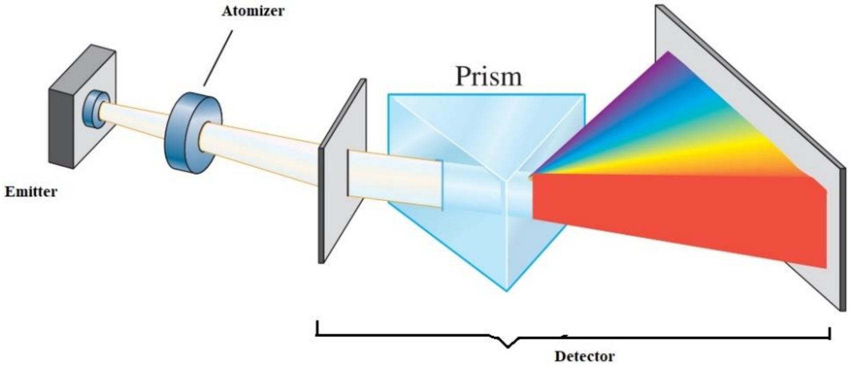


Figure 1.1 Block schematic of an AAS setup [6]

concentrations of arsenic, this method is expensive, time consuming and suffers from interference from other chemical processes [6,7].

The HG-AAS technique makes use of zinc or sodium tetrahydroborate for volatilization of the analyte. In acidic medium, zinc or sodium tetrahydroborate produces hydrogen that forms arsine gas (AsH_3) with As(III) present in the analyte.

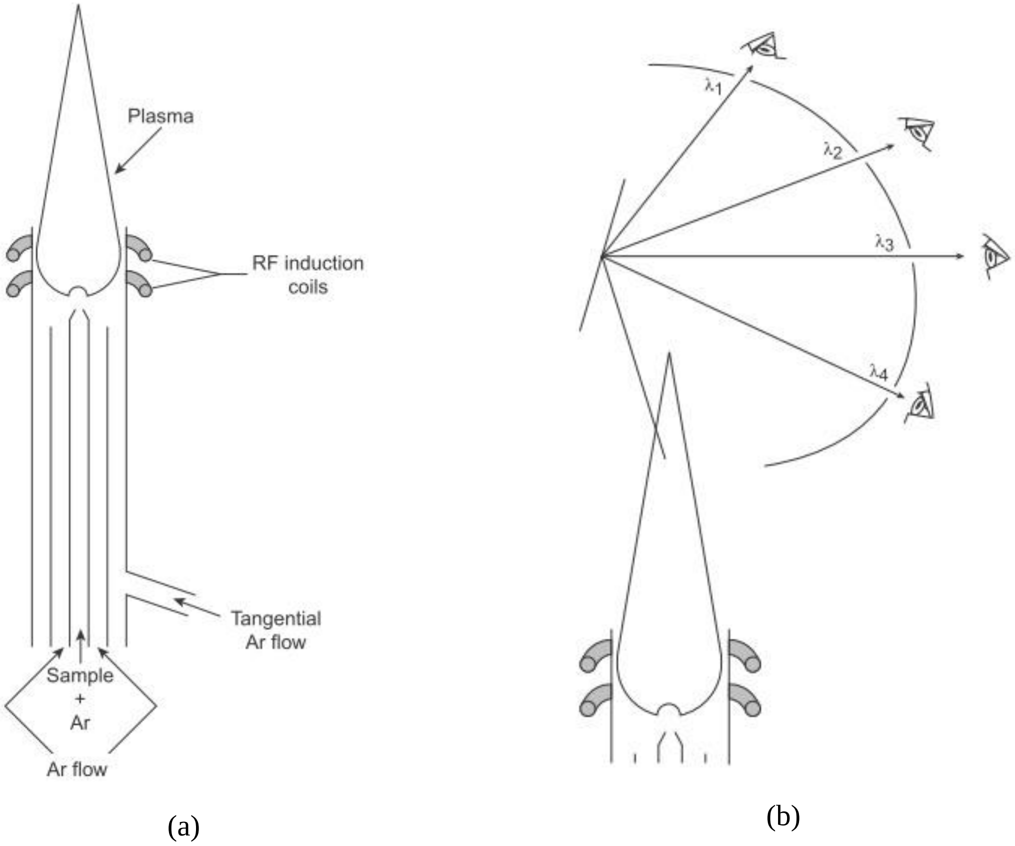
$$6H_2(g) + As_2O_3(aq) \rightarrow 2AsH_3(g) + 3H_2O \qquad 1.1$$

The arsine gas emitted gives direct measure of the quantity of arsenic present as it is directly proportional to the concentration of arsenic present in the sample. However, formation of arsine gas is very slow with As(V). Therefore, it is a regular practice to first reduce As(V) to As(III) before analyzing the sample. Concentrations as low as 2 µg/L can be detected using this technique.

Major limitation of AAS based techniques is the requirement of the lamp that emits the light, which falls in the spectrum of the analyte. Therefore it is expensive to maintain various lamps one each for an analyte [7,8].

1.2.2 Inductively Coupled Plasma Based Techniques

This is the foremost technique that involves absorption/emission of energy at atomic level. Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) or ICP – OES (for Optical Emission Spectroscopy), as the name indicates, works on detection of the emission from the analyte atom in contrast to AAS techniques, which works on detection of the light portion absorbed by the analyte atom. This technique involves a torch arrangement, which acts as the atomizer. Sample is introduced into the torch along with argon gas as a carrier, which is heated by RF magnetic coils to very high temperature as much as 10,000 K (Figure 1.2 (a)). This generates the required plasma for the experiment. The analyte is then nebulized and introduced into this plasma resulting in complete volatilization of the sample. The shell electrons of the analyte atoms then sent to cooler portions of the flame where they come back to lower energy levels by emitting photons with wavelength corresponding to the difference in energy levels. The wavelength is a characteristic of the analyte and the intensity of that particular wavelength gives direct information about the amount of analyte present in the sample. ICP-AES is very efficient in detecting multiple analytes simultaneously; as many as 20 (Figure 1.2 (b)). However, the detection limits achieved are upto 35 µg/L, which is way above the WHO limit.



(a) (b)

Figure 1.2 (a) Schematic of an ICP-AES torch (b) Schematic showing photons filtered at various wavelengths at the detector [7]

Though ICP-OES individually cannot be employed for arsenic analysis in drinking water, we can couple this technique with Mass Spectrometry (MS) to achieve lower detection limits as low as 0.1 µg/L. In ICP-MS technique, the output from ICP-OES is introduced into a chamber under the influence of magnetic field, which causes deflection of the waves. The defected path depends on the analyte concentration. With such a low detection limit for arsenic, ICP-MS is also accepted by analysts for testing drinking water. However, this technique is also restricted to laboratory as the case with AAS.

1.2.3 Field Test Kits Based on Colourimetry (Gutzeit Method)

Most of the field kits commercially available in the present day for arsenic testing in drinking water are Gutzeit method based. The technique involves reducing As in the sample to arsine gas (AsH_3) proportional to the quantity of arsenic present in the sample. The arsine gas is allowed to pass over a test paper strip coated with mercury bromide, which changes color according to the quantity of arsine gas it is exposed to. The intensity of the color is an indicator of the arsenic concentration in the sample.

The chamber where As is reduced, contains zinc in acidic medium, which releases H_2 and reduces arsenic for the production of arsine gas as given in Eq. 1.1. The generated arsine is passed through a chamber containing glass wool treated with lead acetate that traps any interfering hydrogen sulfide from the gas if present. As (V) is slower in forming arsine gas – there to get best results, it is a regular practice to reduce any As(V) present in the sample to As (III) with KI and $SnCl_2$.

Though Gutzeit method based field kits are the most used owing to their high portability, they suffer from major limitations such as poor accuracy, low sensitivity and higher detection limits (usually 10 to 50 µg/L). Large-scale deployment of these kits did not happen owing to toxic mercury and lead containing waste generated from them. Moreover, the arsine gas generated in the process is a hazardous gas injurious to the health of the operator.

1.2.4 Limitations of Analytical Methods Proposed by WHO

All the analytical methods proposed by WHO (except Gutzeit method) are laboratory based, involve heavy investment cost and hence cost per sample analysis is very high. They are not portable and hence are operated far from the sample site, which drastically increases the turnaround time for analysis of samples. Moreover, trained personnel are required to operate that equipment. The operator who uses Gutzeit method is at the risk of getting exposed to toxic arsine gas. Also, there are storage issues of the mercury and lead wastage produced by Gutzeit method. Owing to the high toxic nature of these elements, careful leak-proof disposal mechanism should be in place [9–12].

1.3 Voltammetric Techniques for Arsenic Detection and Electronic Tongue

Anodic Stripping Voltammetry (ASV) is the most popular voltammetric technique employed for arsenic detection in aqueous samples [13–19]. This technique involves controlling a redox reaction with the help of an externally applied voltage on an electrode. This is done in two steps. Firstly, an adequate negative potential is applied to reduce the "electroactive" analyte present in the ambient solution on the electrode.

$$M^{n+} + ne^{-} \rightarrow M^{0} \qquad 1.2$$

In the second step, the voltage on the electrode is being swept in the positive direction starting from the negative voltage. This causes the deposited metal on the electrode to "re-oxidise" and dissolve into the solution.

$$M^{0} \rightarrow M^{n+} + ne^{-} \qquad 1.3$$

During the experiment, the instantaneous input voltage value and the corresponding current out from the solution are recorded and plot with input voltage on x-axis and observed current pattern on y-axis. The resulting plot is called a voltammogram. The peak current from a voltammogram is a characteristic of the analyte and the height of the peak is directly proportional to the amount of analyte present in the sample.

ASV is discussed in greater detail in Section 2.2.2.1. Presently, ASV is the only analytical method approved by USEPA for in situ testing of drinking water for arsenic [20]. This technique has a bunch of merits as compared to other analytical techniques such as being very economic to set up, highly portable, rapid analysis time and requires no pretreatment of the sample. The detection limits with ASV are as low as 0.1 µg/L. Though there were attempts to manufacture field kits based on ASV, they did not perform satisfactorily and suffer from lack of accuracy [21].

With millions of aquifers and tube wells across the world as sources of drinking water, presently there is no feasible, economic and fast enough analytical method that could be employed to diagnose and brand whether a water source is good for consumption. The delay in identifying a contaminated water source is causing more people to consume drinking water from it and thereby exposed to risk of arsenic poisoning. The WHO prescribed analytical methods are very expensive to setup, lab-bound (generally far away from the field of test), methods require extensive training to handle the equipment and demand longer analysis times. Electronic tongue (e-tongue) based detection of arsenic has been constantly gaining popularity over these conventional analytical methods. An e-tongue is an array of sensors (electrodes) that respond through characteristic current responses, which help in analyzing various species in a solution. Favorable factors such as relatively simple instrumentation ease of operation, not so expensive set up, reproducible results with great accuracy and rapid analysis times have made electrochemical techniques to be considered as an alternative to ICP-MS and AAS. Also, electrochemical analytical methods have got potential for large-scale deployment.

1.4 Objective

The prime motive of the research is to develop an economic, reliable, portable, easy-to-use and accurate field kit that can analyze and quantify arsenic in bulk in aqueous samples with rapid analysis time.

1.5 Scope of the Work

The following scopes were laid to accomplish the objective.

- To develop a proof-of-concept model of an e-tongue employing commercial potentiostat that would successfully analyze aqueous samples for arsenic detection and quantification
- To reduce the cost of the e-tongue by replacing the functionality of the commercial potentiostat with cheaper instrumentation that would significantly reduce the cost of the e-tongue setup by 90%
- To validate the results produced by the newly developed e-tongue setup with those produced by AAS.
- To study the interference, if any in the e-tongue based detection and quantification of arsenic.

1.6 Outline of the Thesis

The proposed work is purely inter-disciplinary. Therefore, the contents of the thesis have been drafted with an intention to help electronics engineers/ chemical engineers/chemists, environmental engineers by providing the complementary and necessary information that might be needed if they wish to venture into electrochemical analysis using anodic stripping voltammetry. It was found that not all information required to start-off in this field was available at one place. Hence, deliberately, essential elementary concepts/laws required to understand the work are also presented wherever necessary. This dissertation is organized in five chapters. Figure 1.3 is the pictorial representation of the organization of thesis.

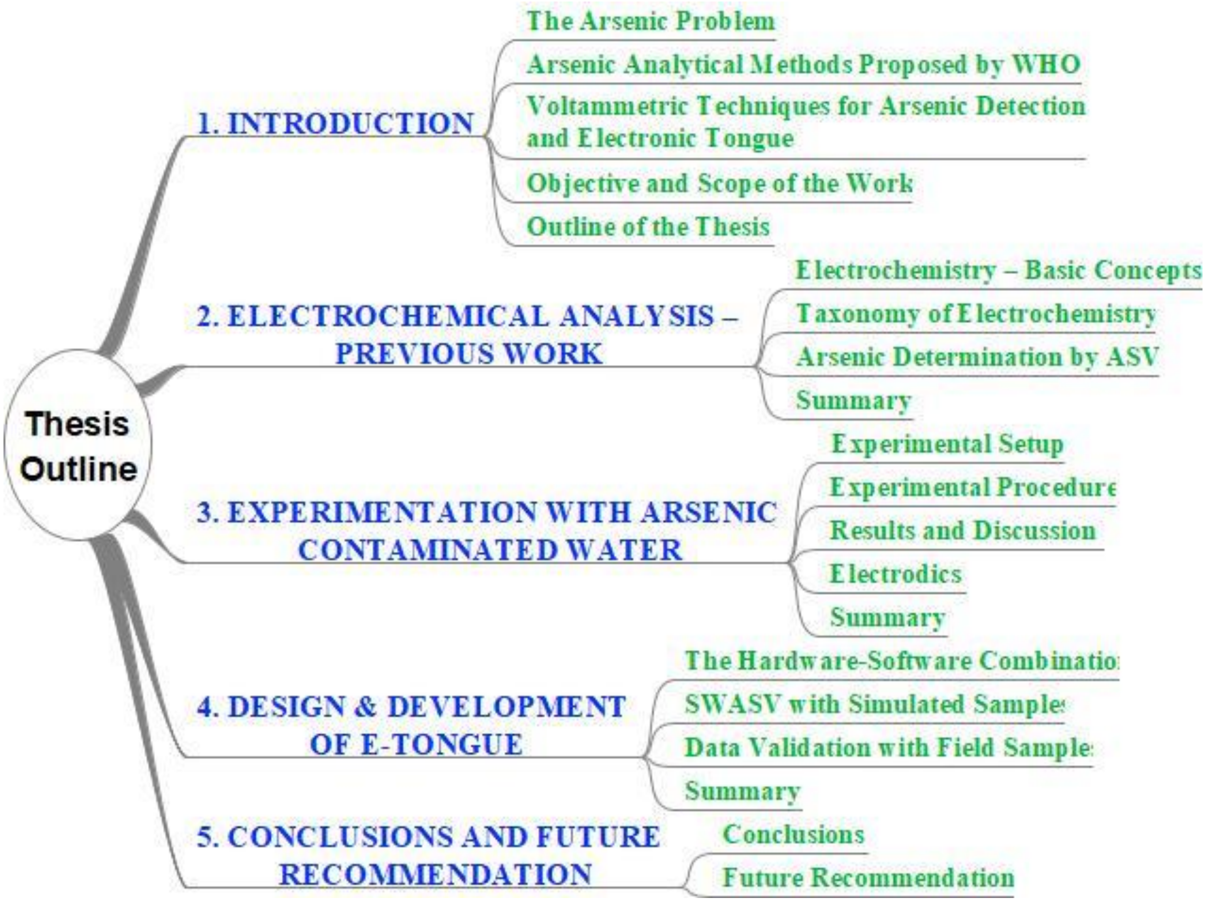


Figure 1.3 Outline of the thesis

First chapter sets background behind the motivation of the present work. It gives a gist of how deep and serious is the case of arsenic poisoning across the globe. This chapter also summarizes various WHO proposed analytical methods for arsenic detection along with merits and demerits. The chapter ends by defining the objective and scope of the research.

Second chapter discusses in detail, anodic stripping voltammetry and cyclic voltammetry experiments on which the current research is solely based. Before that, the basic key terminology related to electrochemistry are introduced in the same chapter. The chapter then discusses previous works done in the area of anodic stripping voltammetry for detection of arsenic in water samples.

Third chapter explains how e-tongue setup using commercial potentiostat was used in arriving at optimal parameter set to conduct anodic stripping voltammetry on simulated water samples for detection of arsenic. Results obtained while studying copper interference during detection of arsenic are presented. The chapter also presents various practical aspects that affect the performance of the experiment.

Fourth chapter contains the detail of the replacement of commercial potentiostat by an economic hardware-software combination or indigenously developed e-tongue. The chapter shows the results produced by the newly developed solution for detection of arsenic. Copper interference study results are also portrayed. In the end, the chapter presents the validation of the results with AAS and gives a comparative table of cost of various analytical techniques.

Fifth chapter gives the conclusion drawn out of the present research and presents the possible future recommendations for further extension of the work.

.

2 ELECTROCHEMICAL ANALYSIS – PREVIOUS WORK

Electrochemistry marks a revolution in analysis of trace metals in aqueous samples, which has unfolded numerous ventures in the field of analytical chemistry. Owing to cheaper investment and rapid analysis times, electrochemistry has been the most popular choice as an alternative to established expensive analysis methods such as atomic absorption spectroscopy (AAS), inductively coupled plasma (ICP), laser induced breakdown spectroscopy (LIBS) and surface enhanced Raman spectroscopy (SERS). Ever since its inception, various techniques, which employ electrochemistry, have found industry applications in varied fields. Few applications to name are fuel cells, electroplating against corrosion, grading of soya, honey, tea, milk, wine, beer and detection of electroactive elements/compounds at parts-per-billion/parts-per-trillion concentrations in aqueous samples [22,23]. This chapter quickly introduces basic concepts of electrochemistry and various popular techniques that use electrochemistry and summarizes the previous work done in the detection of arsenic using electrochemistry. Detection of arsenic is discussed in two aspects – chemistry perspective (electrochemical arsenic analysis) and engineering perspective (e-tongue based detection).

2.1 Electrochemistry – Basic Concepts

Electrochemistry is a branch of study in physical chemistry, which uses electricity for conducting reduction/oxidation reactions for determining concentration of analyte or for characterizing chemical reactivity of the analyte by measuring potential, charge or current. The following section introduces various conventions, terms and standard definitions related to electrochemistry.

2.1.1 Terminology and Standard Definitions

2.1.1.1 Oxidation-Reduction Reactions

Every experiment in electrochemistry involves oxidation of a species and reduction of a species in the analyte solution. Oxidation involves loss of electrons that has “charge” and reduction involves absorbing these electrons. In electrochemistry, we are interested in analyzing what results in movement of these charged particles by measuring current and potential, which is a characteristic of analyte's concentration or chemical reactivity.

2.1.1.2 Elementary Charge:

Elementary Charge or simply, Charge, denoted by *q* or *e* is a fundamental physical constant which has approximately a value of 1.602×10^{-19} C (coulombs). This is the charge carried by an electron.

2.1.1.3 Faraday Constant

A mole of electrons contains 6.022×10^{23} electrons. The collective charge of 1 mole of electrons, therefore is $(1.602 \times 10^{-19})(6.022 \times 10^{23}) = 9.649 \times 10^{4}$C which is called a **Faraday constant**, represented by F. The charge *q*(Coulomb), number of moles *n*(mole) and Faraday constant (Coulomb/mole) are related by the equation given below.

$$q = n F \qquad 2.1$$

2.1.1.4 Electric Current

Electric current or simply, current, denoted by *i* or *I*, is the flow of charge per unit time measured in amperes (A) or coulombs/second. One ampere current at a reference point means that one coulomb of electrons is passing from that point per second.

2.1.1.5 Potential

Potential, denoted by *E* or *V*, is a relative quantity and measured as a potential difference between two points. It is equal to the amount of work done in moving a charge between those two points and is measured in volts (V).

2.1.1.6 Free Energy Change

The maximum possible electrical work that can be done on its surroundings by any chemical reaction which is conducted at constant temperature and pressure defines free energy change for that reaction. Free energy change is represented by ΔG and is prefixed by a negative sign as the work is done on surroundings and diminishing in nature. The electrical work done is defined as the amount of work done in moving a charge *q* through a potential difference of *E*.

Therefore,

$\Delta G = -(\text{work done}) = -(E \cdot q)$

Now, applying equation 2.1 in the above relation, we get

$$\Delta G = -nFE \tag{2.2}$$

2.1.1.7 Electrochemical Cell

An electrochemical cell or simply cell, is a glass housing that is used to accommodate all the components required to conduct electrochemical experiments such as analyte solution and electrodes. They may also have provisions to bubble any gas into the enclosure as per the requirement of the experiment. The reaction phenomena in a cell is represented in terms of two half-cell reactions – one half representing the oxidation reaction and the other half representing the reduction reaction.

2.1.1.8 Electrolyte/Supporting Electrolyte

Electrolyte is the solution, which contains the analyte and enables movement of electrons across the cell. In some experiments, where analyte solution is not supportive of conducting, supporting electrolyte solution is added to enhance the movement of ions. Solutions with low ohmic resistance such as ionic solutions (e.g., NaCl), molten salts and ionic polymers (e.g., Nafion) are the most popular choices for electrolyte solution. Various mineral acids such as HCl, H_2SO_4, $HClO_4$ are widely used as supporting electrolytes as well.

2.1.1.9 Electrode

Electrodes are the conductors that enable application of potentials and flow of electrons across the cells. Generally, 2-electrode or 3-electrode cells are very popular among electrochemical experiments. Electrodes in practice vary in sizes from macro (few mm in length) to micro to Nano scale. The electrode where oxidation occurs is termed as *anode* and the electrode where reduction occurs is called as *cathode*. The nature and material of the electrode differs according to the purpose of the electrode. Electrode reaction kinetics are affected by the electrode surface cleanliness, surface microstructure, and surface chemistry. Various types of electrodes are explained in detail in the subsequent sections.

2.1.1.10 Electrical Conduction

Movement of electrons or ions cause the current in the cell. This movement can be conducted in two ways. Metallic conduction that occurs at the electrode's surface and ionic/electrolytic conduction that occurs because of movement of ions across the solution in the cell. The positive ions move towards negatively charged electrode and the negative ions move towards the positively charged electrode.

2.1.1.11 Faradaic Current

The transfer of electrons is monitored during almost all of the electroanalytical experiments. Faradaic current is caused by the change in oxidation state of the electroactive species in the solution and can be directly related to the rate of the redox reaction in the cell. This is the current, which is of interest during any electrochemical experiment.

2.1.1.12 Voltammogram

After the experiment is conducted, the measured (faradaic) current samples from the cell are plot against the excitation potential applied across the electrode. The resulting current-potential plot is known as voltammogram. The nature of the plot (such as magnitude of current response and shape) of the voltommaogram is dependent on the reactions that occur at the electrode. However practically, not all the current measured is faradaic current. Along with the faradaic currents (of both sample solution as well as blank solution), non-faradaic background currents add up to the measured current.

2.1.1.13 Charging/Background Current

Background current corresponds to the movement of all non-faradaic charges. Other processes contribute as well to non-faradaic charges. Diffusion of electrolyte ions, reorientation of solvent dipoles, adsorption or desorption that occur at electrode-electrolyte interface can be related to the non-faradaic currents. For instance, if an electrode is at zero charge and we instantaneously change its potential to negative charge. The anions near the electrode's surface repel and move away from the electrode while cations would attract and move towards the electrode surface. This movement of ions continue until the negative charge on the electrode's surface equals the positive charge of the interfacing solution near the electrode surface. The movement of these ions (charged particles) also causes a current that is non-faradaic. This is called charging current or background current. This phenomenon occurs every time the electrode's potential is changed. The migration of ions also leads to an electrical double layer formation across the electrode-solution interface.[24]

2.2 Taxonomy of Electrochemistry

All electrochemical techniques, as the name indicates, involve processes that make use of electricity to understand chemistry of electroactive species – the chemical parameters being evaluated are in relationship with the electrical quantities measured such as charge, current or potential. The major difference between other chemical measurements and electrochemical measurements is that the former makes use homogenous bulk solutions while the latter involves processes, which occur at electrode-solution, interface.

A minimum of two electrodes, an electrolyte solution in an electrochemical cell are required to conduct an electroanalytical experiment. The electrode-solution interface can be viewed as a transition point between metallic conduction and ionic conduction. One of the electrode hosts the chemical reactions and responds to the target analyte in the solution, and is called the working (or indicator electrode). The second electrode, independent of the solution's composition, all measurements are done with respect to this electrode – called as counter electrode. Ideally, potential across the counter electrode is expected to be constant so that any change in the overall cell potential will occur at the working electrode. However, in practice, changes in current through counter electrode result in changing potential across the electrode and hence counter electrode's potential is not constant. Therefore, it is replaced with two electrodes: an electrode whose potential stays constant irrespective of the current in the cell (reference electrode) and an electrode that is used to complete the electrical circuit (counter/auxiliary electrode) [6].

Electrochemical cells can be categorized into two kinds [6]:

i. **Voltaic or Galvanic Cells:** In which oxidation-reduction reactions occur spontaneously without the need of application of any external energy. In fact, they produce electrical energy because of this spontaneous flow of electrons. They find direct applications in electrical batteries and fuel cells.

ii. **Electrolytic Cells:** In which an external energy needs to be applied in order to facilitate and study the oxidation-reduction reactions. All electroanalytical cells are electrolytic cells. They are used in variety of industry applications such as electroplating and grading of beverages. The cell employed for the present research is an electrolytic cell.

Further, the electroanalytical techniques can be broadly classified into two categories – Potentiometric Measurements and Voltammetric Measurements.

2.2.1 Potentiometric Measurements

Potentiometry is considered a static technique because the potential of the electrochemical cell is measured at zero current. Owing to zero current flow, the chemical composition in the cell stays unaltered which makes potentiometric measurements ideal for quantification. In practical conditions, a very negligible current flows in the cell. Figure 2.1 shows a typical potentiometric electrochemical cell. The cell is made of two half-cells. Both the cells contain solution with an electrode dipped in it. The composition of the ions in the cell will influence the potential across the electrode. The “electrical connection” between these two half-cells is made using a salt bridge containing an inert electrolyte, such as Potassium Chloride (KCl). The salt bridge is fit with porous frits at both the ends to ensure only ions move through but not the solution. The circuit is complete electrically because of the charge carrying ions moving freely across the bridge between the half-cells. When the electrochemical

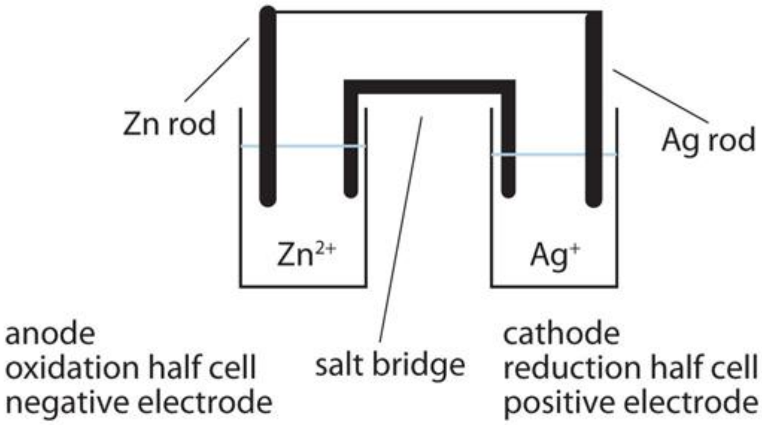


Figure 2.1 A potentiometric electrochemical cell

cell is represented by two half-cell reactions, one represents the reference potential while the other is a potential which is a direct indicative of the concentration of the analyte [25].

By convention, the electrode where oxidation reaction occurs is called as the anode thus

$$\mathrm{Zn(s)} \leftrightarrow \mathrm{Zn^{2+}(aq)} + 2\ \mathrm{e^-} \qquad 2.3$$

The reduction reaction is assigned to the electrode in the right half-cell and is called as the cathode.

$$\mathrm{Ag^+(aq)} + \mathrm{e^-} = \mathrm{Ag(s)} \qquad 2.4$$

The net potential of the cell shown in Figure 2.1 can be obtained from the reaction formed by combining two half-cell reactions 2.3 and 2.4 as below:

$$\mathrm{Zn(s)} + 2\ \mathrm{Ag^+(aq)} \leftrightarrow 2\ \mathrm{Ag(s)} + \mathrm{Zn^{2+}(aq)} \qquad 2.5$$

Potentiometric electrochemical cells are also defined so that working electrode is represented by the cathode and the reference electrode by anode. The shorthand notation for a potentiometric electrochemical cell is

$$\text{reference electrode} \parallel \text{working electrode}$$

$$\mathrm{Zn(s)} \left| \mathrm{ZnCl_2}\ (\mathrm{aq}, a_{\mathrm{Zn^{+2}}} = 0.0167) \parallel \mathrm{AgNO_3}\left(\mathrm{aq}, a_{\mathrm{Ag^+}} = 0.100\right) \right| \mathrm{Ag} \qquad 2.6$$

The shorthand notation is the representation of cell that has two parts as with two half-cells. Both parts are separated by a double vertical slash (||) as a symbolic representation of the salt bridge between the two half-cells. The electrode-solution interface where the potential develops is represented by a vertical slash(|) and the species in the same phase are separated by a comma.

The net potential of the cell, E, can be written as:

$$E_{\mathrm{cell}} = E_{\mathrm{we}} - E_{\mathrm{re}} + E_{\mathrm{jp}} \qquad 2.7$$

where, E_{we} is the working electrode potential, E_{re} is the reference electrode potential and E_{jp} is the potential developed across a liquid junction that forms when two compositionally different ionic solutions coexist for which ion mobility are different. Therefore E_{jp} can be eliminated by choosing an electrolyte solution, which has similar ion mobility as the solution in the cell. The characteristic of an ideal reference electrode is to maintain a constant potential that can be used as a reference for other potentials measured across the cell. With E_{jp} eliminated and E_{re} maintained at a constant value, any changes seen in E_{cell} will therefore be attributed to analyte's effect on the working electrode potential E_{we}. Standard Hydrogen Electrode (SHE), Saturated Calomel Electrode (SCE), and Silver/Silver Chloride Electrode are the most common reference electrodes while ion-selective electrodes (ISE) and metallic electrodes are employed as indicator/working electrodes.

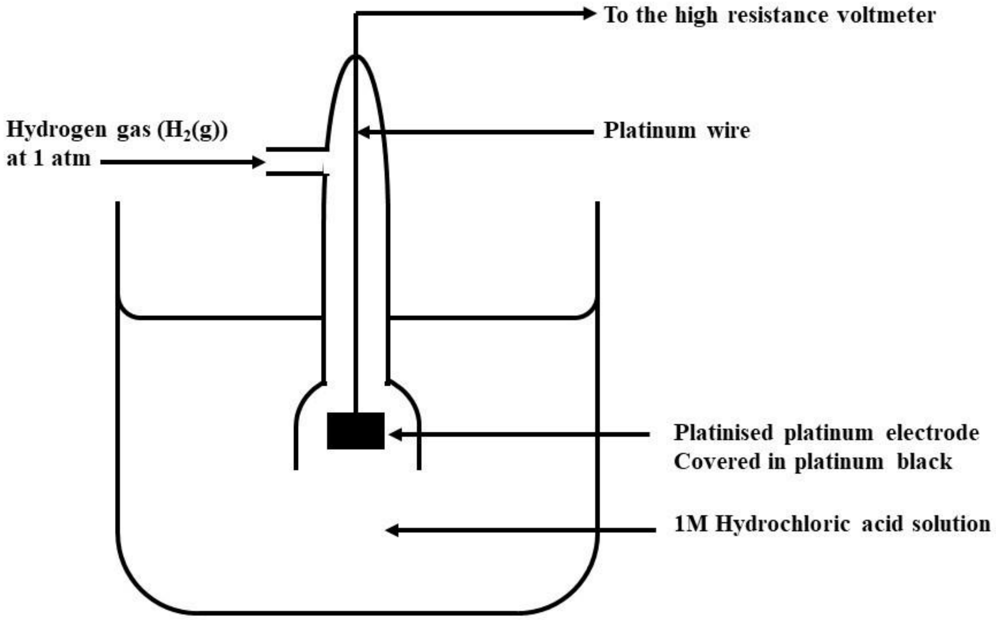


Figure 2.2 Schematic diagram of standard hydrogen electrode

Standard Hydrogen ElectrodeError! Reference source not found.Figure 2.2 shows a schematic of SHE which has a platinum electrode in a 1M acidic solution and hydrogen gas is bubbled through a gas enclosure over the electrode. The working electrode whose standard potential is to determined is connected to SHE through the salt bridge. The half-cell notation can be written as:

$$\mathrm{Pt(s), H_2(g, f_{H_2} = 1.0)|H^+(aq, a_{H^+} = 1.0)} \qquad 2.8$$

and the standard-state potential for the reaction $\{\mathrm{H^+(aq) + e^- = {}^1/_2\, H_2(g)}\}$ is, by definition, 0.0 V at 25^{o}C. The working electrode potential for SHE is given by the Nernst equation as below:

$$\mathrm{E = E_0 + 0.05916.\log\frac{[H^+]}{[H_2]^{1/2}} = 0.05916.\log[H^+]} \qquad 2.9$$

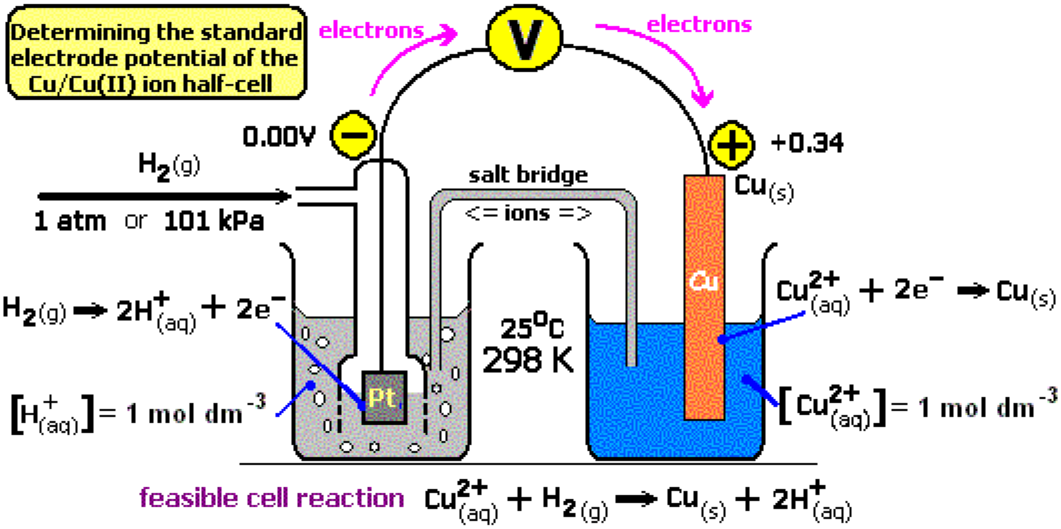


Figure 2.3 A typical setup to measure standard reduction potential
(Image source: http://www.docbrown.info/page07/equilibria7b.htm)

Owing to difficulty in preparation and maintenance, SHE is rarely employed in electrochemical experiments. Major application of SHE is to setup standard reduction potentials for various electrodes.

Standard Reduction Potentials

As mentioned earlier, the SHE is arbitrarily assigned zero potential at 25°C and standard reduction potentials of various metal electrodes are calculated by connecting the SHE half-cell to the negative terminal of a voltmeter (potentiometer) and half-cell of the metal electrode to the positive terminal of the voltmeter. The reading on the voltmeter would give a measure of the standard reduction potential. Figure 2.3 shows such a typical setup for measurement of standard reduction potential of copper. In this setup, the copper half-cell shows +0.34V on voltmeter with respect to the SHE. The direction of current will be from more negative half-cell to more positive half-cell. In this case, electrons flow from H_2/H^+ to Cu/Cu^{2+}. If the reading on the voltmeter is negative, then the electrons flow in the reverse direction (i.e., from metal electrode half-cell to SHE). A large negative reduction potential means the metal is a good reducing agent. Conversely, a large positive reduction potential indicates the metal is a good oxidizing agent.

2.2.1.1 Saturated Calomel Electrode

Hg and Hg_2Cl_2 are used as the redox couple for SCE:

$$Hg_2Cl_2(s) + 2e^- = 2Hg(l) + 2Cl^-(aq) \qquad 2.10$$

The SCE comprises of a platinum wire dipped in saturated KCl solution along with a paste of mercury and mercury chloride (solid and solution) as shown in Figure 2.4 (reproduced from [26]). The conventional salt bridge is replaced by the porous wick placed at the bottom of the outer tube and the electrical connectivity between the inner and outer tube solutions is achieved by the small hole at the bottom of the inner tube. The fill hole on the outer tube can be used to drain and refill the electrode with fresh KCl solution.

The short hand notation for SCE shown in the figure is:

$$Hg(l)|Hg_2Cl_2(s), KCl(aq, sat'd) \parallel \qquad 2.11$$

The corresponding Nernst equation is

$$E = E^0_{Hg_2Cl_2/Hg} - \frac{0.05916}{2}\log(a_{Cl^-})^2 = 0.2682V - \frac{0.05916}{2}\log(a_{Cl^-})^2 \qquad 2.12$$

The concentration of Cl^- in the KCl solution has direct influence on the potential of an SCE. The potential is determined by the activity of Cl^- in equilibrium with Hg and Hg_2Cl_2. It is therefore directly dependent on the ambient temperature of the electrode as well because with increase in temperature, solubility of KCl also increases which results in reduction of

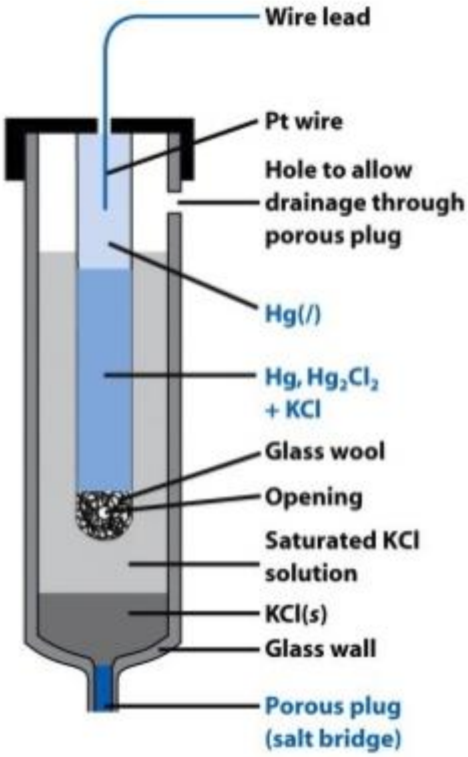


Figure 2.4 Schematic diagram of saturated calomel electrode

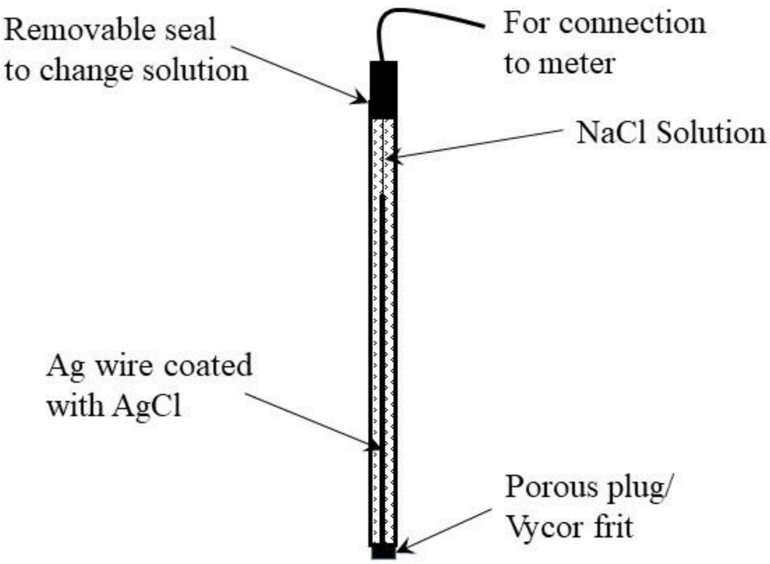


Figure 2.5 Schematic diagram showing an Ag/AgCl electrode

electrode potential and vice versa. This is a major limitation for SCE. Saturated KCl solution is chosen because evaporation will not result in change in the activity of Cl^- and hence will not affect the electrode potential. Another limitation of SCE is that it uses Hg and its compounds, which are hazardous to health.

2.2.1.2 Silver/Silver Chloride Electrode

Ag/AgCl electrode is the most popular and most widely used reference electrode. Here, Ag and AgCl form the redox couple.

$$\mathrm{AgCl(s) + e^- = Ag(s) + Cl^-(aq)} \qquad 2.13$$

The electrode comprises of a silver wire dipped in saturated KCl (or NaCl) solution. The silver wire is coated with AgCl at its end. Similar to SCE, Ag/AgCl electrode uses a porous plug/frit that doesn't allow leakage of the solution, but allows movement of ions and thus enabling electrical connectivity (Figure 2.5). Short hand notation for Ag/AgCl electrode is

$$\mathrm{Ag(s)|\ AgCl(s), KCl\ (aq, a_{Cl^-} = x)\ \|} \qquad 2.14$$

As with the case of SCE, the Cl^- concentration plays a major role in the determination of potential of Ag/AgCl electrode. The Nernst equation governing this electrode is given by:

$$\mathrm{E = E^0_{AgCl/Ag} - 0.05916\ log(a_{Cl}{}^-) = 0.2223V - 0.05916\ log(a_{Cl}{}^-)} \qquad 2.15$$

2.2.1.3 Ion-Selective Electrode

ISEs are used as indicators or working electrodes. As indicated by their name, ISEs respond to specific ions in the solution. They develop potentials that are a proportional measure of the activity of ions in the solution. ISEs find their application in systems in equilibrium and no current flows through the cell. There are a variety of ISEs used in various electrochemical measurements such as glass electrodes, membranes, enzyme electrodes as well as solid-state electrodes. pH electrode is an ISE.

2.2.1.4 Metallic Electrodes

Metallic electrodes are used in variety of forms in making potentiometric measurements. In one kind, the metal electrode is dipped in its own solution as cation and is in equilibrium involving $M^{n+}/M(s)$ redox couple. Such electrodes can be used only on deaerated solutions because they tend to oxidize other metals as well. Also these electrodes suffer from a limitation that they respond to other cations as well. Another kind of metallic electrode is a wire of inert metal (such as Pt, Au, etc.) which do not participate in the electrochemical reactions, but completes electrical connection of the cell by passing the current. They are apt for redox titrations.

2.2.2 Voltammetric Measurements

Voltammetric measurements are controlled-potential techniques, which are based on electrochemical cells with non-zero current. Therefore, the analytical part involves study of current flow at the electrode-solution interface. These techniques make use of the electrode potential to trigger the oxidation-reduction reactions and measure the resulting current. Hence, voltammetric techniques can be successfully deployed for measurement of any electroactive chemical species – i.e., which can be oxidized or reduced upon application of external force. The knowledge of standard potential of the target analyte helps to design the input potential to the cell that can generate the currents, which are a characteristic of the analyte's concentration. In few situations where analyte is not electro-active, indirect procedures are employed where the analyte is allowed to form a compound, which is electro-active, and then measure the analyte indirectly through the compound.

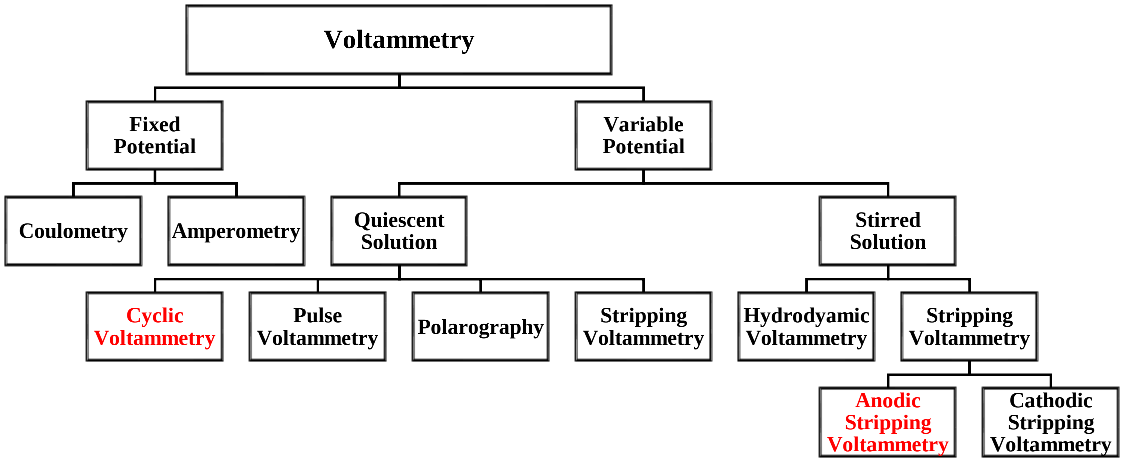


Figure 2.6 Controlled-potential techniques

Voltammetric measurement techniques have become extremely popular during the last few decades owing to many merits such as high sensitivity (detection limits as low as parts-per-trillion), conveniently portable, rapid response, lot cheaper than many other analytical equipment for establishment, availability of a wide-range of electrodes and ability to quantitate a wide range of species. Voltmmetry can be combined with other analytical methods to achieve higher sensitivity.

Figure 2.6 enlists various voltammetric techniques in practice [25]. They are broadly classified under two categories in which the input potential is either fixed or variable. With variable potential, experiments can be conducted with either quiescent solution or stirred solution. Discussion of all the techniques is not in the scope of the present dissertation. However, cyclic voltammetry and anodic stripping voltammetry (marked red in the figure) are detailed in the next subsection as the research is based on these techniques.

2.2.2.1 Anodic Stripping Voltammetry

An ASV experiment is performed in two (or three) steps:

i. **Preconcentration/Deposition/Plating step** – During this phase, arsenic in the sample solution to be analysed is allowed to reduce to As(0) by applying a potential which is more negative than the standard potential of arsenic at working electrode. The reduced As gets deposited on the electrode. Typical deposition times are from 30s to 300s.

ii. **Equilibration/Settling step (optional)** –The sample solution may be stirred during pre-concentration for mass transfer to enable uniform concentration around the electrode during deposition step. After the deposition time is over, the stirring action is stopped and the solution is allowed to settle. This equilibration step typically from 5s to 30s. This step is optionally performed only when the sample is stirred.

iii. **Stripping step** – After deposition step, the deposited arsenic is "re-dissolved" back into the analyte solution by causing its oxidation. This is achieved by applying a linear ramp potential across the working electrode, thus causing "stripping" of arsenic. The resulting anodic current from oxidation is recorded.

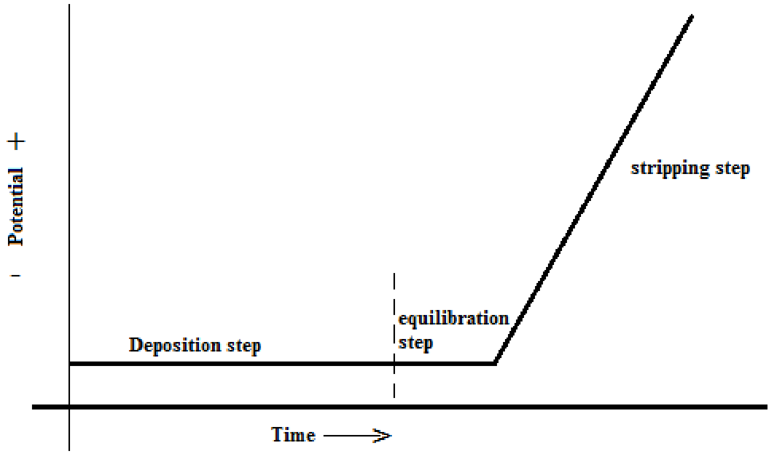


Figure 2.7 A typical potential-time sequence used in ASV

The input potential-time sequence during ASV is depicted in Figure 2.7. During the deposition step, the working electrode is held at a slightly negative potential that would cause the analyte in the solution to get deposited. The solution is stirred during deposition step, the stirring action is stopped a few seconds before the end of deposition period in order to allow the analyte solution settle (equilibration step). After the equilibration step, input potential is swept from lower to higher potential within a predefined range at a specific sampling rate and the current responses from the cell are recorded/observed in the computer with the help of (data acquisition software) DAS. The length of deposition, equilibration and stripping steps differ as per the optimum parameters decided for each analyte. The plot drawn with input voltage against anodic current is called voltammogram. The peak current is of high interest in the voltammogram because peak current is a function of amount of arsenic present in the analyte solution.

The reduction and oxidation reactions occurring at the working electrode are as below:

Reduction (Deposition): $As(III) + 3e^- \rightarrow As(0)$

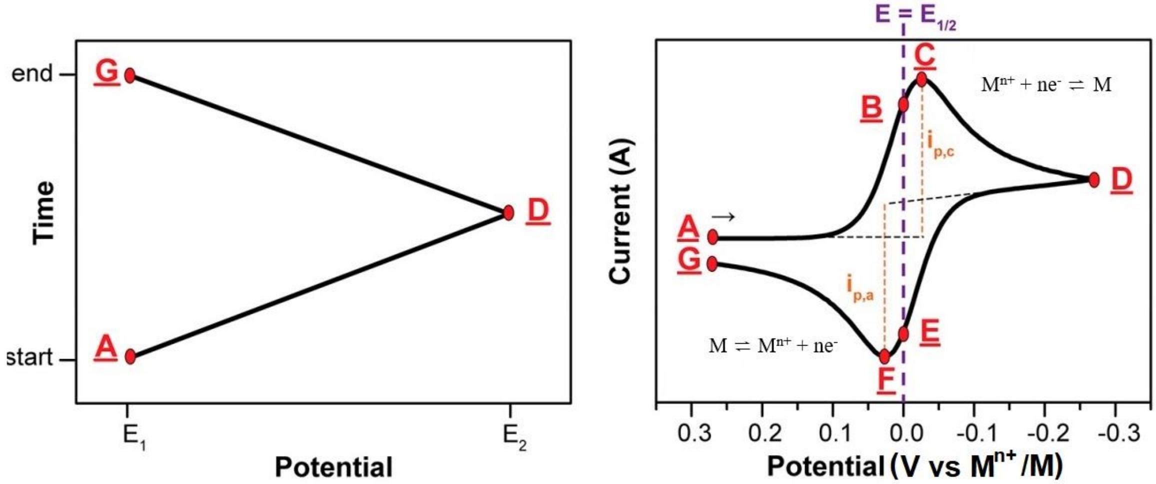
Oxidation (Stripping): $As(0) \rightarrow As(III) + 3e^-$

2.2.2.2 Cyclic Voltammetry

In voltammetry, the only major difference between various techniques is the nature of the input potential applied across working electrode and the study of the current signatures that emanate out of the electrochemical cell as a result of the input potential sequence. For instance, the input voltage is swept in positive direction linearly to perform anodic stripping voltammetry and in the case of cyclic voltammetry, the input potential is scanned in both positive and negative directions. CV requires completing scan in forward and backward directions. Another major difference is that ASV is performed on a stirred solution and CV requires the analyte solution to be in quiescent state [25,27]. Figure 2.8 (a) shows the relationship between time and applied potential, with the potential axis as the x-axis to see the relation with the corresponding voltammogram in Figure 2.8 (b). In this example, in the forward scan, the potential is swept negatively from the starting potential E_1 to the switching potential E_2. This is referred to as the cathodic trace. The scanning direction is then reversed, and the potential is swept positively back to E_1, referred to as the anodic trace. Both reduction and oxidation reactions occur at the electrode surface and the solution in contact with the electrode surface. As the potential is scanned negatively (cathodically) from point A to point D, $[M^{n+}]$ is steadily depleted near the electrode as it is reduced to M:

$$M^{n+} + ne^- \rightleftharpoons M$$

At point C, where the peak cathodic current ($i_{p,c}$) is observed, the current is dictated by the delivery of additional M^{n+} via diffusion from the bulk solution. The volume of solution at the surface of the electrode containing the reduced Fc, called the diffusion layer, continues to grow throughout the scan. This slows down mass transport of M^{n+} to the electrode. Thus, upon scanning towards more negative potentials, the rate of diffusion of M^{n+} from the bulk solution



(a) (b)

Figure 2.8 (a) The Potential-Time curve of a typical CV input voltage sequence (b) A typical cyclic voltammogram [26]

to the electrode surface becomes slower, resulting in a decrease in the current as the scan continues (C → D). When the switching potential (D) is reached, the scan direction is reversed, and the potential is scanned in the positive (anodic) direction. While the concentration of M^{n+}at the electrode surface was depleted, the concentration of M at the electrode surface increased. The M present at the electrode surface is oxidized back to M^{n+} as the applied potential becomes more positive.

$$\mathrm{M} \rightleftharpoons \mathrm{M}^{n+} + ne^-$$

At points B and E, the concentrations of Fc+ and Fc at the electrode surface are equal, $E=E_{1/2}$. This corresponds to the halfway potential between the two observed peaks (C and F) and provides a straightforward way to estimate the E^0 for a reversible electron transfer, as noted above. The two peaks are separated due to the diffusion of the analyte to and from the electrode.

Scanning the potential in both directions provides us with the opportunity to explore the electrochemical behavior of species generated at the electrode. This is a distinct advantage of cyclic voltammetry over other voltammetric techniques. Figure 2.9 shows the cyclic voltammogram for the same redox couple at both a faster and a slower scan rate. At the faster scan rate, two peaks are seen. At the slower scan rate in Figure 2.9 (b), however, the peak on the reverse scan disappears. One explanation for this is that the products from the reduction of

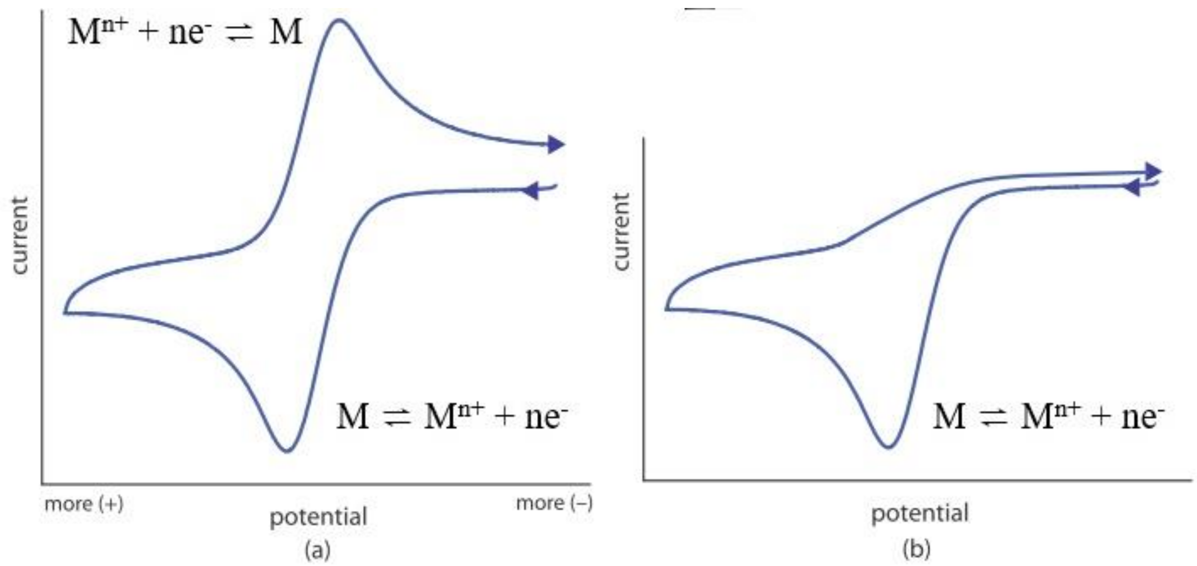


Figure 2.9 Voltammograms obtained for M (a) at a faster scan rate (b) at a slower scan rate [25]

R on the forward scan have sufficient time to participate in a chemical reaction whose products are not electroactive.

2.3 Arsenic Determination by ASV

Ever since "stripping analysis" was introduced in 1931 [28], it gained immense popularity because it made analysis of elements like arsenic which are present in ultra-trace amounts in samples using simple instrumentation. Of the stripping analysis techniques, anodic stripping voltammetry has been more popular for quantification of arsenic. Innumerous works have been reported and currently in progress to address the problem of rapid analysis of arsenic in aqueous samples. Almost entire reported research is centered around development of novel working electrode for detection of arsenic using ASV that would detect arsenite at nano molar levels. Few works have made attempt to reduce the cost of working electrode as well. A review of the existing literature is presented in this section.

Section 2.3.1 discusses research contributions, which reported development of new materials to be used as working electrodes for detection of arsenic using ASV while section 2.3.2 discusses works done with respect to "hardware" required to perform ASV.

2.3.1 Literature Review – Chemistry Perspective

Majority of research pursued for arsenic detection using ASV was for synthesis of novel working electrode that could further reduce the limit of detection of arsenic in the aqueous sample. There are a rich set of working electrodes synthesized during the past few decades to address either the limit of detection or interference from other elements during detection. The following subsections are an attempt to give an overview of the research done in that direction.

2.3.1.1 Macro Electrodes

These have been the most popular choice for conducting ASV analysis of As. They vary from solid metal wire (of few mm in diameter) to disk-type to film-type to nano particles deposited on a substrate. A significant amount of research has been dedicated to increase the efficiency of these electrodes and achieve lower limits of detection.

Forsberg et al. made a pioneering research with usage of gold electrode in place of platinum for arsenic detection using ASV and differential pulse ASV (DPASV). In their comparative study with platinum electrode, gold electrode exhibited superior performance with more sensitivity, higher hydrogen voltage and a detection limit of 0.02 µg/L with perchloric acid as supporting electrolyte. Experiments were conducted with both HCl and $HClO_4$ as supporting electrolyte at varying molarity. It was also reported that beyond 0.7V (vs SCE), gold and platinum electrodes perform poorly because of damped electron transfer kinetics. The most common problem with macro electrodes has been reproducibility. Due to repeated usage, the electrode's surface suffers fouling and without proper restoration of the original surface, the responses would be highly unreliable. The authors have reported that when the electrode was left in 6M HNO_3 before analysis was performed, they obtained improved and reproducible results [29]. Though there were successful attempts using platinum [30] and silver [31,32] electrodes as working electrode, gold electrode has been the mostly used macro electrode for arsenic analysis [33–36].

Gold modified electrodes were also extensively used for arsenic detection like Au modified boron doped diamond (BDD) electrode [37,38]. They detected arsenic in presence of 0.1M phosphate buffered saline solution at a deposition potential of -0.4V (vs SCE). Arsenate was reduced in two steps – arsenate to arsenite; then to arsenic at -1.5V (vs SCE). Gold modified graphite electrode [39,40] was also experimented for arsenic quantification in mixed EDTA-phosphoric acid and achieved a detection limit of 7 µg/L.

Gold film deposited on glassy carbon substrate [36,41,42] was also successfully employed for trace detection of arsenic as low as 0.19 µg/L with a deposition time of 4 minutes in sea water samples [41]. A low cost bismuth film deposited on an exfoliated graphite electrode was successfully used to detection of arsenic upto a limit of 5 µg/L without copper interference. The study has also reported that addition of Cd to the analyte solution has resulted in positive shift of arsenic peak [43].

After gold, carbon is the most popular choice in the recent years for voltammetric analysis. Carbon forms an ideal substrate owing to its low cost, wide potential range, inert chemical nature, fast response rate, flexibility in fabrication and low background current. Carbon paste electrode (CPE) is the most widely used electrode because of the aforementioned advantages and also because of ease of modification and renewal of electrode surface area. Numerous modifications have been tested and reported with CPEs in order to increase the sensitivity of the electrodes. Those modifications were both biological as well as chemical in nature achieved mainly by applying modifier on the surface of electrode (adsorption or covalent binding) or mixing modifier during preparation of the paste (dissolution or direct mixing). CPEs are less costly and easier to handle than the gold macro electrodes. However not much work has been reported on application of CPEs for arsenic detection using ASV. CPEs can be made more sensitive to arsenic by modifying the process of paste making. Carbon nanotubes (CNTs) and carbon nanoparticles (CNPs) have demonstrated very low detection limits and these are the versions of carbon electrode with highest sensitivity [44–46]. Though the detection limits as low as 0.05 µg/L have been reported, the application of CNTs have been limited because of involvement of time-consuming preparation of chemical modifiers in the process.

2.3.1.2 Microelectrodes

Microelectrodes (ME) or sometimes referred to as ultra-microelectrodes (UMEs) are the electrodes with dimensions in micrometer/sub-micrometer scale. Specifically, whose dimensions are comparable or almost same as that of diffusion layer. MEs are preferred to macro electrodes in the present day research owing to their advantages such as high mass transport. Also, because of smaller surface area, they have low immunity to ohmic drop, less

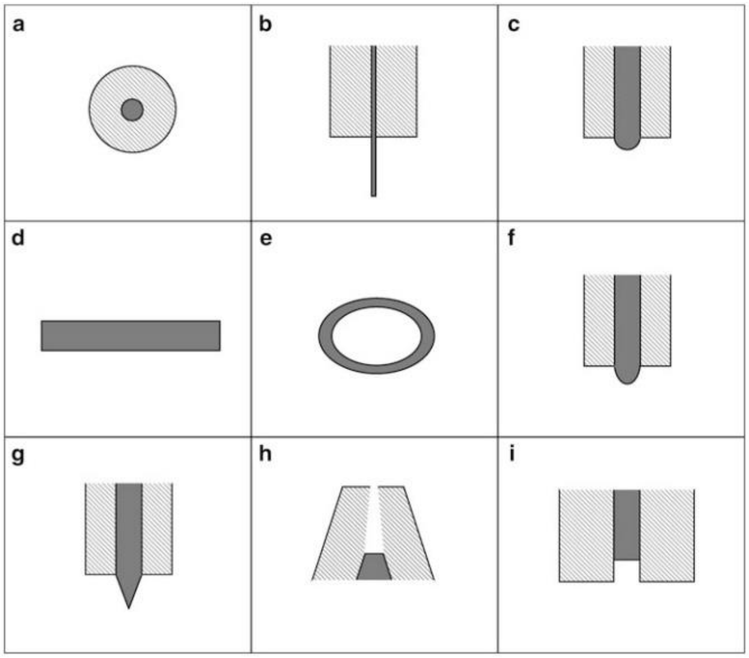


Figure 2.10 Microelectrode configurations: (a) disk, (b) cylinder, (c) hemisphere, (d) band, (e) ring, (f) sphere cap, (g) cone, (h) nanopore, and (i) recessed microelectrode

background current and improved signal to noise ratio [47]. Figure 2.10 (directly adapted from [47]) shows various configurations in which MEs are synthesized.

Gold ME/gold micro wire electrode has been the most popular choice as working electrode for arsenic detection using anodic stripping voltammetry [9,48–54]. The sensitivity of the MEs can be enhanced by reducing the diameter of the ME in application. Chi Zhou and et al. have reported an improvement by 1.5 times in sensitivity by reducing the diameter of gold ME from 25.67 to 15.41 µm while detecting As(III) in 0.5M H_2SO_4. They have also reported a 2.8 times reduction in detection limit for As(III). For As(V) detection in 0.25M HCl, they have reported an improvement of 1.6 times in selectivity and an improvement of 2.5 times in detection limit. They reported detection limits of 2.6 µg/L and 3.9 µg/L.for As(V) and As(III) respectively.

2.3.1.3 Nanoparticple/Nanostructure Based Electrodes

Most research found GCE as a suitable substrate for gold nanoparticle (AuNP) or gold nanostructure deposition [46,55–59]. Screen printed electrodes (SPEs) are the next popular choice for AuNP deposition [60–62]. AuNP deposited SPEs and Ibuprofen-Au nanostructure electrodes have achieved arsenic detection limits of 0.4 µg/L and 0.018 µg/L respectively

The nano gold crystal violet (Au-CRV) film deposited on GCE and indium tin oxide glass electrode was examined and it is found that nano-Au-CRV film on GCE had greater sensitivity and achieved detection limit of 15 µg/L in both simulated as well as drinking water samples [63]. In the most recent work, Trachioti et al. have prepared gold nanoparticles from eutectic Au/Si alloy (Au - 97%, Si - 3%) by passing a 1.2 kV electric discharge between Au and screen-printed electrode. When compared with gold nanoparticles synthesized from only metal - gold(AuNP), eutectic gold nanoparticles (eAuNPs) were approximately 2.4 times more electroactive and 5 times more sensitive. The analysis time was also lesser for eAuNPs as compared to AuNPs and achieved an LOD of 0.2 µg/L [60].

Gold electrode has been the dominant choice across all the research in detection of As using ASV. However, presence of other heavy metals in the sample being analyzed hampered the sensitivity of arsenic detection. Metals such as antimony, bismuth, copper, iron, mercury, selenium, silver and zinc, when coexist with arsenic in the analyte solution, tend to interfere with the stripping peak produced by the ASV experiment [11]. Of these metals, copper poses a serious problem with interference. It is because copper is also present in water sources almost as abundant as arsenic and the stripping peaks of arsenic and copper are seen in same potential window while detected by ASV. Also, during the deposition (pre-concentration) phase of the ASV experiment, copper forms an intermetallic compound – copper arsenide that could produce an overlapping peak with that of arsenic.

Numerous works have been reported in an attempt to mitigate the interference caused by Cu (II) during the detection of As (III). The solutions provided could be categorized into the following:

2.3.1.4 Electrode Modification

Many materials have been modified to be used as working electrode for increased sensitivity and immunity towards interference. Few examples are solid metals, carbon nanostructures, metal oxides, organic ligands, enzymes, polymers, bi-metallic and biomolecules [64]. Variants of gold electrode such as mercaptoethylamine modified Au electrode [65], L-Cysteine modified gold electrode [66], Au microwire electrode [35,67]and lateral gold electrode [68]were used successfully to demonstrate arsenite detection without interference from copper. Various gold nanoparticle (GNP) modified electrodes were also of great interest to study the interference of Cu (II) in determination of As(III). Few of the recent works in this area are GNPs deposited on glassy carbon electrode and basal plane pyrolytic graphite electrode [69], GNP modified screen printed electrode [61], nanorod like α-MnO_2 decorated with ~ 5 nm GNPs [55] and glassy carbon electrode modified with internal-electrolysis deposited GNPs [70]. Some contribution has been reported using platinum nanoparticle modified glassy carbon electrodes [71] and most recently using thoria nanoparticle-carbon paste electrodes [72].

2.3.1.5 Choice of Supporting Electrolyte

Mineral acids such as sulfuric, nitric, perchloric, phosphoric, and hydrochloric acids with varying molarities were used more commonly as supporting electrolytes across majority of the research contributions in determination of As (III). Of them, HCl have been the preferred choice. However, interesting results have been reported mentioning less or no interference of Cu (II) when ASV is conducted with a variety of solutions other than pure mineral acids as supporting electrolyte. ASV was successfully conducted in a mixed EDTA-phosphoric acid as supporting electrolyte to detect As(III) in the presence of 30 times Cu(II) [40]. Few other choices made for supporting electrolytes for electrochemical detection of arsenite are HCl containing 8 mM ammonium 2-amino-1-cyclopentene-1-dithiocarboxylate [73], acetate buffer solution (with CV) [45], Britton-Robinson buffer solution with acetylthiocholine iodide stock solution [74], phosphate buffer solution [65,75], HCl with addition of surfactant Triton X-100 [76] and HCl with complexone III[39].

2.3.1.6 Enhanced Mass Transfer

Formation of hydrogen bubbles during pre-concentration phase would severely affect the detectability of arsenic in the experiment[77]. The interfacial region between the working electrode and the solution is the area where accumulation of charges happens. To compensate for the excess charge on the electrode, it attracts a layer of oppositely charged ions near the interfacial region. This results in an “electrical double layer”. Also, the bulk concentration of the analyte in the solution differs to that near the electrode. Therefore, a “diffusion layer” is created. The thickness of the layer could be as much as 10nm depending on the ionic strength. The charge accumulated in the layer is responsible for the “background current” that limits the sensitivity of ASV[78].

The interference from Cu (II) added up to hydrogen bubbles and diffusion layer significantly affects electrochemical determination of As (III). The detectability of the experiment can be enhanced by making sure that concentration around the electrode surface is same as the bulk concentration. A magnetic/mechanical stirrer is employed in the majority of the works to enhance the mass transfer around the electrode. A successful attempt was made using an array of droplets of silicon oxinitride on the surface of a gold electrode which form a protective surface against diffusion and prevents the interfering metal from reaching the electrode [33]. Few other notable works in this area made use of a rotating electrode or made an external rotor/a vibrating motor a part of the electrode making it "vibratable" [9,48,58,77]. Application of ultrasound also had resulted in reduction of copper interference [30]. Another logical approach for the elimination of Cu(II) interference would be to perform sequestration [79]before ASV is conducted on the sample.

2.3.2 Literature Review – Engineering Perspective

Potentiostat is an indispensable component of an e-tongue experimental setup. With a capability to interface with the modern day computers, scan rates those seemed unimaginable two decades ago; are in use now. The advent of technology has resulted in miniaturization of the circuitry and made the entire e-tongue setup highly portable. However, the cost of a commercial potentiostat is still significantly high which can be a limitation for mass deployment. Surprisingly the amount of research reported in reduction of the cost of the equipment required for ASV is a very small fraction as compared to the work reported on development of novel working electrodes. Almost entire work reported on design and development of low cost potentiostat is very specific to a particular application and run either linear sweep voltammetry or cyclic voltammetry. This section explains some notable contributions that attempted to provide economic solutions for setting up e-tongue experimental systems.

George Lauer et al reported pioneering work in design of a potentiostat for running double step chronocoulometry in an attempt to automate the data acquisition system using a digital computer [80]. Figure 2.11 shows the schematic of the system proposed in the work. The electrochemical cell is interfaced to a computer and an analog to digital converter (ADC) through an analog cell-control instrument. The computer, with help of additional digital

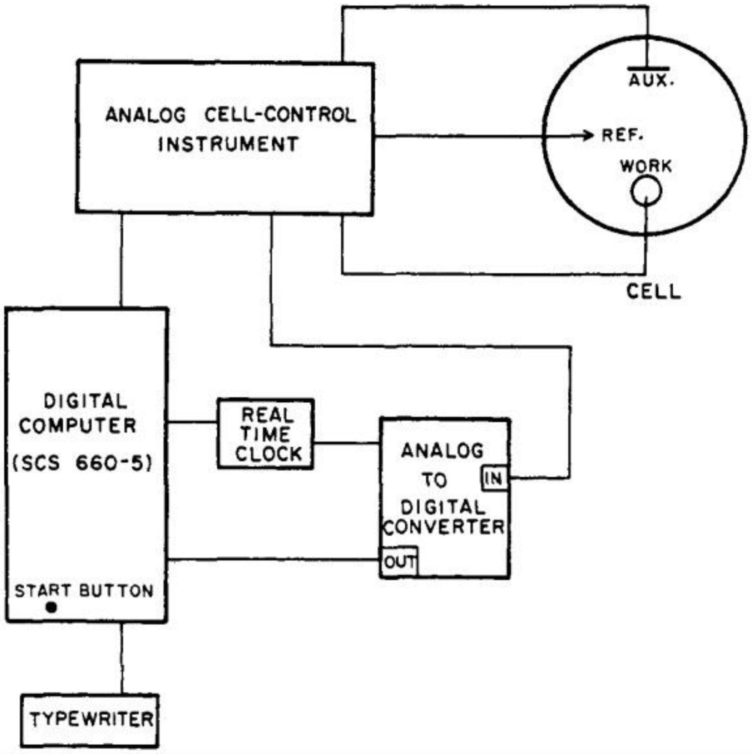


Figure 2.11 Schematic of data acquisition and analysis stem proposed by George Lauer et al.

circuitry, applies the necessary input voltage potential through the analog cell-control instrument and the current responses from the cell are fed into the ADC, which transforms the analog current signal to discrete digital sample that could be stored conveniently as a number in the computer.

The design of data acquisition and analysis system proposed in the work is in line with present day potentiostat designs even after five decades. Present research effort had rightly foreseen that the adaptation of computers into electrochemical experimental setup would solve a multitude of problems with rapid analysis times analyzing complex data received from various experiments. Soon enough lot of innovations and design changes were introduced and a potentiostat interfaced computer is so embraced by the research fraternity that electrochemical analysis is one of the most popular technique for the analysis of electroactive species [81,82,91–100,83,101–110,84,111–113,85–90].

Most common application of a potentiostat is in lab-on-a-chip/system-on-a-chip solutions such as glucose meters. Minimal size, light-weight, low power consuming potentiostat is the need in these devices [85,88,100,102,104,106,112].

The next popular application of a potentiostat is to run linear sweep voltammetry or cyclic voltammetry [80,89,116–118,101,102,105,109,110,110,114,115]. Few attempts were reported to provide low cost implementation for potentiostat to make them affordable for high-school and promote the course of electrochemistry [98,102,110]. There were research articles reporting potentiostats for monitoring/detection of heavy metal ions as well; however, limited to either linear sweep voltammetry or cyclic voltammetry [87,90,92,95,111].

Umar et al in their report, claim that the low cost potentiostat presented can be used for monitoring heavy metal ions in water [111]. However, validation for the field deployment of the solution is yet to be evaluated. Cheapstat, an open-source potentiostat developed by Aaron et al produce promising results for detection of arsenic in water samples using ASV [98]. They devised the product to be versatile which can perform CV, LSV and stripping voltammetry. They have also demonstrated application of Cheapstat for detection of As (V) using ASV. Whether Cheapstat could be employed for detection of As(III) across various concentrations without interference from other elements is yet to be tested and validated.

Another notable work in detection of As(III) using e-tongue (though not ASV) was reported by Philip Wu et al [107]. They have developed Aquasift – a low cost potentiostat for electrochemical detection of contaminants in drinking water. They made use of differential pulse voltammetry for the purpose. They have demonstrated that the increasing current peaks along with the increase in arsenite concentration is an indication that the device could be used for electrochemical determination of arsenite up to 50 µg/L beyond which the current response is saturated.

2.4 Summary

In terms of cost of investment, time taken for analysis, portability, accuracy, safety-to-use and expertise required, ASV has a clear edge over other conventional analytical techniques such as AAS, ICP-MS and Colorimetry. Most of the research done in the field of ASV has been concentrated around reducing the detection limits of ASV. However, not much notable work had been taken up so far in reducing the cost of the ASV experimental setup. The present dissertation intended to fill this gap so that with cheaper instrumental cost, mass deployment of arsenic detection activity could be initiated.

3 EXPERIMENTATION WITH ARSENIC CONTAMINATED WATER

The prime motive of this research was to develop a novel and an economic electronic tongue experimental setup that can reliably detect and estimate the amount of arsenic present in a given aqueous sample. Copper is as abundantly present as arsenic in aquifers and causes interference during electrochemical detection of arsenic. Therefore, the arsenic quantifier to be developed should also be immune to the copper interference. A lot of research is being pursued in this direction to address the arsenic problem. Innumerable contributions have been reported proposing a large variety of working electrodes that are synthesized to detect ultra-trace amounts of arsenic as low as part-per-trillion. However, this research was focused on development of an economic e-tongue that could detect arsenic levels as low as 2 ppb which is well below the WHO proposed guideline limit of 10 ppb for arsenic and costs almost one-tenth of the commercially available potentiostat used for performing anodic stripping voltammetry (ASV).

This chapter delineates the practical aspects of experiments conducted employing commercially available potentiostat for detection and quantification of arsenic in water samples using indigenously developed software. The optimal set of parameters used are provided along with details of the materials and equipment used. ASV was performed using a 3-electrode e-tongue. The performance of gold wire as working electrode was analyzed with varied supporting electrolytes, varying concentrations of supporting electrodes, varying deposition voltages and sampling frequencies before arriving at the optimal set of parameters for ASV. Observations made during study of copper interference in quantifying arsenic are also presented.

The experiments conducted using the setup explained in this chapter are a proof-of-concept for development of an economic field deployable e-tongue setup which is discussed in Chapter 4.

3.1 Experimental Setup

Figure 3.1 depicts a typical e-tongue setup to perform ASV. The following is a brief description about various major components of the ASV experimental setup:

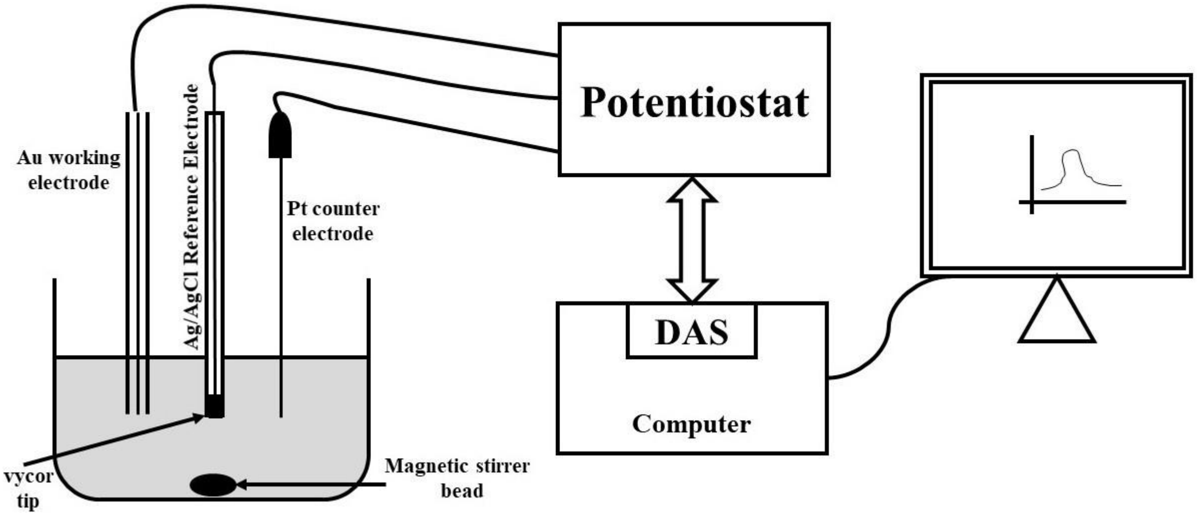


Figure 3.1 Schematic of a typical e-tongue experimental setup (not drawn to scale)

3.1.1 Electrochemical Cell

The electrochemical cell is the placeholder of the sample analyte solution where all the required electrochemical reactions occur. The cell is generally a small glass container with enough room to accommodate the analyte solution and the electrodes necessary. It also contains a provision to pump-in a gas (such as nitrogen) to provide an inert environment during the experiment. This research used Dr. Bob’s electrochemical cell procured from Gamry Instruments (USA) for conducting all the ASV experiments. Figure 3.2(a) shows image of the cell and Figure 3.2(b) shows image of the cell with various electrodes inserted for conducting the experiment. The analyte solution is needed to be stirred for providing uniform concentration around the electrode’s surface during the ASV experiment. Therefore, the cell setup shown in Figure 3.2(b) was placed on top plate of a magnetic stirring setup with the magnetic bead placed inside the cell.

The electrochemical cell holds the simulated arsenic contaminated solution, a magnetic bead and the following three electrodes:

i. A 24-carat gold wire (length: 5mm, width: 0.6mm) used as working electrode

ii. Commerical Ag/AgCl in 3M NaCl (Model No. 012167 RE – 1B, ALS Co., Ltd.) used as reference electrode

iii. A platinum wire (length: 5mm, width: 0.4mm, part no. 935-00056, Gamry) used as counter electrode

A detailed description of the purpose and function of these electrodes are given in Chapter 2. These electrodes are connected to various leads of a potentiostat.

(a) (b)

Figure 3.2 (a) Electrochemical cell (b) A typical electrochemical cell with required electrodes inserted to conduct the experiment.

3.1.2 Potentiostat

A potentiostat is the central control unit for any electrochemical experiment. A feedback amplifier that is instrumental in maintaining a fixed voltage between working electrode and the reference electrode. The present-day commercial potentiostats are versatile instruments that can apply a variety of input voltage patterns across the working electrode and also record the current responses from the electrodes in digital form. This research employed Reference 600, a commercial potentiostat procured from Gamry Instruments, USA (shown in Figure 3.3). The potentiostat is connected to various electrodes through appropriate leads on one end and is connected to a PC through USB at the other end. There are six leads available – working, working-sense, counter, counter-sense, reference and ground. During experimentation, working and working-sense leads are connected to the working electrode, counter and counter-sense leads are connected to the auxiliary electrode, reference lead is connected to the reference electrode and the ground lead is generally connected to a faraday cage. The required voltage patterns are applied to the working electrode by the potentiostat upon directions given using a PC as needed through a data acquisition software (DAS).

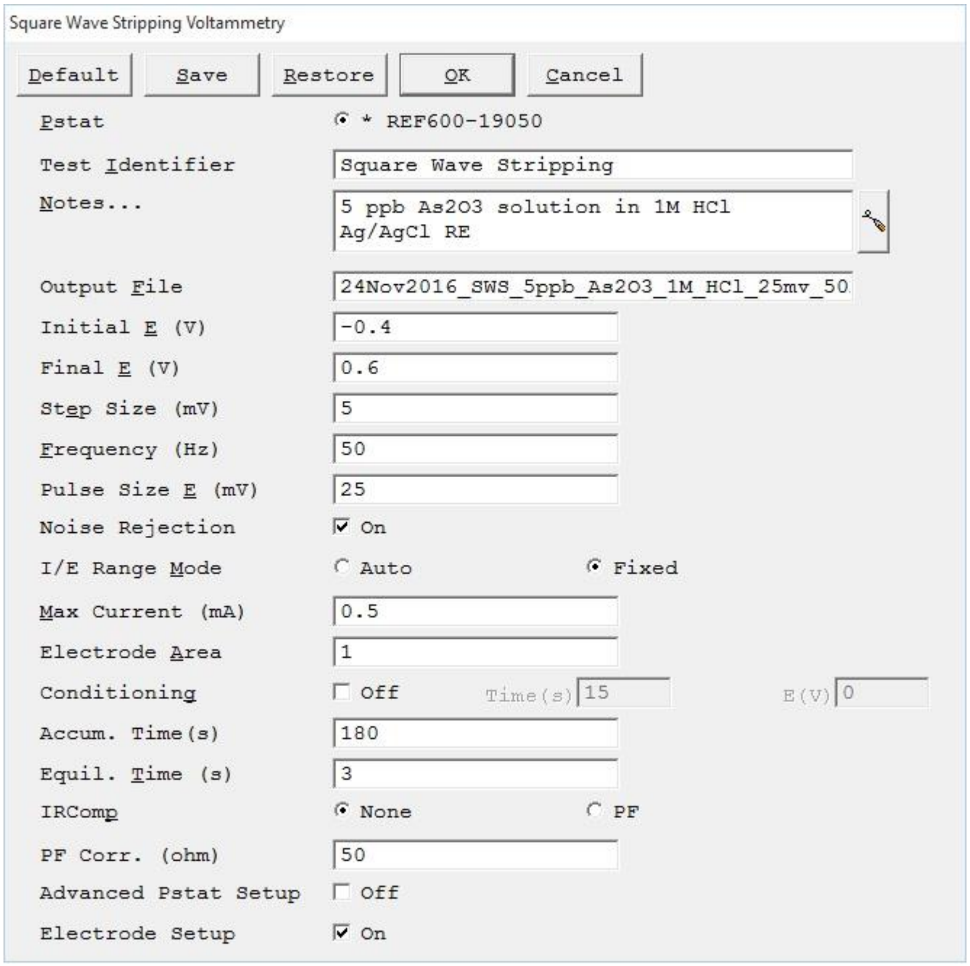
Figure 3.3 Reference 600 potentiostat
(Image source: www.gamry.com)

3.1.3 Data Acquisition Software (DAS)

DAS is a driver software that can be used to instruct the potentiostat to behave as required by the user. A DAS also has additional capabilities. The DAS is used for generating the series of voltage signals across working and reference electrodes and then for recording the electrochemical signals generated by the cell. Every commercially available potentiostat is accompanied with its corresponding DAS. Gamry too has provided DAS that contained two software modules:

i. **Framework** – that can be used to choose the electrochemical experiment to be performed, set up various parameters required to run the experiment, initiate the experiment and during the experiment, record the current signatures as received from the potentiostat into a file for further analysis. This module is bundled with two packages, Physical Electrochemistry Experiments (PHE200) and Pulse Voltammetry (PV220). These packages contain various electrochemical or voltammetric experiments that can be performed using the potentiostat. They provide dialog boxes, which can be used to set up parameters as per the requirement and run the experiment. Figure 3.4 shows a sample dialog box.

ii. **Echem Analyst** - That can be used to load data from the files created by Framework module and analyse. The module provides various useful features such as finding peak current, subtracting background, linear fitting of data, etc. Figure 3.5 shows a sample screenshot of the package.

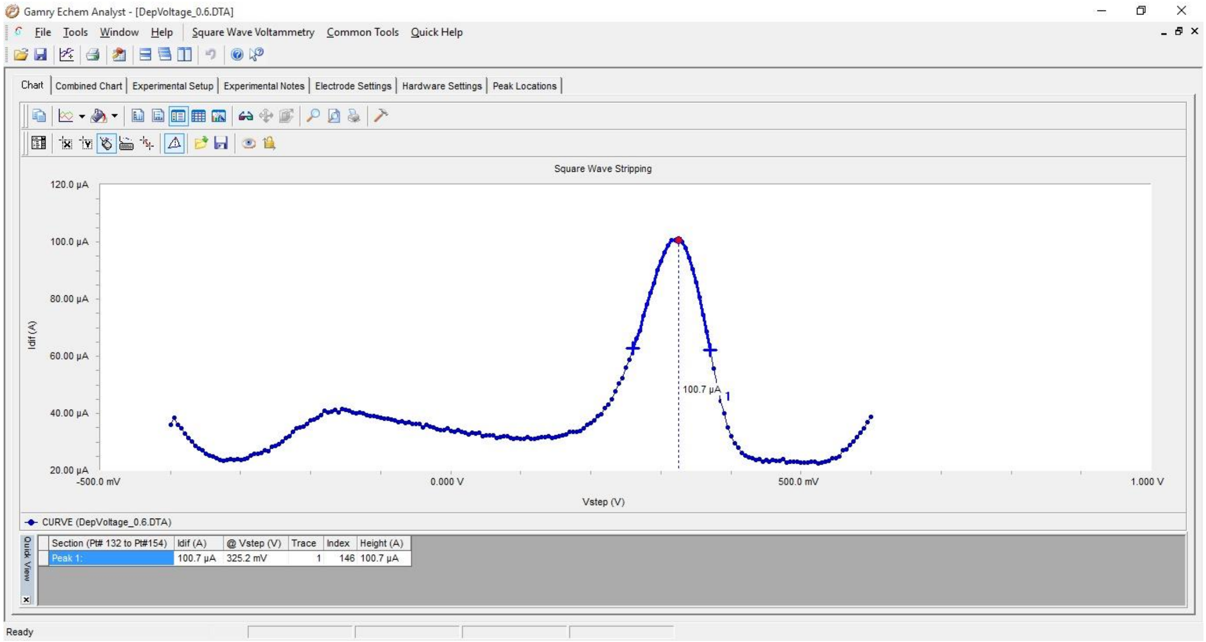


Pstat	● * REF600-19050		
Test Identifier	Square Wave Stripping		
Notes...	5 ppb As2O3 solution in 1M HCl Ag/AgCl RE		
Output File	24Nov2016_SWS_5ppb_As2O3_1M_HCl_25mv_50		
Initial E (V)	-0.4		
Final E (V)	0.6		
Step Size (mV)	5		
Frequency (Hz)	50		
Pulse Size E (mV)	25		
Noise Rejection	☑ On		
I/E Range Mode	○ Auto	● Fixed	
Max Current (mA)	0.5		
Electrode Area	1		
Conditioning	☐ Off	Time(s) 15	E(V) 0
Accum. Time(s)	180		
Equil. Time (s)	3		
IRComp	● None	○ PF	
PF Corr. (ohm)	50		
Advanced Pstat Setup	☐ Off		
Electrode Setup	☑ On		

Figure 3.4 A sample dialog box from package PV220 for setting up parameters to run square wave stripping voltammetry

3.1.4 Magnetic Stirrer

Magnetic stirrer (Model MC-02, Tarsons) was used to continuously stir the sample analyte during electrodeposition phase of the ASV experiment. Stirring helps to control mass transfer making sure that ideally bulk concentration is maintained and no concentration gradient occurs around the electrode surface. Figure 3.6 is an image showing all the major components of the e-tongue experimental setup employed during this research.



Section (Pt# 132 to Pt#154)	Idif (A)	@ Vstep (V)	Trace	Index	Height (A)
Peak 1:	100.7 µA	325.2 mV	1	146	100.7 µA

Figure 3.5 A sample screenshot of Gamry Echem Analyst

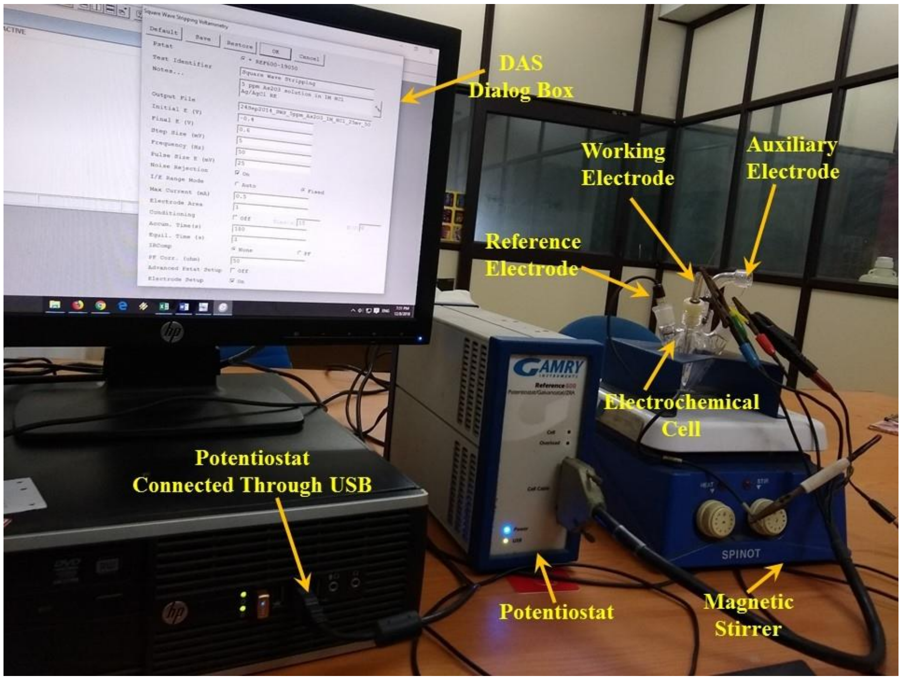


Figure 3.6 E-tongue experimental setup with commercial potentiostat used in the research

3.1.5 Materials and Reagents

Table 3.1 enlists the reagents that were employed to run ASV experiments using the e-tongue setup with commercial potentiostat.

Table 3.1 List of reagents used during arsenic detection using ASV using commercial potentiostat

Description	**Manufacturer**
Arsenic trioxide (As_2O_3)	Loba Chemie Pvt. Ltd
Hydrochloric acid (HCl, 36%)	Fischer Scientific Pvt. Ltd.
Cupric chloride dehydrate ($CuCl_2.2H_2O$)	Rankem
Potassium hydroxide pellets (KOH)	Merck
Hydrogen peroxide (H_2O_2, 30%)	Merck
Masterprep polishing suspension (alumina, 0.05µ)	Buehler
Deionized water (18MΩ)	Milli-Q Ultrapure Water Purification System

Stock Solution Preparation:

A 75 µg/L stock solution of As (III) was prepared by dissolving 19.81 mg of A_s2O_3 in 8.3ml of HCl and then making up to 100ml with MilliQ water.

Similarly, a 75 µg/L stock solution of Cu (II) was prepared by dissolving 50.30 mg of $CuCl_2.2H_20$ in MilliQ water with 1M HCl and further lower concentrations were prepared by dilution method.

For each concentration of arsenic, in order to study the interference pattern of copper over arsenic detection, five different samples with varying levels of copper (1x, 5x, 10x, 50x and 100x times the arsenic present in the sample) were prepared. All solutions were prepared with 1M HCl as supporting electrolyte and stored at room temperature.

3.2 Experimental Procedure

The ASV experiment was conducted as explained in section 2.2.2.1. The objective of the experimentation was to achieve an optimal set of parameters for anodic stripping voltammetry that would yield appropriate quantification of arsenic present in the simulated samples. Later, those ASV parameters were confidently used for designing an “e-tongue-based” indigenous arsenic estimator.

Any experimental investigation at present time needs rigorous design of experiments (DOE) apriori of conducting them. DOE is a systematic and efficient procedure to find the relationship between inputs affecting a process output. The objectives of experimental design are maximum possible inferences through minimum number of experimentation, identifying the most important inputs and interaction among them, reduction of error in measurements with enhanced confidence in results, and quantizing the inputs to optimize (maximize or minimize) the output. There are different types of DOEs’: OVAT, Full Factorial design, Fractional factorial design (Taguchi designs), Response surface design, Mixture design, EVOP (evolutionary operations), and Plackett-Burman Design (two-level fractional factorial design).

OVAT (one-variable-at-a-time) experimentation is popular one. It involves variation in the level of an input (with levels of all other inputs being fixed) to find the level that imparts an optimal output. This procedure is then repeated for each of the remaining inputs. The inputs that were varied in previous sets of experiments are kept at levels that gave optimal responses. OVAT was used to optimize the process output (Current signature) by tailoring the main factors; such as deposition voltage, deposition time, equilibrium time, voltage sweep range/stripping potential, pulse size, and step voltage.

For the present case, to find out a main effect (amount of current) using OVAT, 32 experiments for the lower level of that variable and other 32 experiments for the higher level of that variable keeping other input factors or variables constants. Hence, for six factors total 384 numbers of experiments had to be conducted. The OVAT approach necessitates more experiments than the factorial design plans. Experiments were triplicated and averaged, which ensured the reduction in measurement errors. The OVAT approach does not provide information on the impact of the interaction among inputs on the response.

The following is the list of parameters that affect the current response generated from the sample solution during ASV experiment.

i) Deposition potential:

This is the negative potential applied at the working electrode during deposition step of ASV experiment. The deposition potential should be near to the half-wave potential of the analyte. During this research -0.4V was found to be optimal value for deposition potential.

ii) Deposition Time:

Time during which the analyte (As) is allowed to undergo reduction and get deposited on the electrode. This is the duration of the preconcentration step. The sample solution can be optionally stirred during the deposition phase.

iii) Equilibration Time

This is the time after which stirring action is stopped and the analyte solution is allowed to settle before stripping step begins. Typical equilibration time duration is 5 to 30 seconds. Five-second duration was chosen as equilibration time for all the experiments performed.

iv) Stripping Potential Range

This is the input potential range that is applied at the working electrode, which involves a positive-going potential scan to cause re-oxidation of the metal deposited during deposition step. Various ranges of input potential ranging from -0.8 to -0.2V were tried out across all concentrations and the scan potential range from -0.4 to +0.6V generated reliable current signatures that would enable to distinctly quantify the arsenic content in the contaminated water.

v) Pulse Size

Pulse size is the incremental value that is added to the present input potential to generate next input potential until the highest value in the stripping potential range is reached. The current responses were closely observed by varying pulse size from 10 mV to 50 mV. A pulse size of 25mV was found to be the optimal value across all concentrations.

Electrode Preparation:

To prepare for the experimentation, weekly once, the gold electrode was put in a mixture of 50mM KOH and 25% H_2O_2 for 10 minutes followed by potential sweep from -200mV to -1200mV in 50mM KOH. Then after rinsing well with Milli-Q water, the electrode was sonicated for 10 minutes, dried and polished using a 0.05µ polishing grade alumina on a polishing pad and finally the electrode was rinsed to remove the traces of adhering alumina particles.

Simulated Arsenic Solution Samples:

Samples of lower concentration of arsenic were prepared (250 ppb, 225 ppb, 200 ppb, 175 ppb, 150 ppb, 125 ppb, 100 ppb, 50 ppb, 25 ppb, 10 ppb and 5ppb) by dilution method from the stock solution. The concentration 5 ppb was chosen as the lower limit for testing as it is sufficiently below the WHO guideline of 10 ppb for arsenic in drinking water. Required amount of HCl was added to each sample as supporting electrolyte [119].

Experimentation:

A 25ml of analyte solution was transferred into the cell and various leads of the potentiostat were connected to the electrodes. The `SWASV procedure was run with parameters as given in Table *3.2* and the resulting voltammogram was recorded into a file by the DAS. The voltammograms were recorded three times for each sample and their mean was considered for analysis. In between the experimentation, for every sample, the electrode was buffed with polishing pad with alumina (0.05µ) and rinsed well with Milli-Q water.

Study of Cu(II) interference:

To analyse the interference of Cu (II) during electrochemical detection of As (III), for each concentration of arsenite its variants containing different concentrations (1x, 5x, 10x, 50x and 100x times the concentration of arsenite) of Cu (II) were prepared and SWASV was performed on all the samples.

All the potentials mentioned throughout the thesis are measured against Ag/AgCl (3M NaCl) reference electrode.

Table 3.2 Optimised parameters for SWASV experiment

Parameter		Value
Deposition voltage	:	-0.4V
Deposition time	:	180s
Voltage sweep range	:	-0.4 to +0.6V
Pulse size	:	25 mV
Step voltage	:	1 mV
Sampling frequency	:	25 Hz
Supporting electrolyte	:	1 M HCl

3.3 Results and Discussion

3.3.1 Optimization of SWASV parameters

To arrive at the optimized set of parameters, numerous trials of experiments were conducted by varying important parameters of the experiment. This section explains how these parameters affect the detection of arsenic using SWASV and why a particular value was chosen as an optimal value. All experiments were conducted in triplicate and only the mean of three trials are considered for plotting. Since all the experimental data shown in various plots is the mean data, error bars are not shown.

3.3.1.1 Arsenic Concentrations under Test

Constant care was taken throughout the research that the optimized set of parameters are chosen such that SWASV performed using these parameters would successfully detect and quantify arsenite across all the concentrations under consideration even in the presence of copper in the analyte solution. The various arsenic(III) concentrations considered during the study were 5 ppb, 10 ppb, 25 ppb, 50 ppb, 100 ppb, 125 ppb, 150 ppb, 175 ppb, 200 ppb, 225 ppb and 250 ppb.

3.3.1.2 Choice of Supporting Electrolyte

HCl has been the most popular choice for SWASV of arsenic in water samples throughout the literature. During the present work, H_2SO_4 and $HClO_4$ were also tested as supporting electrolyte. For the same concentration, HCl has the highest sensitivity (higher peak current recorded per concentration) as compared to the other two mineral acids. The increased sensitivity for HCl can be attributed to the theory that the Cl^- ions facilitate the reduction of arsenite by acting as an ionic bridge between the working electrode and the arsenious ions as per the following reactions:

$$\mathrm{As(OH)2 + Cl- + \overline{e} \rightarrow As(OH)Cl + (OH)-} \qquad 3.1$$

$$\mathrm{As(OH)Cl + Cl^{-} + \overline{e} \rightarrow As(I)}$$

$$\mathrm{As(I) + \overline{e} \rightarrow As}$$

HCl was used as the supporting electrolyte during this research.

3.3.1.3 Molarity of Supporting Electrolyte

Study was made on the variation of peak current with increasing molarity of the supporting electrolyte. Supporting the theory of Cl^- facilitating reduction of arsenite, the recorded peak currents increased along with the increasing molarity of HCl. Trend of the peak current along with change in HCl molarity is depicted in Figure 3.7. Though 2M and 3M concentrations of HCl yielded higher currents, 1M HCl was chosen to be the optimized concentration because with samples containing higher concentrations of arsenic, the current response was getting saturated owing to high current responses generated and therefore affecting the linearity relation between peak currents and arsenic concentrations.

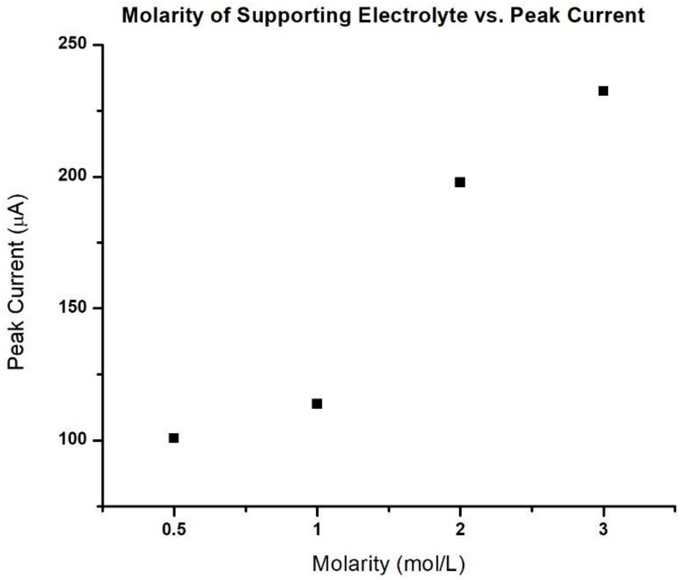


Figure 3.7 Variation of peak current with molarity of supporting electrolyte – ASV runs performed on solutions containing 5ppb arsenic.

3.3.1.4 Deposition Time

Deposition time is the duration during which the arsenite in the analyte solution is allowed to get deposited on the working electrode. Experiments were conducted to study the effect of change of deposition time on ASV. Current signatures were recorded varying deposition time from 30 seconds to 5 minutes. The sample solution was constantly stirred using a magnetic bead during the deposition time. Figure 3.8 shows the trend of current peak variation with increasing deposition time.

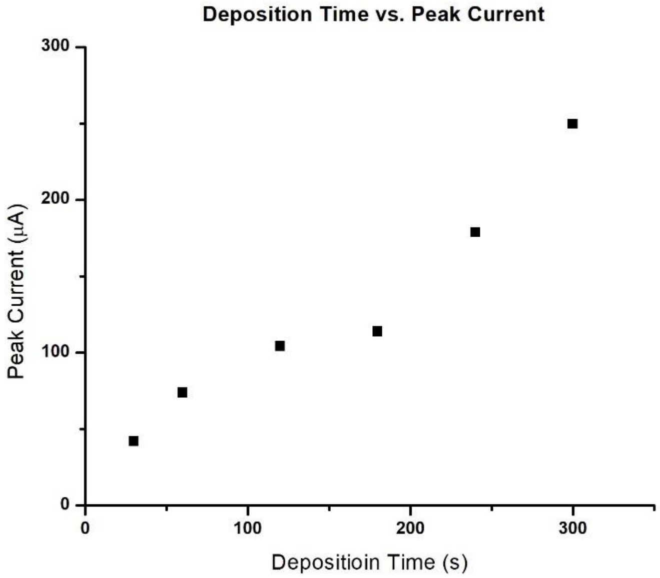


Figure 3.8 Variation of peak current with different deposition times – ASV runs performed on solutions containing 5ppb arsenic.

As can be seen from the figue, the peak current recorded is directly proportional to the duration of the deposition time. Highest peak current (250 μA) was recorded for 300s of deposition time. However, it was observed that the deposition times 240 and 300s produced higher peak currents that saturated the output of the potentiostat for subsequent higher concentrations of arsenic above 5 ppb and hence found not suitable for maintaining linearity relation between peak currents and arsenic concentrations. 180s was chosen as an optimum value for deposition time as it resulted in linear response of ASV of arsenic across all the concentrations under test.

3.3.1.5 Deposition Potential

Deposition potential is responsible for the electrochemical deposition of arsenic on the working electrode. This was chosen to be more negative than the standard reduction potential of arsenic. Study was made on effect of variations in deposition potential on the detection of arsenic. Figure 3.9 shows the peak current responses recorded as per the variations in deposition voltage from -0.7 to -0.1V. The data was collected by running SWASV on 5 ppb arsenite solution with 1M HCl as supporting electrolyte. The same is summarized in Table 3.3. Upon inspection, it was found that the deposition potential of -0.4V produced the highest peak current. More negative deposition potentials did not produce higher peak currents because of generation of hydrogen bubbles hampering electrodeposition of arsenic. -0.4V was chosen as optimal value for deposition potential.

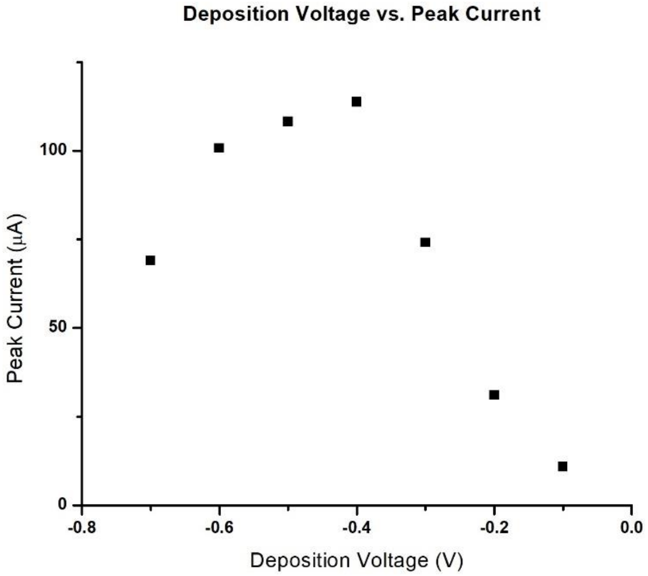


Figure 3.9 Peak current as a function of deposition potential – SWASV run on 5 ppb As (III) solution

Table 3.3 Peak currents recorded during SWASV of 5 ppb arsenic solution for various deposition voltages

Deposition Voltage (V)	Peak Current (µA)
-0.1	11
-0.2	31
-0.3	74
-0.4	114
-0.5	108
-0.6	101
-0.7	69

3.3.1.6 Equilibration Time

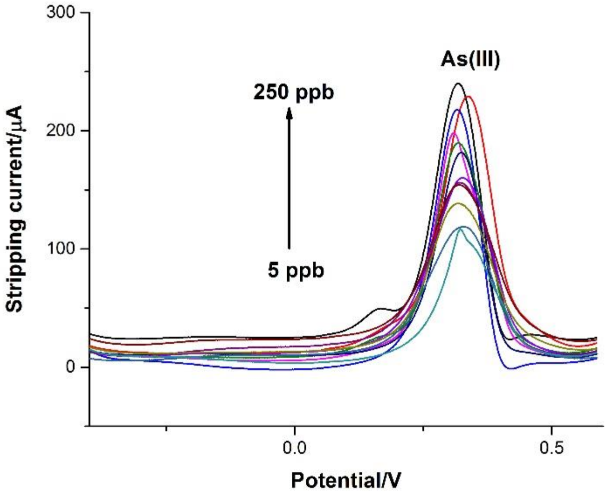


Figure 3.10 SWASV responses of As (III) concentrations varying from 5 ppb to 250ppb.

This is the time during which the solution is allowed to settle after stirrer is turned off before the arsenic is stripped off the working electrode. It was found that a 5-second duration would suffice for the solution to get settled before stripping step begins. Equilibration step helps in two ways – it allows solution to attain quiescent state thereby avoiding movement of ions because of convection and it is reported that maintaining the working electrode at deposition potential during equilibration time will result in significant reduction in non-faradaic (background) current thereby increasing the sensitivity of the experiment [120].

3.3.1.7 Sampling Frequency

The rate at which the samples are measured defines the sampling frequency. Experiments were performed with sampling rates varying from 10 Hz to 100 Hz. It was found that the lower peak currents were recorded as 10 Hz and 100 Hz runs picked up noise. Therefore, a sampling frequency of 25 Hz was chosen as optimal value.

After the optimal set of parameters are obtained, SWASV was performed on simulated water samples with parameter set as per Table 3.2. The experiments were conducted in two phases: once on water samples containing only arsenic and then on water samples containing arsenic along with varying concentrations of copper.

3.3.2 SWASV on Water Samples Containing Only Arsenic

Experimentation was done on simulated arsenic samples varying concentrations from 5 ppb to 250 ppb. The voltammogram showing current responses of the samples is shown in Figure 3.10. The numerical data pertaining to the figure is presented in Table 3.4.

The peak currents were recorded as 114 µA and 240 µA for concentrations 5ppb and 250 ppb respectively. All peaks were around the voltage range from 0.3 to 0.34V as can be observed from the table. The calibration curve for the entire concentration range is shown in Figure 3.11

Table 3.4 Data for SWASV of samples containing only arsenic (using commercial potentiostat)

As(III) Concentration (ppb)	Peak Voltage (V)	Peak Current (µ A)
5	0.3225	114
10	0.3275	124
25	0.3205	131
50	0.3185	143
75	0.3205	156
100	0.3255	160
125	0.3245	180
150	0.3175	190
175	0.3095	198
200	0.3155	218
225	0.3365	229
250	0.3165	240

Quantification of Arsenite In An Unknown Sample

For quantification using PCA, a data matrix is created by recording current signatures of various known concentrations of arsenic varying from 250 ppb to 5 ppb. The data matrix resulted from the collected experimental time series signatures was 603×10. Mean of three samples were taken for each category of arsenic solutions, hence, a data matrix of 201×10 was considered for PCA decomposition. The resulted scores were projected along two principal component directions as shown in the Figure 3.12. The percentage variances captured were 67.2%, 21.1%, and 6.5 % by PC1, PC2, and PC3, respectively. Since, the first two principal

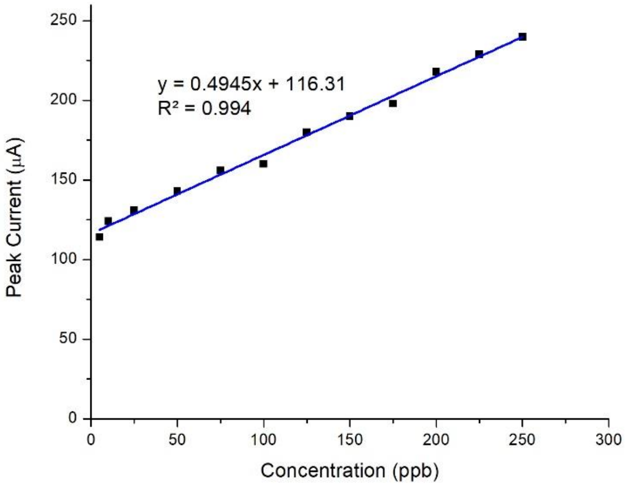


Figure 3.11 Peak Current as a function of As(III) concentration

components (PCs') captured 88 % of the total variance of the data considered, the scores were calculated using first two PCs' only. The data belonging to the different concentration of arsenic samples find themselves segregated in different clusters possessing individual cluster centers. When an unknown arsenic sample is considered, and the data is projected into PCA space, the unknown sample finds its place into an appropriate cluster following the nearest neighborhood principle.

Figure 3.12 reveals the fair amount of separability among the data pertaining to different concentrations in ppb level and the authentication of unknown sample. The unknown arsenic contaminated solution was simulated by incorporating 5 % noise to any of the 10 category data (mean of the 3 samples). This very figure represents the authentication performance of unknown 75 PPb arsenic solution. In Figure 3.12, 10 ppb, 75 ppb or 25 ppb are some attributes or features to the PCA based authentication algorithm. It can't discriminate to put them in a hierarchy of concentrations. The algorithm could correctly authenticate the unknown sample of arsenic to place it to the nearest neighborhood.

The Euclidean distance of each of the data points from the origin were calculated. Then the distances were correlated with arsenic concentrations using cftool (MATLAB). The resulting model is as follows:

$$f(x) = ax^b + c, \text{ Goodness of fit: R-square: 0.9692} \qquad 3.2$$

Coefficients (with 95% confidence bounds):

a = 5.463e-013 (-8.87e-012, 9.963e-012)

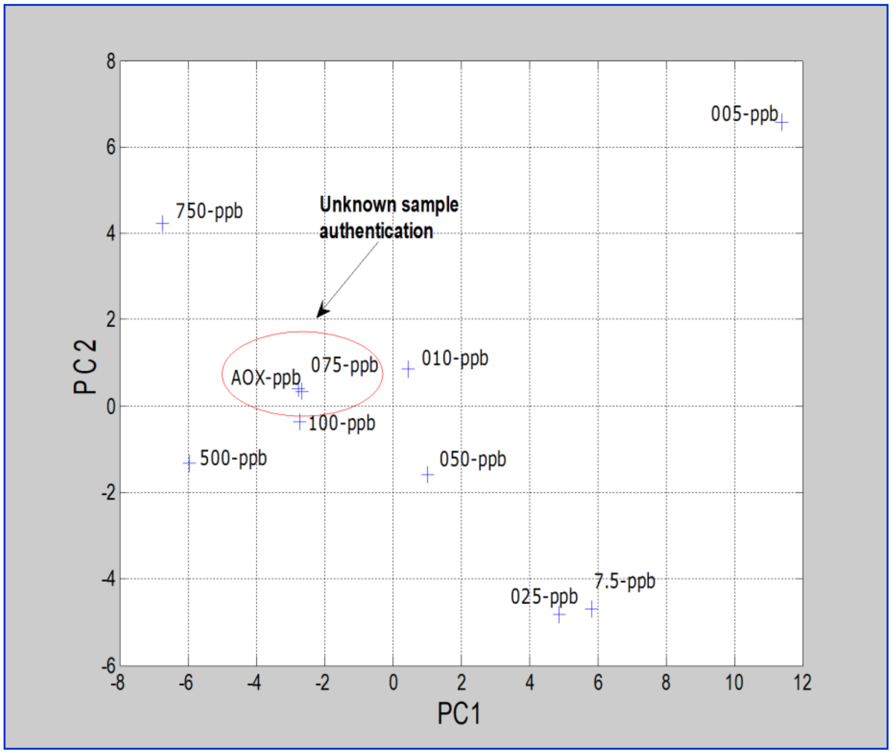


Figure 3.12 Unknown arsenic sample (75 ppb) authentication

b = 16.14 (8.148, 24.14)

c = 35.87 (-13.44, 85.19)

The parameters b and c seem to be statistically insignificant, which can't be denied. For developing a good quantifier, the range of concentration should not be that large and the arsenic concentration ranging from 100 ppb down to the 5 ppb level is crucial to be quantified and monitored. An exhaustive data collection within that range will ensure the successful quantifier development.

3.3.3 Study of Interference of Copper during SWASV of Arsenic

Other cations like Bi, Cr, Cu, Pb, Sb, Se, Sn, Te and Zn are known to interfere during the electrochemical detection of arsenic. Of these, Cu is the most common interfering element. This research was hence centered around studying the influence of presence of copper during detection and estimation of arsenic using SWASV. For each concentration of arsenic tested, five samples of the same concentration containing 1x, 5x, 10x, 50x and 100x times copper

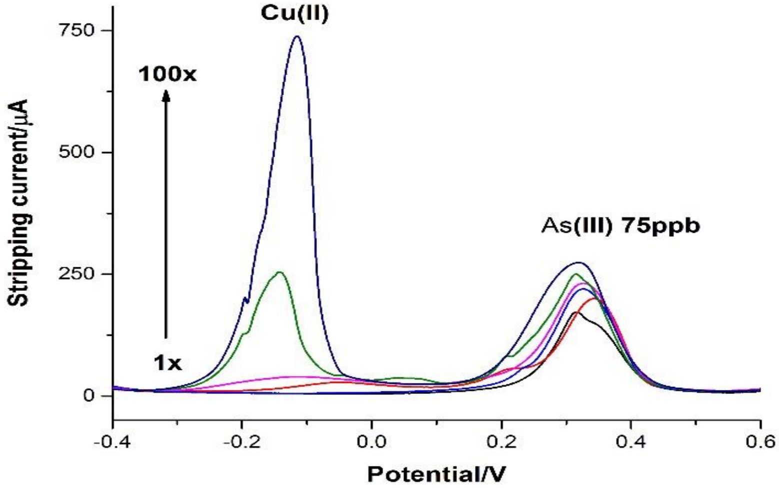


Figure 3.13 SWASV of 75 ppb As(III) with Cu(II) added in the quantities of 1x, 5x, 10x, 50x and 100x times of As(III) concentration.

were prepared. SWASV runs were performed on all of these samples and current signatures were recorded. Figure 3.13 shows one such case with 75 ppb of As(III) and its variants containing Cu(II) concentration equal to 1x, 5x, 10x, 50x and 100x times of As(III).

As seen from Figure 3.13, the Cu (II) and As (III) peaks are distinctly produced with a minimum distance of 250 mv between them. As (III) produced slightly higher peak in the presence of Cu (II) than pure As (III). We attribute this slight increase in the height of the peak to the contribution of copper arsenide that would have formed.

Similar trend was observed across all concentrations of As (III) studied with Cu (II) presence and a summary is shown in Figure 3.14. Figure 3.14(a) shows SWASV response of pure As (III) solutions of concentrations from 5 – 250 ppb. The maximum peak currents for 5 ppb and 250 ppb are 116.5μA and 240μA respectively. Figure 3.14(b) corresponds to voltammograms of As (III) solutions of same concentrations under study with equal amount (1x) of Cu (II) added. The peak currents have been recorded as 165.2μA and 279.9μA respectively for 5 ppb and 250 ppb, which are slightly more than those recorded by pure As (III) solutions. Figure 3.14 (c) presents current signatures recorded after adding tenfold (10x) Cu(II) to As(III) solutions and current peaks are at 180μA and 433.7μA while with hundredfold (100x) Cu(II) added, the peaks were recorded at 240.8μA and 540μA (Figure 3.14 (d)). A trend is seen such that with the increase in concentration of Cu (II), the peak heights produced

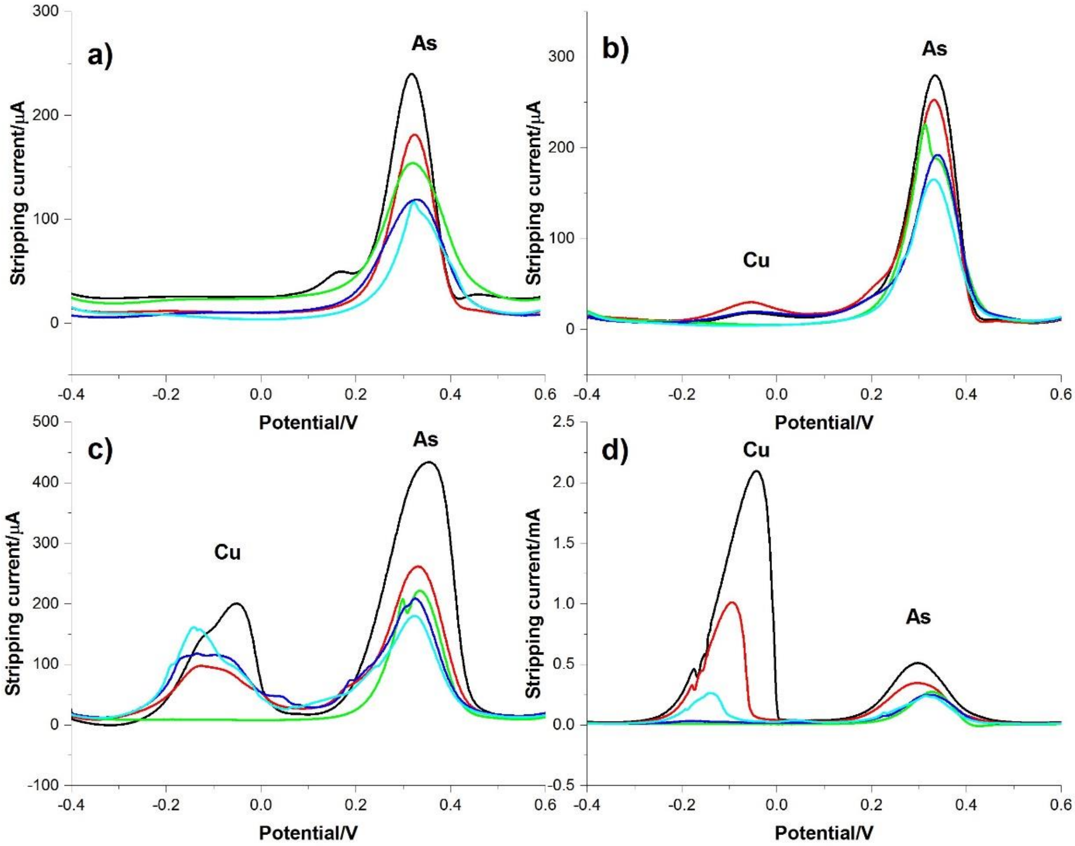


Figure 3.14 SWASV responses of samples containing: a) pure As (III) b) As with 1x times Cu(II) c) As with 10x times Cu(II) d) As with 100x times Cu(II)

by As (III) also increased. Cu (II) did not produce any significant peak when present in equal concentration (1x) with As (III). However, at higher concentrations (10x, 50x and 100x) Cu (II) peaks reached as high as 2.2mA.

Figure 3.15 depicts the trend in change of peak currents produced by various As (III) concentrations with varying Cu (II). It was observed that the peaks produced by As (III) in presence of Cu (II) are higher than those produced by solutions containing only As (III). However, this trend was observed to be less influential on lower concentrations of arsenic.

3.4 Electrodics

Electrodics deals with the physical chemistry of electrically charged interfaces. It deals with the study of interface between the electrode surface and analyte solution, and the processes that arise due to bringing those interfaces together. Electrodics has a vast scope for

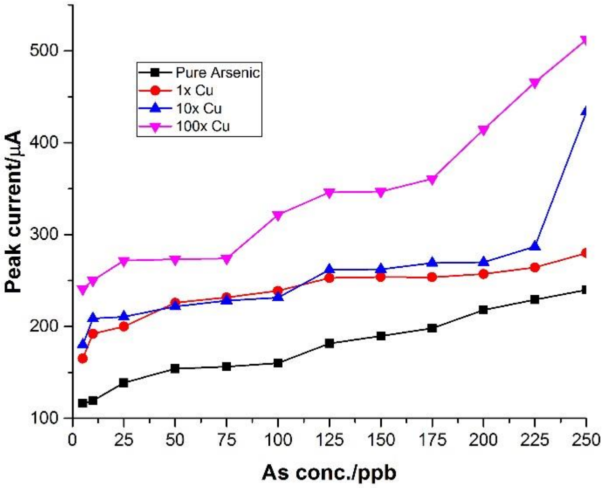


Figure 3.15 Plot showing trend in change of SWASV peak currents in presence of Cu (II)

discussion as it encompasses a great deal of mechanisms that occur at the electrode-solution interface such as the electrical double layer, charge diffusion, convection current, etc. However, the discussion in this section is limited only to the practical aspects which might help researchers who are looking into venture into electrochemistry – especially SWASV.

Reliability, reproducibility and accuracy should be the primal conditions that should be fulfilled by any analytical method to be employed for detection and quantification of arsenic. Same applies to SWASV as well. Working electrode, reference electrode and auxiliary electrode are the three electrodes in an SWASV experimental setup. The success of an SWASV experiment lies majorly on the performance of these electrodes.

3.4.1.1 Auxiliary electrode (or counter electrode)

Auxiliary electrode serves the purpose of completing the circuit and thereby enables current flow. It is generally made of an inert metal (platinum in the present research for instance). The counter electrode doesn't participate in any redox reaction that occurs inside the electrochemical cell.

3.4.1.2 Reference electrode

A reference electrode is an electrode of known constant potential and no redox reactions occur at this electrode. All voltages measured in SWASV experiment are with respect to that of reference electrode. An ideal reference electrode does not change its potential

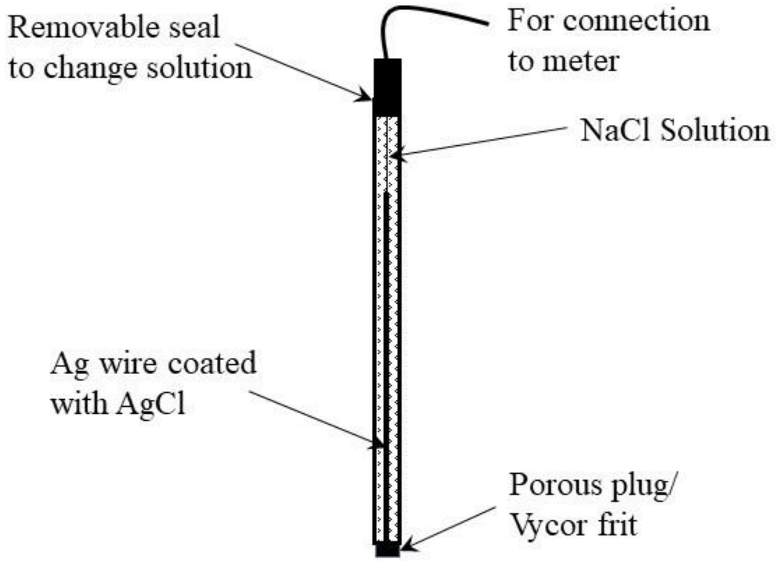


Figure 3.16 Schematic diagram of Ag/AgCl reference electrode

even though current flows through it. Saturated calomel electrode (SCE) and Ag/AgCl electrode are the two reference electrodes that are employed as reference electrode for decades. Ag/AgCl is the most recommended and the most used reference electrode of the present day because of simple design, low cost and construction using non-toxic components. This research employed Ag/AgCl reference electrode in all the experiments and therefore the same is discussed in this section.

The main characteristic of an ideal reference electrode is that the electrode should be "non-polarizable" – meaning the electrode's potential does not vary with the current flow through it. However, the practical reference electrode cannot behave ideally. Therefore, it is operated in the potential range where its behavior is almost ideal. It is not exaggeration that when an electrochemical experiment does not produce a current output as expected, then most probably the problem lies with the reference electrode. An improperly maintained reference electrode causes incorrect results in electrochemical experiments. Knowledge about constructional details and practical aspects of the electrode will help maintain it properly and thereby mitigate undesirable results in the electrochemical experiments.

Figure 3.16 shows a schematic diagram explaining various components of the Ag/AgCl reference electrode employed in this research. A silver wire coated with silver chloride is enclosed in a thin glass tube of around 4mm filled with 3M NaCl solution. One end of the tube is fitted with a porous plug or a vycor® frit. The plug/frit will only allow the movement of ions but not the NaCl solution (acts as a salt bridge). Another end is closed with a rubber/plastic seal, which can be opened and closed; so that fresh NaCl solution can be added, or the wire can be removed for maintenance. Another popular choice of filling solution is either 3M KCl or saturated KCl.

The redox couple between silver and silver chloride is as given below:

$$AgCl(s) + e^{-} \rightleftharpoons Ag(s) + Cl^{-}(aq) \qquad 3.3$$

The potential of the reference electrode ($E_{AgCl/Ag}$) is directly related to the concentration of Cl^{-} involved in the preparation of the electrode. Their relation is given by the equation below:

$$E_{AgCl/Ag} = 0.2223 - 0.05916 \log [Cl^{-}] \qquad 3.4$$

where 0.2223V is the standard state reduction potential for AgCl/Ag electrode. Therefore, it is evident that any change in the concentration of chloride ions will result in change in electrode's potential.

The remaining section details various factors that affected the electrode's performance during electrochemical experiments and the generic maintenance done during this research to avoid erroneous results.

Chloride Ion Concentration:

It is imperative that the reference electrode potential should be constant throughout the SWASV experiments if their results are to be compared and the potential of the electrode depends directly on the concentration of chloride ions in the filling solution. During the SWASV experiment, there is a large gradient of chloride ions across the porous plug/vycor® frit with bulk Cl^{-} ions on one side of the frit and the sample analyte solution on the other side. This gradient causes slow diffusion of chloride ions from the filling solution to the analyte solution upon prolonged usage – which means change in chloride ion concentration in the electrode solution and therefore, change in electrode potential. Another reason for change of potential can be natural evaporation of water from the filling solution.

Proper maintenance of the chloride ion concentration is very essential for correctness in measurements during the experiments. Constant check was done on the electrode potential during research. The potential of the electrode under use was compared periodically with another internal reference electrode and whenever the difference was above 0.002V, the filling solution was replaced with freshly prepared 3M NaCl solution and left overnight to stabilize before it was used for running experiments. Also care was taken to not to put the electrode to prolonged usage in the sample solution. When not in use, the electrode was stored in 3M NaCl solution. Also, in between the experiments, reference electrode was removed from the electrochemical cell and was placed in the solution.

Effect of Temperature:

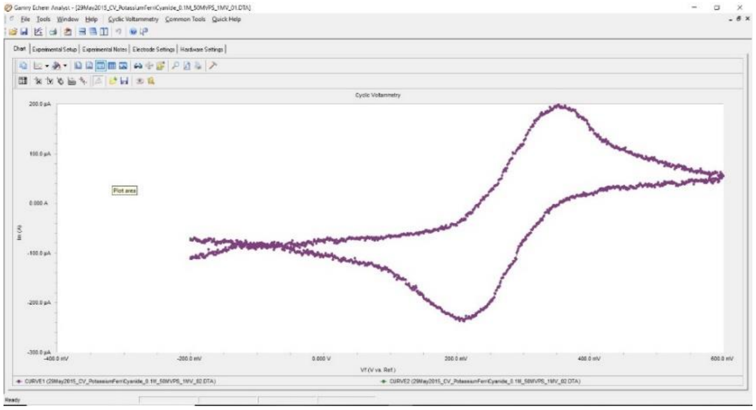
The reference electrode potential is directly dependent on temperature. There can be variation of as much as 10mV in the accuracy of measurements if experiments are not run at a constant temperature. All the experiments in this research are executed at a constant temperature of 25^{o} C.

Internal Impedance of Reference Electrode:

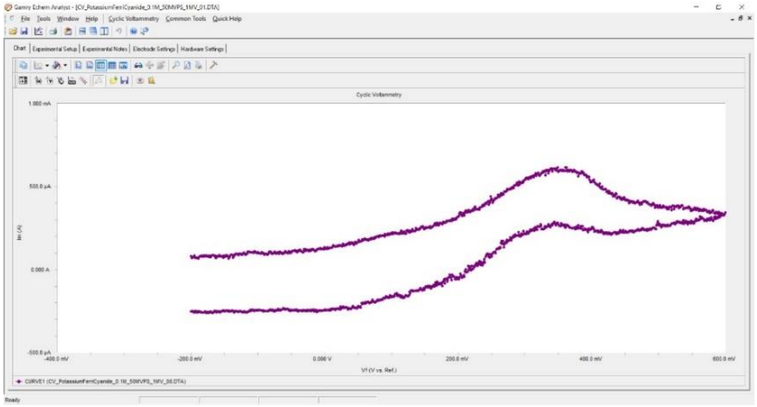
The reference potential of the electrode is directly proportional to its internal impedance. The lower the impedance of the electrode, the better is its performance. Change in impedance of electrode means change in reference potential. Therefore, precautions must be taken to counter any changes in the internal impedance of reference electrode. There are two major reasons for increase in electrode's impedance:

i. The salt in the filling solution (NaCl or KCl) precipitates around the frit due to natural evaporation of water from the solution or because of formation of precipitates with the sample solution due to prolonged use. Deposition of such precipitates will increase impedance of reference electrode and alters the reference potential.

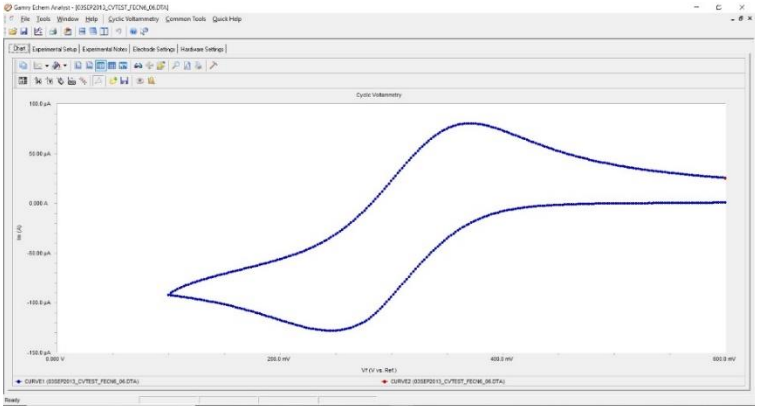
ii. Contamination of the frit due to prolonged usage of electrode is one more reason. The vycor frit/porous plug loses its porosity because of cumulative contamination caused during experimentation over a period of time.



(a)



(b)



(c)

Figure 3.17 Cyclic voltammograms of 0.1mM $K_3Fe[CN]_6$ reduced in 1.0 M KNO_3 as a supporting electrolyte (a) and (b) run with high impedance Ag/AgCl reference electrode (c) run after the noise was removed

Increase in impedance of the reference electrode results in recording of noisy current responses and this slows down the response of the potentiostat as well because the scan rate has to be slower to reduce noise in the current signal. Whenever, regular maintenance of the electrode is done, its performance was verified by running cyclic voltammetry with a standard solution such as potassium ferricyanide. Figure 3.17 (a) and (b) shows cyclic voltammograms, which were recorded using noisy reference electrodes on 0.1 mM potassium ferricyanide, reduced in 1 M potassium nitrate. Figure 3.17 (c) represents voltammogram recorded after the vycor frit was replaced and fresh NaCl was filled in and the electrode was allowed to stabilize before cyclic voltammetry was performed.

3.4.1.3 Working Electrode

Working electrode surface is the area where all redox reactions happen in an electrochemical cell. There are a variety of working electrodes in practice to detect arsenic in trace amounts using SWASV. This research focused mainly on reduction of the cost of potentiostat and increase the mobility of the experimental setup to enable in-situ analysis of the water sources. So, an off-the-shelf electrode which doesn’t require complex procedure to prepare for experimentation at the field level was needed to be used as working electrode. Gold wire was the choice of this research. However, there are known limitations of using a metallic macro electrode for ASV experimentation. The response of the gold wire electrode is dependent on the “quality of the electrode surface”. The electrode surface suffers contamination from past usage history, method of pretreatment used and also the oxide films that form because of experimentation. Presence of oxide layer on the surface of the working electrode is a serious problem for an ASV experiment because it inhibits the stripping process. This problem is called passivation of the electrode.

Giacomino et al have proposed usage of cyclic voltammograms to study the inconsistencies on the electrode’s surface and also to electrochemically activate the electrode. For instance, cyclic voltammogram in Figure 3.18 was run on gold wire with linear potential sweep from -0.4 to 1.2V. The oxidation peak that can be observed from the figure indicates the Au electrode surface is optimal to run SWASV. Whereas in the cyclic voltammogram shown in Figure 3.19, the absence of any significant peaks conveys the information that the

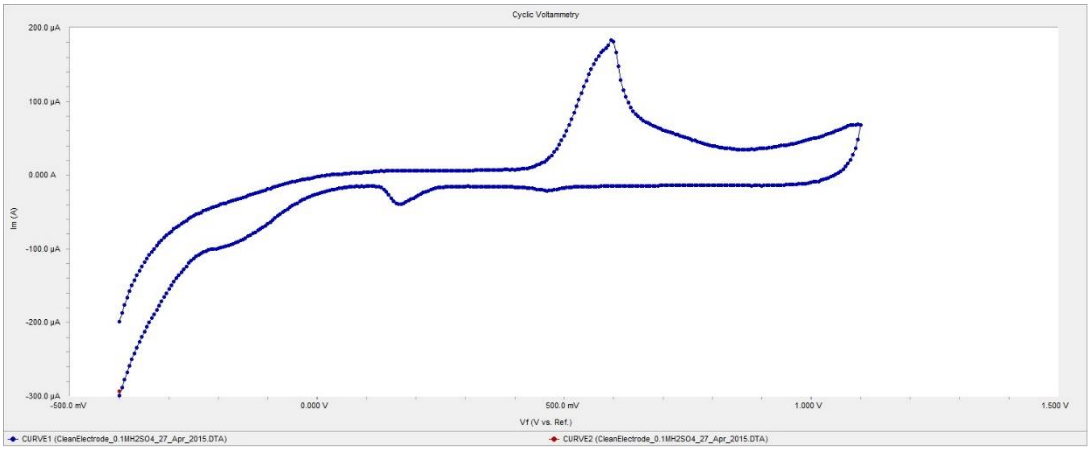


Figure 3.18 Cyclic voltammogram of Au electrode with clean surface

electrode surface is severely passivated and hence cannot be used for stripping analysis experiments.

Therefore, proper preparation method is to be followed to make working electrode ready for the experimentation before each run. In order to replenish surface quality of the gold wire, cleaning procedure as explained in section 3.2 (Electrode Preparation) was followed.

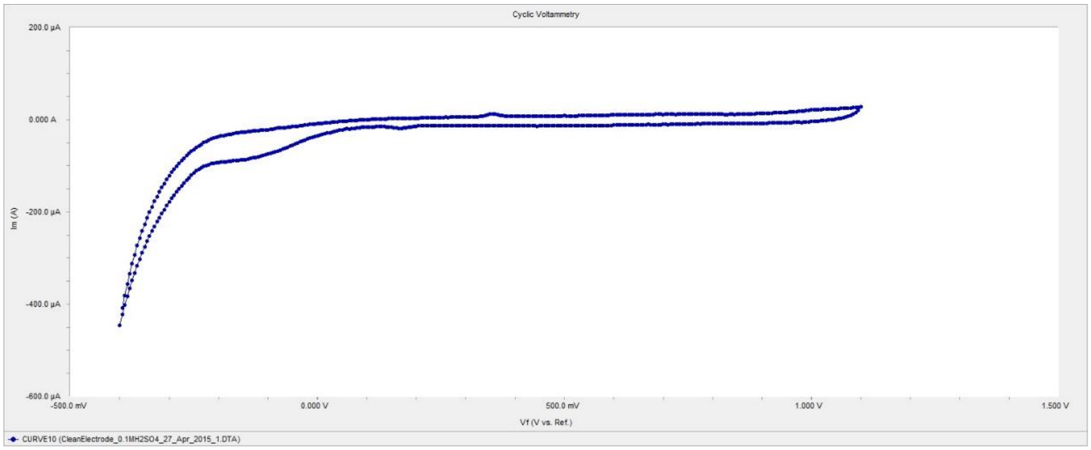


Figure 3.19 Cyclic voltammogram of passivated Au electrode surface

3.5 Summary

In the process of development of an economic version of potentiostat for detection and quantification of arsenic using SWASV, firstly proof of concept was established by successfully detecting arsenic using commercially available potentiostat. Gold wire was used as working electrode, Ag/AgCl electrode (3M NaCl) as reference electrode and platinum wire as counter electrode. Concentration ranges from 250 ppb to 2 ppb of arsenite were tested and calibration curve was prepared. Any unknown sample could be analyzed using the data available from the known solution concentrations followed by mapping the data from unknown sample using multivariate statistical analysis techniques (principal components analysis). With the proposed electrochemical experimentation setup, arsenic detection and quantification was unaffected by the presence of copper concentrations up to as much as 100 times that of arsenic. Various practical problems that might arise with electrodes during SWASV experiments were also discussed and practices to mitigate those problems were suggested.

4 DESIGN & DEVELOPMENT OF E-TONGUE

The crux of this research lies in developing a reliable, economic version of commercial potentiostat that can be employed in running SWASV experiments for on-field detection and estimation of arsenic in given drinking water sample. After achieving proof-of-concept of arsenic detection using SWASV with the 3-electrode setup using commercial potentiostat, the next phase was to replace the potentiostat with a cheaper instrumentation that performs the same functionality as the potentiostat and costs almost one-tenth of the potentiostat cost.

This chapter describes the design process of the hardware-software combination that replaced the commercial potentiostat from the e-tongue setup. The e-tongue experimental setup with the new circuitry was then used to detect arsenic concentrations from 250 ppb to as low as 2 ppb. The e-tongue presented in this section was also immune to any interference from copper during arsenic detection using SWASV. The last section presents results obtained while analyzing water samples collected from various sites of 24-paraganas district (West Bengal state, India) validated against those from AAS.

4.1 The Electronic Tongue

This section reveals the incremental development of low-cost, field deployable electronic tongue setup for detection and quantification of arsenic in aqueous samples. This was achieved by eliminating the usage of commercial potentiostat in SWASV experiments.

Figure 4.1 shows the e-tongue system that employs a potentiostat for generating input potential sequence and recording current signatures. A data acquisition software (DAS) controls the operation of the potentiostat. The potential sequence to be applied to the electrochemical cell through potentiostat is directed through the DAS and it is responsible for recording the current-analogous-voltage output produced by the potentiostat into a file. Hence, the potentiostat is the interface between the PC and the analyte for recording current signatures. However, a commercial potentiostat contributes to almost more than 90% of the total cost of the e-tongue setup.

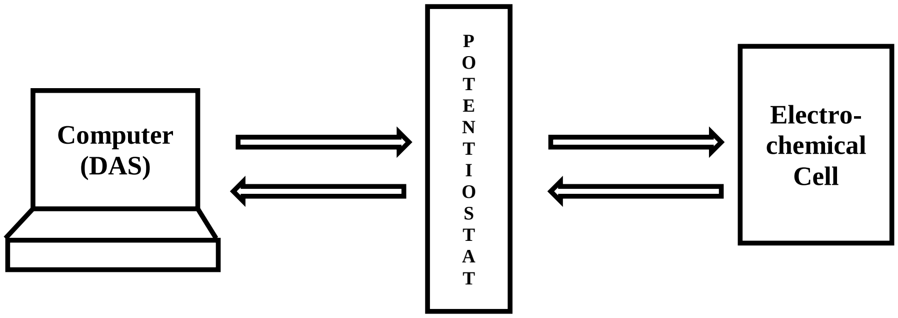


Figure 4.1 Typical e-tongue experimental setup

A phenomenal reduction in cost of e-tongue system is implied if the commercial potentiostat is replaced by an economic solution to perform electrochemical experimentation. Few contributions have reported the replacing of potentiostat by cheaper version of electronic circuits. However, almost all of them are restricted to pulse voltammetry and cyclic voltammetry and there is no significant contribution made for anodic stripping voltammetry so far.

Broadly, a potentiostat takes care of the following two tasks in an electrochemical experiment:

Generation of required input voltage patterns – the DAS records the experimental parameters input by the user and directs potentiostat accordingly. The potentiostat then generates input signal (to the electrochemical cell) with the required pattern that would be applied across working electrode and the reference electrode.

Collect current/voltage responses from the electrochemical cell – After applying the required input voltage pattern to initiate electrochemical reaction in the cell, the potentiostat receives the current response from the cell, converts the analog current samples into equivalent digital (discrete) voltage values and transfer these values to DAS so that they may be recorded into a file for further analysis.

This research concentrates on simulating the above functionality of a commercial potentiostat with the help of a software module and interfacing electrochemical cell to the PC through a data acquisition card (DAQ) as shown in Figure 4.2; thus eliminating the potentiostat

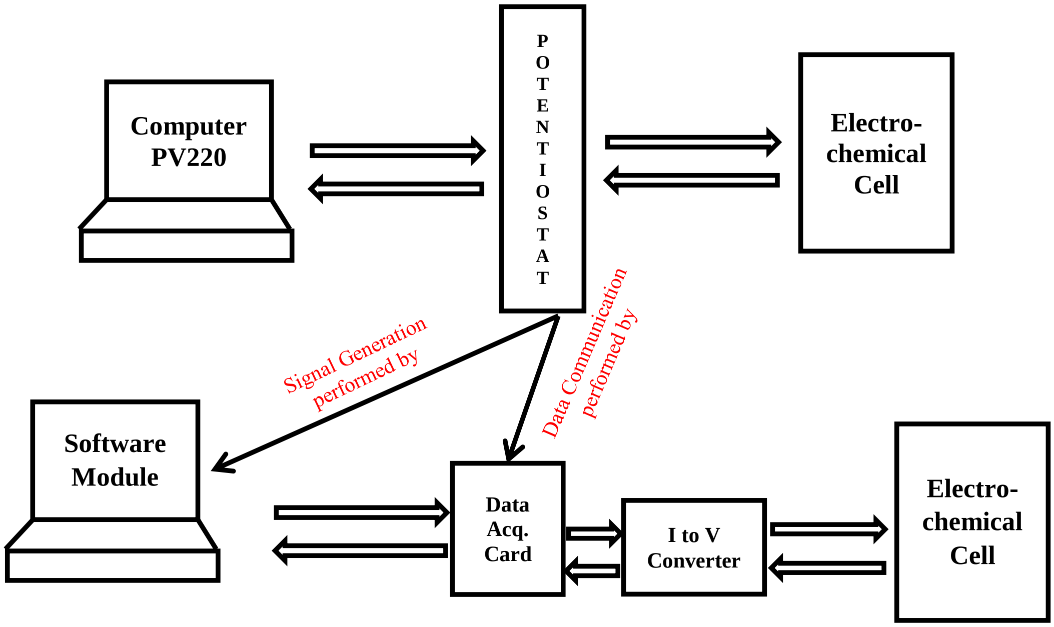


Figure 4.2 An alternative solution to potentiostat functionality in e-tongue experimental setup

from the e-tongue experiment scenario thereby reducing the cost of the setup to almost one-tenth of the cost with commercial potentiostat.

The functionality of the potentiostat was implemented by a hardware-software combination where an USB-based data acquisition card (DAQ) with an I-to-V (current-to-voltage) converter module is the hardware part and software module contains the program to generate signal waveform and to record the output current pattern as received from the data acquisition card. The data acquisition card takes care of the communication between the cell, the software module – such as the generated excitation signal is applied across the electrodes of the cell, and the current pattern produced by the cell is sent back to the software module. The in-house developed I-to-V converter module is the analog circuit that acts as interface between data acquisition card and the electrochemical cell. The I-to-V converter receives current output from electrochemical cell and generates proportional voltage output. The software part is also a machine-learning algorithm (developed using MATLAB) that helps in detection and quantification of arsenic in simulated and real samples.

4.1.1 Hardware Module

The hardware module constitutes an USB-based DAQ along with an in-house developed I-to-V converter module.

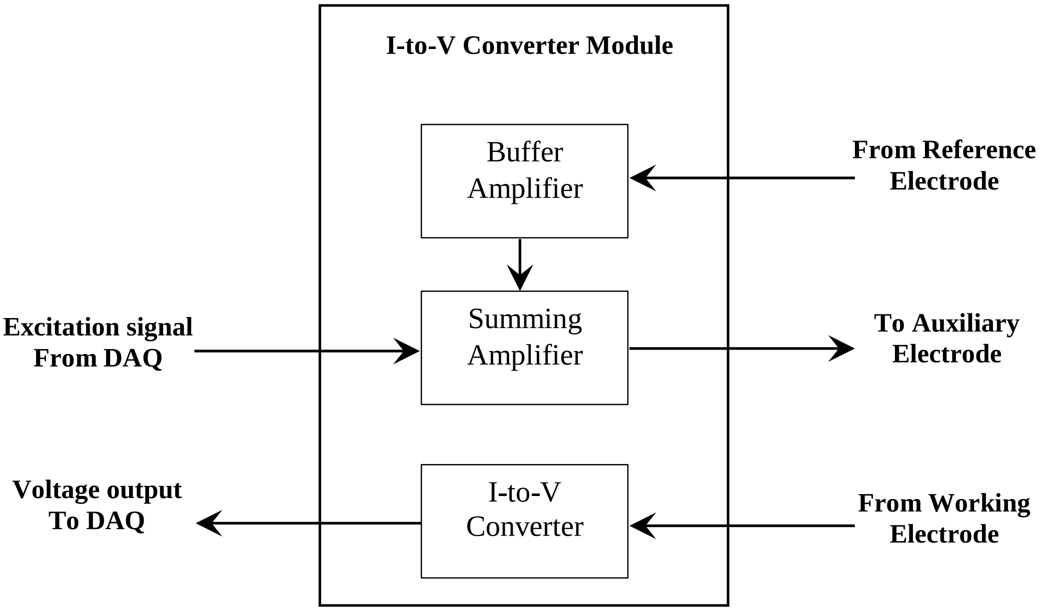


Figure 4.3 Block diagram showing various functional blocks of I-to-V converter module

4.1.1.1 I-to-V Converter Module

The I-to-V converter module is an op-amp based analog circuit that interfaces the electrochemical cell with the DAQ.

The major functions of the I-to-V converter module are:

- To maintain constant voltage between reference electrode and working electrode
- To be able to measure the current response from the working electrode
- To operate irrespective of current direction through working electrode

Figure 4.3 show various functional blocks inside an I-to-V converter module. The reference electrode is connected as input to the buffer amplifier. The output of buffer amplifier and the excitation signals as received from DAQ are fed to a summing amplifier and its output is connected to the auxiliary/counter electrode. The output current from the electrochemical cell is passed into an op-amp circuit working in current-to-voltage converter configuration and the output of the circuit is connected to one of the analog inputs of the DAQ for storage into a file.

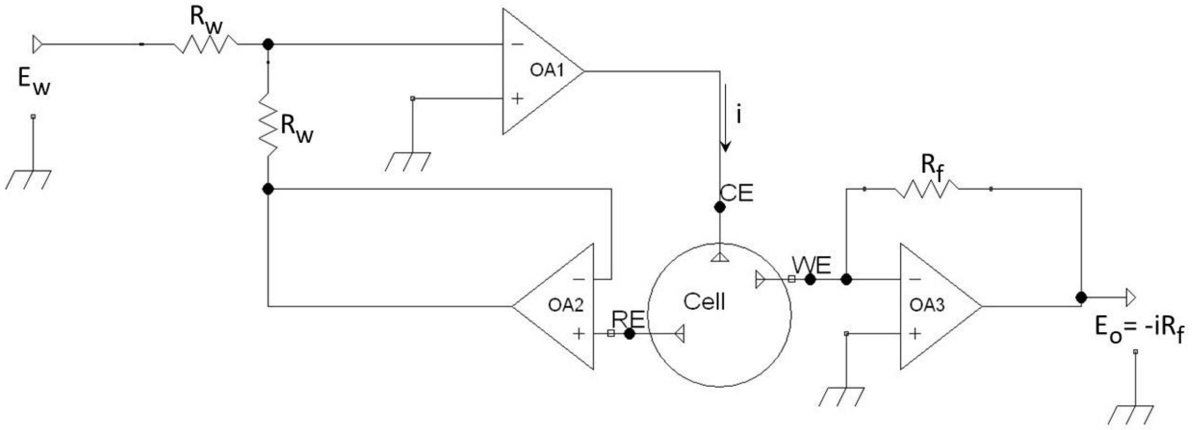


Figure 4.4 Schematic of I-to-V Module

The summing amplifier along with the buffer amplifer is responsible for the actual potentioistatic action. The buffer amplifier is connected directly to the reference electrode and draws almost no current from it.

The various components of I-to-V converter module can be op-amp based analog circuits. Figure 4.4 shows schematic of a generic I-to-V converter module with each block replaced by simple op-amp circuits. Additional components can be included in the circuit based on the gain and noise reduction requirements.

Counter electrode supply any current/voltage required by the working electrode to drive the reactions in the cell. Therefore, counter electrode acts as current source as well as voltage supply. Reference electrode's job is to measure the potential of the solution near the working electrode and to supply a reference potential point. That reference point is connected to the non-inverting input of OA2, which is wired up in voltage follower configuration. Therefore, it acts as a buffer for the potential, which means input of OA2 has very high impedance. E_w (external working voltage) and voltage through resistor R_w from OA2 are applied at inverting input of OA1 and OA1 is a summing amplifier with a feedback. The current flows through the counter electrode, and the feedback loop includes solution resistance. The output current of OA1 will be equal to input current of OA3. No current flows in or out of an operational amplifier. Yet the WE is connected directly to the inverting input of OA3. This means that the current has to come through the feedback resister R_f. Suppose, for e.g., a 1.0 μA current was flowing into the op-amp from the WE. If the feedback resistor is 1.0 MΩ, then a voltage of +1.0 V would have to exist on the output of OA3. If the output voltage rises too high, the positive-going potential feeds back to the inverting input and forces the voltage back down; the reverse happens if the output falls too low. The output voltage is therefore exactly proportional to the current; the proportionality factor is the value of the feedback resistor R_f in ohms. Importantly, the inverting input is held very close to ground by the operation of the amplifier- so the working electrode appears to be connected to ground. Therefore, the current at inverting input of OA3 eventually flows through R_f to reach output as Eo.

Autodesk® Eagle CAD software was used to design the printed circuit board (PCB) for the I-to-V converter module. The gerber files were then used to get the PCB manufactured from a local manufacturer. There were a series of such PCBs manufactured in the process of arriving at the final version of the I-to-V converter module. Figure 4.5 is the circuit diagram for the I-to-V converter module. Figure 4.6 is the hardware schematic made before it was sent out for manufacturing on a PCB, and Figure 4.7 shows photograph of a PCB after manufacture and soldering done with the components.

4.1.1.2 Data Acquisition Card (DAQ)

The DAQ chosen was USB-4711A (make: Advantech). A gist of features of the DAQ are presented in Table 4.1. Various pin assignments are given in Figure 4.8. Desirable features like availability to SDK and API available for development across various languages, a maximum sampling rate of 150kS/s, availability of sufficient number of analog input and output channels made 4711A a convenient choice for the research. Also, like many of the commercially available DAQ cards, 4711A doesn’t need an external power supply – it draws required power from the USB connection it is interfaced with. During the experimentation, USB-4711A was used in the -10 to +10V output mode.

With usage of appropriate APIs, the DAQ can be directed to apply a voltage pattern through analog outputs as per the requirement of the experiment. Similarly, APIs are provided to read voltages appearing at analog input pins through software. The software module manages the communication between the PC/Laptop and the DAQ.

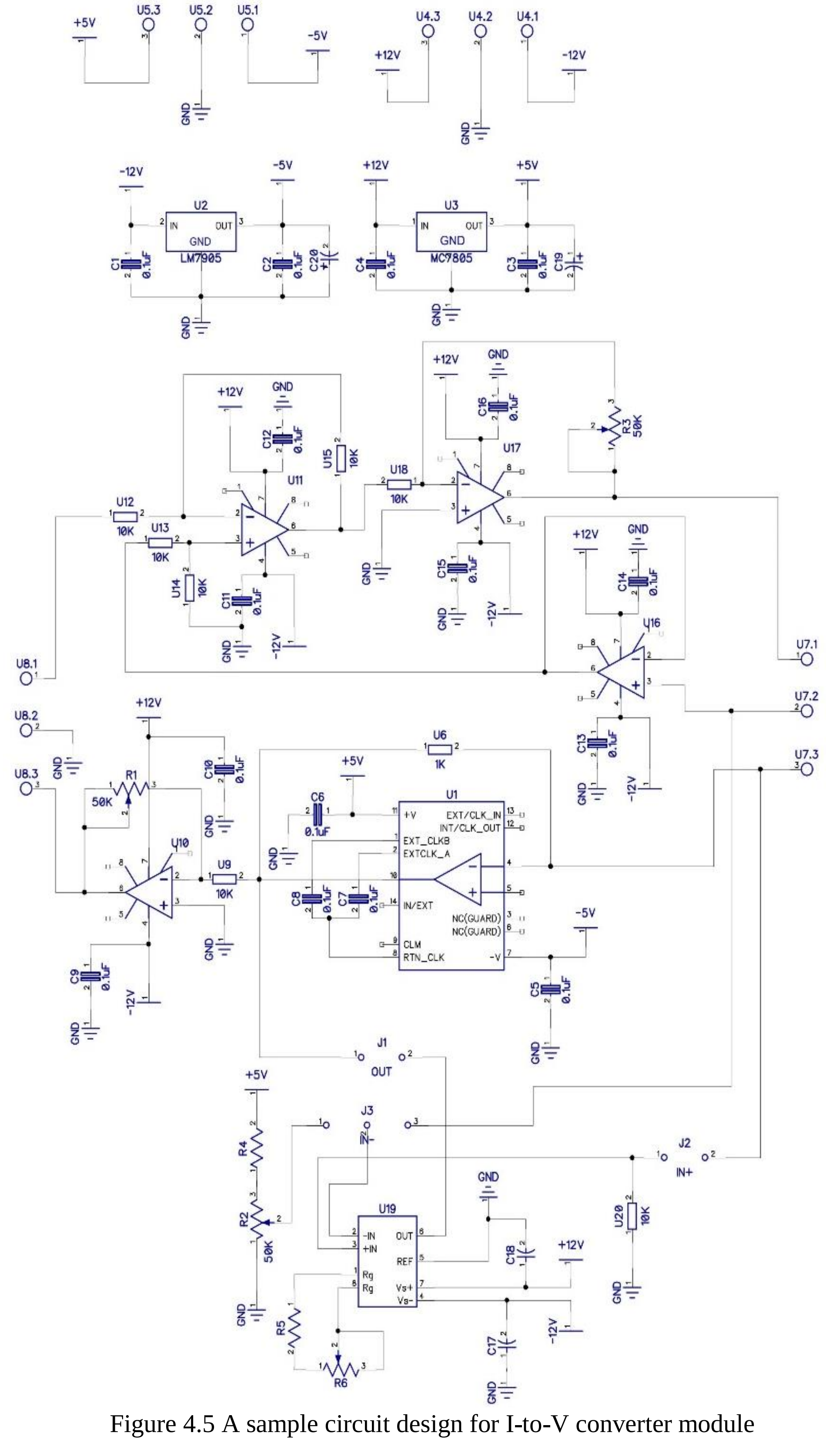


Figure 4.5 A sample circuit design for I-to-V converter module

4.1.2 Development of Software Module

The responsibility of the software module is to apply the excitation signal to the I-to-V converter module through the DAQ and also to receive the voltage signal from the analog output of the DAQ and store it in a file for future analysis. USB-4711A is provided with a rich set of SDK and APIs to support software development across various programming languages. LabVIEW was the first choice of language to develop the software module.

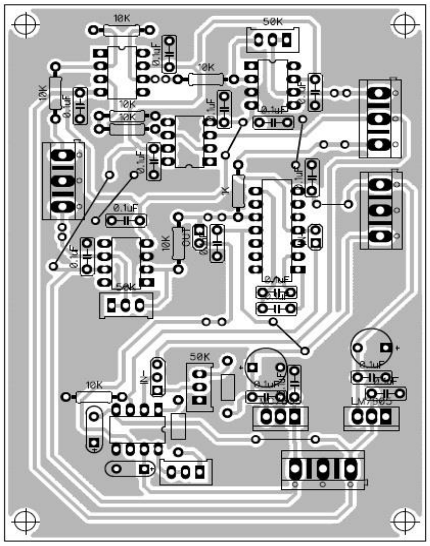


Figure 4.6 Hardware schematic of I-to-V converter module

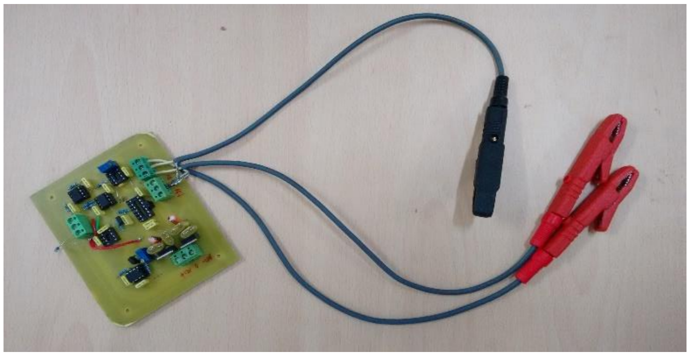


Figure 4.7 Photograph of an I-to-V converter module PCB

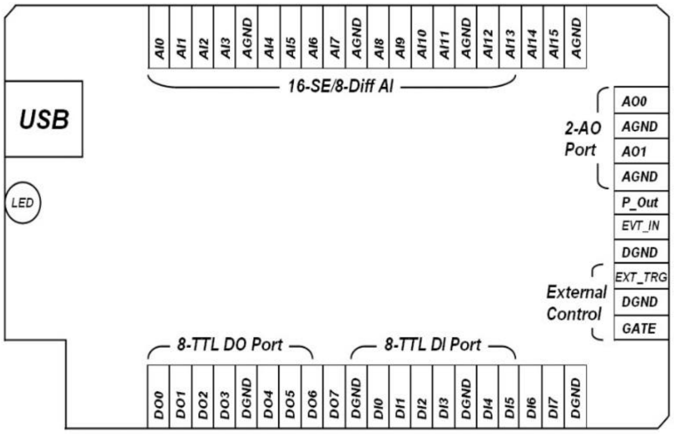


Figure 4.8 I-O Pin connector assignment of USB-4711A

Table 4.1 Relevant features of Advantech DAQ USB-4711A

Feature	Description
Analog Inputs	16 analog input channels (AI0 – AI15) are available. The same can be used as 8 analog input channels with differential inputs. A reference analog ground AGND is also provided.
Analog Outputs	Two analog output channels (AO0, AO1) are available with a reference analog ground AGND.
Analog Output Range	Works in four different modes: 0-5V, 0-10V, ±5V, ±10V with a driving capability of 5mA output current.
Digital Inputs	8 digital inputs (DI0 - DI7) are available with a reference digital ground DGND.
Digital Outputs	8 digital outputs (DO0 – DO7) are available with a reference digital ground DGND.
ADC	12-bit resolution on-board Analog to Digital Converter.
External Trigger	Signal that acts as trigger for analog to digital conversion. This is a negative-edge triggered input.
Sampling rate	Supports operation up to 150 kSamples/s.
Buffer	Has a FIFO buffer of 1024 samples.
Power consumption	Bus (USB) powered and consumes 450mA @ 5V.
Internal timer	Provides one 16-bit programmable/timer.
Software support	SDK and API available for a wide range of programming languages such as LabVIEW, C#, Delphi, Visual Basic.

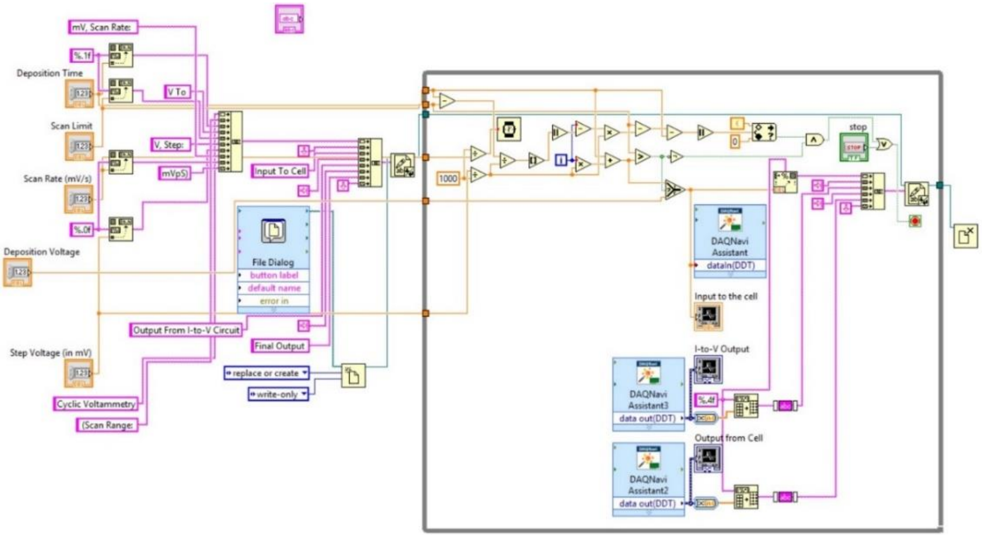
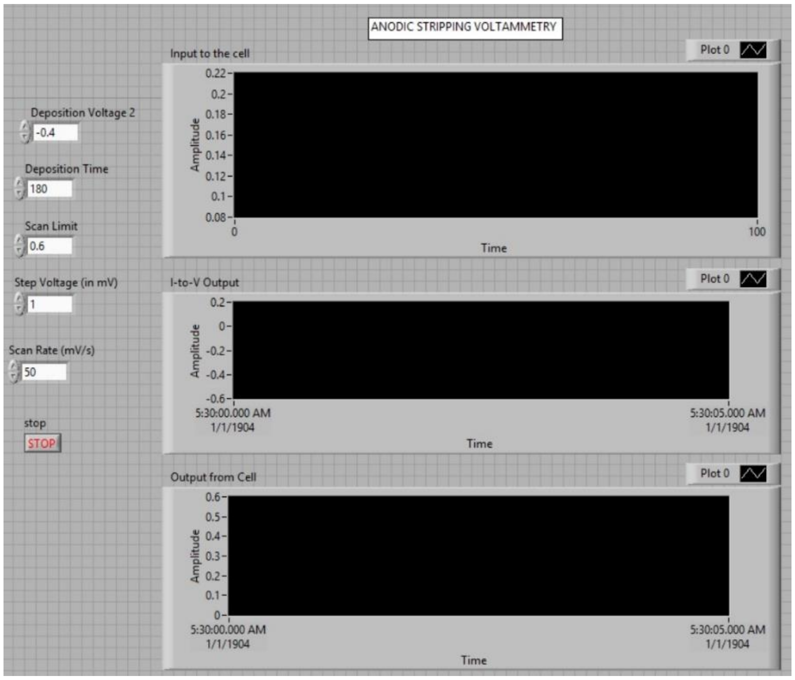


Figure 4.9 Screenshot of LabVIEW VI for running SWASV

Figure 4.9 is a screenshot of LabVIEW VI written to perform SWASV experiment with 4711A interfaced through USB. The user has to type-in the various parameter values required for running the SWASV experiment and run the VI. Figure 4.10 Shows the screenshot of the UI of the VI shown in Figure 4.9.

Though the software module developed using LabVIEW was fully functional, it suffered with the following limitations:


ANODIC STRIPPING VOLTAMMETRY

Deposition Voltage 2: -0.4

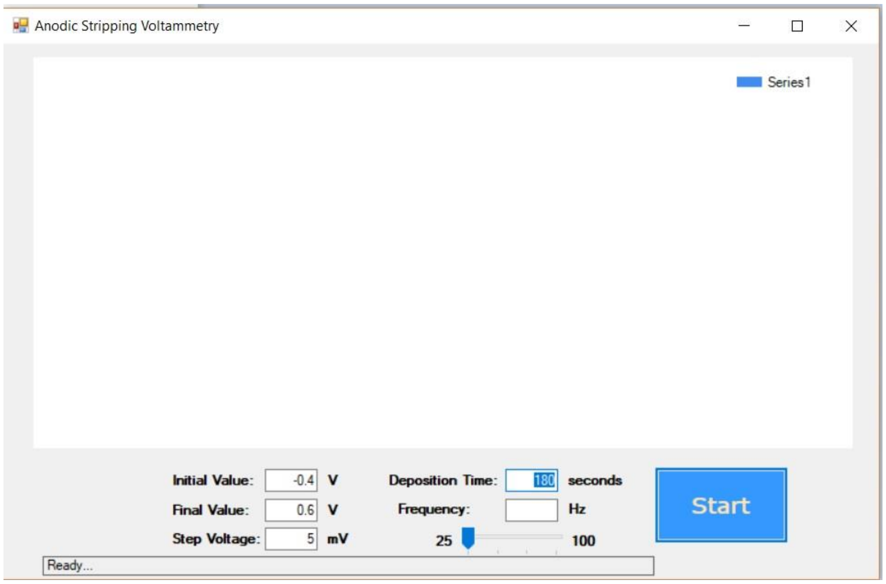
Deposition Time: 180

Scan Limit: 0.6

Step Voltage (in mV): 1

Scan Rate (mV/s): 50

Figure 4.10 UI for the LabVIEW VI developed to run SWASV



Initial Value: -0.4 V
Final Value: 0.6 V
Step Voltage: 5 mV
Deposition Time: 180 seconds
Frequency: Hz
Ready...

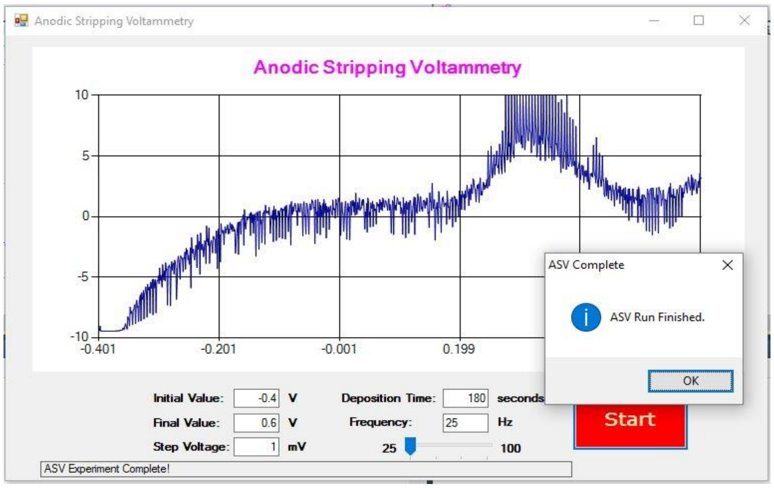
Figure 4.11 UI of the application developed using C#

i. The module requires LabVIEW runtime environment for deployment. The size of the runtime environment is very large (more than 100 MB) and often time-consuming to deploy.
ii. Few components of LabVIEW VI required runtime license to be purchased for execution. This would increase the cost of the overall solution.

Therefore, after careful consideration, C# was chosen for the development of software module as an alternate solution. Figure 4.11 shows the UI of application developed using C# that accepts the required parameters for running SWASV.

The development of the e-tongue system was done incrementally. During the development, the hardware as well as software modules have undergone lot of tweaking to make sure the current signatures were recorded without noise. Figure 4.12 is a screenshot of an UI taken during one such moment when the output produced by the I-to-V converter module was noisy and the same was shown in the UI as well.

Figure 4.13 is screenshot grabbed from a video that demonstrates working of the new e-tongue system with commercial potentiostat replaced and output produced was free from noise. The C# application makes use of the APIs provided by the Advantech DAQ USB-4711A to apply required potential through the analog output pins, receive the potential value through the analog input pins and store the received value into a text file for further analysis.


Anodic Stripping Voltammetry

ASV Complete

ASV Run Finished.

Initial Value: -0.4 V

Final Value: 0.6 V

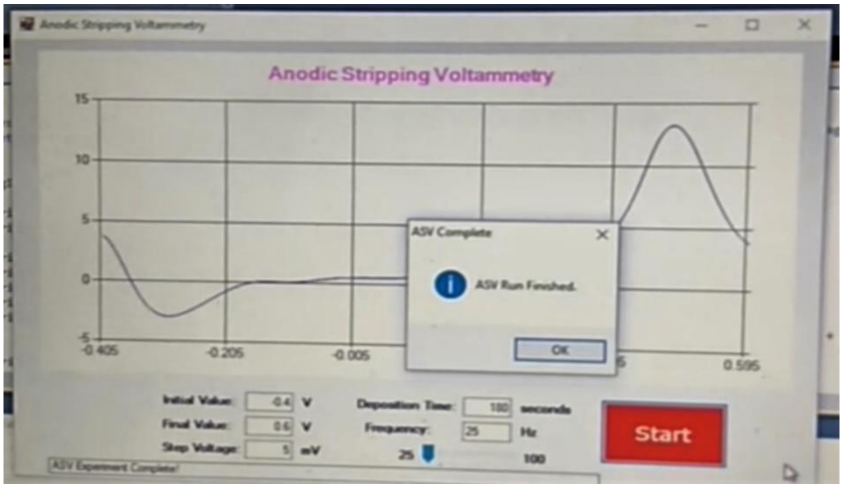
Step Voltage: 1 mV

Deposition Time: 180 seconds

Frequency: 25 Hz

ASV Experiment Complete!

Figure 4.12 Screenshot of C# application after ASV run is finished with noisy current output


Anodic Stripping Voltammetry

ASV Complete

ASV Run Finished.

Initial Value: -0.4 V

Final Value: 0.6 V

Step Voltage: 5 mV

Deposition Time: 180 seconds

Frequency: 25 Hz

ASV Experiment Complete

Figure 4.13 Screenshot captured from a video showing working of the e-tongue without noise

4.2 SWASV With Simulated Samples

Simulated samples were prepared with varying concentrations of arsenic (250 ppb, 200 ppb, 150 ppb, 100 ppb, 50 ppb, 25 ppb, 10 ppb, 5 ppb and 2 ppb). All solutions were prepared with 1M HCl as supporting electrolyte. SWASV experiments were conducted using these simulated samples with the developed e-tongue system and optimized parameters shown in Table *3.2*. The current responses recorded are shown in Figure 4.14 and the corresponding current peak data is presented in .Table 4.2

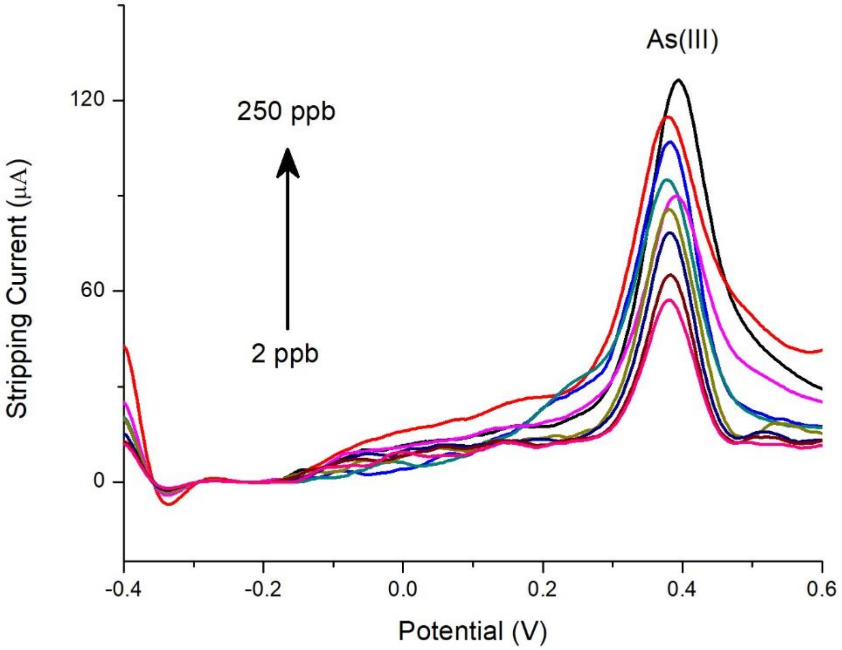


Figure 4.14 SWASV responses of As(III) concentrations varying from 2ppb to 250 ppb using newly developed e-tongue system

Table 4.2 Data for SWASV of samples containing only arsenic

As(III) Concentration (ppb)	Peak Voltage (V)	Peak Current (μ A)
2	0.38	57
5	0.383	65
10	0.383	78
25	0.38	86
50	0.392	90
100	0.377	95
150	0.383	107
200	0.38	115
250	0.395	126

As can be observed from the data, the current peak increases with the arsenic concentration in the analyte. The distinct peaks produced by each concentration without overlap is an indication that the new solution can be employed for arsenic detection and quantification without including commercial potentiostat in the experimentation.

4.2.1 Study of Copper Interference

Similar study was performed as done with the commercial potentiostat to analyse if the presence of copper will affect the detection and quantification of arsenic with the newly developed solution. The current responses recorded during the SWASV experiments are

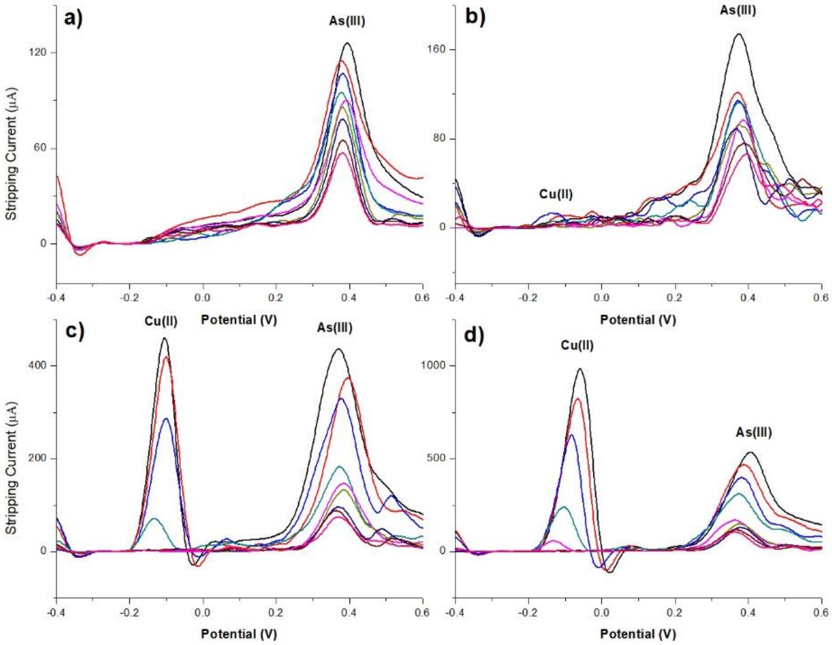


Figure 4.15 SWASV responses recorded using newly developed e-tongue system with samples containing: a) only As (III) b) As with 1x times Cu(II) c) As with 10x times Cu(II) d) As with 100x times Cu(II)

shown in Figure 4.15. As in the case with the commercial potentiostat, it was observed that the new solution also is immune to the presence of copper. All the concentrations ranging from 2 ppb to 250 ppb were tested by adding copper concentrations varying from 1x to 100x. The voltammogram from Figure 4.15(b) show that copper presence did not produce any significant current peak when it is present in equal amount as arsenic (1x). The SWASV responses in Figure 4.15(c) and Figure 4.15(d) explain that the copper and arsenic peaks are separated by at least 400mV. Therefore, it can be deduced that copper will not interfere with arsenic detection using the new hardware-software combination solution.

The trend in these observations were in line with those made with commercial potentiostat and presented in section 3.3.3. It was also observed that with the increase in the concentration of copper in the arsenite solutions, higher current peaks were produced as compared to those produced by solutions containing only arsenite. Again, it was observed that the influence of copper was less in lower concentrations. The trend of arsenic peaks produced with varying concentrations and the data related to these peaks are presented in Figure 4.16 and Table 4.3 respectively.

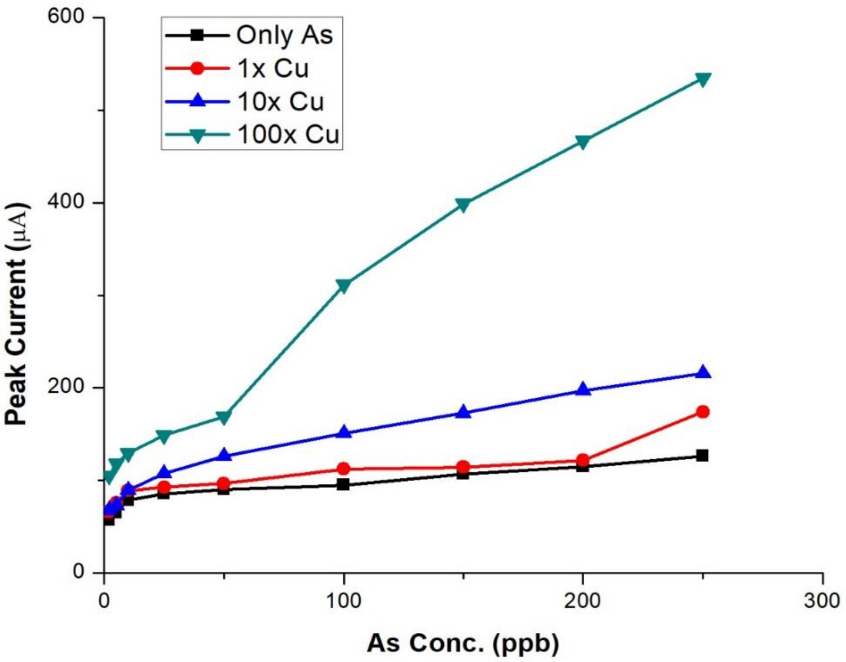


Figure 4.16 Trend of peaks produced by arsenic solutions with varying copper concentration using newly developed e-tongue system

Table 4.3 Peak currents recorded on various arsenic solutions with varying copper concentrations using hardware-software combination

Arsenic Concentration (in ppb)	**Peak Current (in μA) produced by solutions with**			
	Only Arsenic	**As with 1x times Cu**	**As with 10x times Cu**	**As with 100x times Cu**
2	57	66	68	105
5	65	76	73	118
10	78	89	89	129
25	86	93	108	149
50	90	97	126	169
100	95	112	151	311
150	107	114	173	399
200	115	122	197	467
250	126	174	216	535

4.3 Data Validation with Field Samples

There is a significant difference between detection of arsenic with simulated samples and that with field samples. The simulated samples which were used for analysis in the previous sections were all laboratory-prepared to contain arsenite only. However, when it comes to analysis of samples collected from the field, the composition is a lot different. Along with the arsenite, there is a high probability of coexistence of arsenate and other naturally abundant metals such as copper, iron, mercury and lead. The challenge is to perform detection and quantification of total arsenic without the interference of other metals present (if any). Total arsenic content includes both arsenite as well as arsenate present in the water sample. As(V) is electro-inactive and therefore, any arsenic detected using SWASV would be giving the amount of arsenite only. The most employed procedure for detection of total arsenic is to first reduce all arsenate present in the sample to arsenite and then perform detection of arsenic.

4.3.1 Analysis of Field Samples from 24-Paraganas District

The performance of the newly developed e-tongue solution was evaluated by analyzing tube well water samples collected from various sites in the 24 paraganas district (of West Bengal state, India) and the results were compared with those produced by AAS. Method of standard addition was chosen for calibration and detection of the unknown sample as described in the following sub-sections.

4.3.1.1 Experimental Setup:

Gold wire was used as working electrode along with an Ag/AgCl (3M NaCl) reference electrode and a platinum wire as an auxiliary electrode. An electrochemical cell with these three electrodes along with magnetic stirrer was setup. All the electrodes were connected to an analog data card that in turn was connected to data acquisition card interfaced to a PC using a software module developed in Visual C# .Net.

4.3.1.2 Reduction of Arsenate to Arsenite

Prior to analysis, 10% m/v of potassium iodide solution was added to the collected water sample in 4M HCl to reduce any As(V) present in the water sample to As(III). After adding potassium iodide solution, the sample was stirred thoroughly and allowed to settle for four hours.

4.3.1.3 Experimental Procedure:

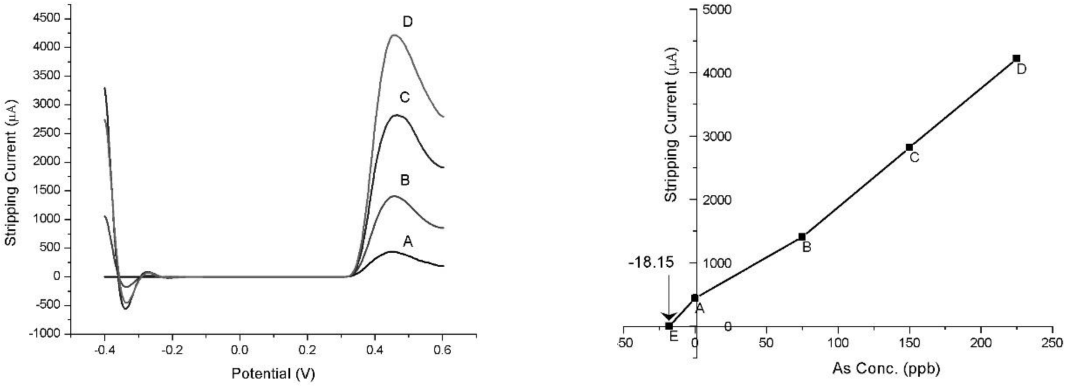
The following procedure described below is common for analysis of all field samples:

Four 100ml volumetric flasks (A, B, C & D) were taken and 20ml of the field sample of water after As(V) pre-reduction was transferred into each of the flasks. From 1 ppm stock solution of As(III), 7.5ml, 15ml and 22.5ml were transferred to volumetric flasks B, C, and D respectively. Then all the four flasks are topped up with distilled water to volume. Hence, flasks B, C and D had 75, 150 and 225 ppb of As(III) respectively along with the unknown concentration of As(III). 4M HCl is used as the supporting electrolyte.

20ml of the sample from flask A was transferred to electrochemical cell. A -0.4V (vs Ag/AgCl) was applied to the gold electrode for 180s for deposition (preconcentration) of As(III). The solution was stirred constantly during preconcentration step at 500 rpm. After deposition, the stirrer is stopped and the solution is allowed to settle for 10s. A sweeping potential was then applied from -0.4V to +0.6V at a frequency of 25 Hz with a step size of 3mV to determine the oxidation current.

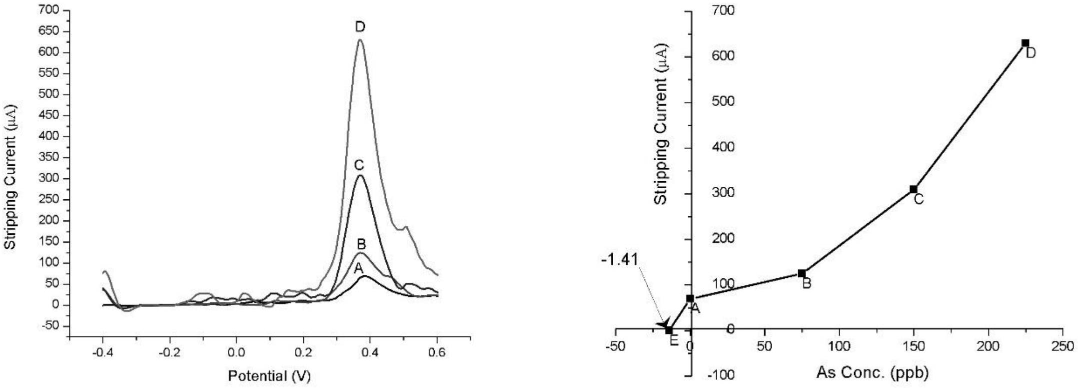
Current vs. potential plot was recorded and peak was recorded. The experiment was repeated under same conditions with samples from volumtertic flasks B, C and D and peaks were recorded on the plot. Cuves A, B, C, D in Figure 4.17(a), Figure 4.18(a) and Figure 4.19(a) are the respective voltammograms of solutions from flasks A, B, C and D for each field sample. Table 4.4 summarises peak currents recording by SWASV experiments on the solutions from flasks A, B, C and D.

The peak current vs. arsenic concentration were plotted separately for preparing the calibration curve. Figure 4.17(b), Figure 4.18(b) and Figure 4.19(b) are the plots showing calibration curves drawn from the voltammograms for field sample-1, field sample-2 and field sample-3 respectively. A linear nernstian plot was observed for each of the field sample and x-intercept of the regression line gives the concentration of the unknown sample solution. The concentration obtained from the calibration curve is then multiplied by 5 (because the sample was diluted 5 times before analysis) to get the actual concentration of the sample under analysis. The concentrations obtained from the standard addition method are compared against those obtained from AAS in Table 4.5.



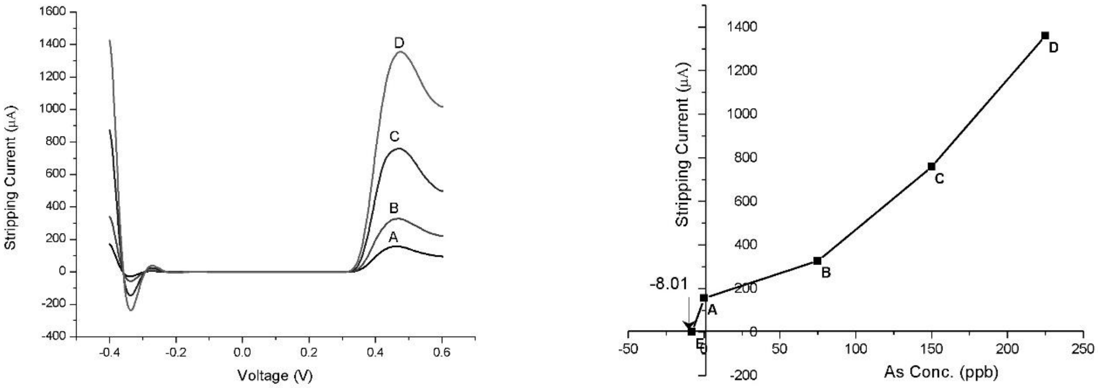
(a) (b)

Figure 4.17 (a) Voltammograms of the samples (b) Calibration curve for field sample-1



(a) (b)

Figure 4.18 (a) Voltammograms of the samples (b) Calibration curve for field sample-2



(a) (b)

Figure 4.19 (a) Voltammograms of the samples (b) Calibration curve for field sample-3

Table 4.4 Peak currents recorded for solutions from various flasks prepared for analysis of field samples

Sample No.	Flask A	Flask B	Flask C	Flask D
Field Sample-1	4.40E-04	1.41E-03	2.82E-03	4.22E-03
Field Sample-2	6.95E-05	1.25E-04	3.09E-04	6.30E-04
Field Sample-3	1.56E-04	3.27E-04	7.59E-04	1.36E-03

Table 4.5 Comparative statement of concentrations of field samples calculated based on the calibration curves and concentrations calculated from AAS

Sample No.	Intercept	Slope	R-Squared	Concen-tration. by Linear Fit (in ppb)	Actual Concen-tration (in ppb) (5x)	Concen-tration from AAS(in ppb)	Deviation (%)
Field Sample-1	3.08E-04	1.70E-05	0.993	-1.81E+01	90.75	92	1.36
Field Sample-2	3.51E-06	2.49E-06	0.908	-1.41E+00	7.05	7.2	2.08
Field Sample-3	4.37E-05	5.39E-06	0.946	-8.10E+00	40.50	39.2	3.32

Note: Deviation (%) = (Concentration from AAS – Actual Concentration)/Concentration from AAS

Table 4.5 presents the concentration of each field sample calculated using the data from the hardware-software combination and as well as from AAS. It was found that the congruence between results obtained from the newly developed solution and those obtained from AAS is more than 95%, which is a fair proof that the newly developed e-tongue solution can be used as an alternative to the AAS. Field sample-2 has arsenic concentration of 7.2 ppb which is well below the WHO approved limit of 10 ppb. This further supports our claim that the new solution could be employed successfully to analyze samples of lower concentration than 10 ppb. Morever, the newly developed e-tongue system as a part of this research has a great cost advantage as compared to the established analytical methods for detection and quantification of arsenic in aqueous samples. A comparative statement of cost per sample is presented in Table 4.6. The estimated cost includes the instrument's price and the cost of the consumables required to perform the experiment[121–123]. As shown in the table, when compared with the established commercial methods of arsenic detection, the solution proposed in this research has both the cost as well as time advantage.

4.4 Summary

An economic alternative has been presented for the expensive commercial potentiostat that is required to run ASV experiment. A novel hardware-software combination was employed to eliminate the usage of commercial potentiostat thereby significantly reducing the cost of the e-tongue setup required for detection and quantification of arsenic in drinking water samples. The design and development of hardware-software combination was detailed and the functioning various blocks of the hardware module was explained with circuit diagrams wherever needed. In addition, the performance of the solution proposed in this research was evaluated against that of AAS by estimating concentrations of various water samples collected from various sites in 24-paraganas district of West Bengal state, India. When compared with all the currently available commercial solutions used for detection of arsenic, the new hardware-software combination is the cheapest analytical solution with the lowest analysis time.

Table 4.6 Comparative statement of cost per sample for various analytical methods to detect and estimate arsenic in aqueous samples

Method	**Cost of equipment (approx. in INR)**	**Approximate cost per sample for one year in INR (@1000 samples/month)**	**Time taken for analysis**
ICP-MS	80 Lakh	900	Few hours
Colorimetric	0.50 Lakh	140	45 minutes
ASV (Commercial Potentiostat)	12 Lakh	100	20 minutes
ASV (Hardware-Software Combination)	**1 Lakh**	**8**	**20 minutes**

4.5 Supplementary Reading – Operational Amplifiers

This section provides a brief description of basic concepts about operational amplifiers (op-amps) and various configurations in which op-amps are employed for development of the hardware module.

4.5.1 Ideal Op-Amp

The operational amplifier or op-amp as it is commonly called, is a fundamental element of analog circuit design. It is most commonly used in amplifier and analog signal processing circuits in the frequency band from 0 to 100 kHz. Though an op-amp internally has complex circuitry involved, it is treated a basic circuit element.

The ideal op-amp is a three terminal device that is modeled as a voltage-controlled voltage source. That is, its output voltage is gain multiplied by its input voltage. The circuit symbol is given in Figure 4.20. The op-amp is a differential gain amplifier, meaning it amplifies the difference of inputs applied to it. The input at terminal marked with “+” is called non-inverting input and the input terminal marked with “-” is called inverting input. The output voltage is measured with respect to the circuit ground and is given by:

$$v_o = A(v_+ - v_-).$$

where A is the voltage gain, v_+ is the voltage at the non-inverting input, and v_- is the voltage at the inverting input.

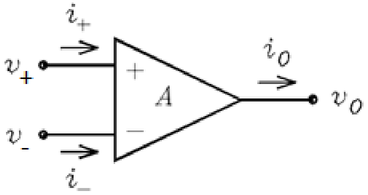


Figure 4.20 Op-amp Symbol

There are three conditions that the terminal characteristics of the ideal op amp satisfy. These are as follows:

1. The current in each input lead is zero. This means that the input resistance to each input is infinite.
2. The output voltage is independent of the output current. This means that the output resistance is zero.
3. An op-amp has a very high gain, ideally infinity. If the output voltage is finite, this means that the difference voltage between the two inputs must approach zero.

The following are the various op-amp circuit configurations that were employed in realizing the hardware module required to implement the new e-tongue system.

4.5.2 The Inverting Amplifier

Figure 4.21 shows the circuit diagram of an inverting amplifier. The input signal is applied through resistor R_1 to the v_- op-amp input. Resistor R_F is the feedback resistor which connects from the output to the inverting input. The v_+ op-amp input is not used and is grounded.

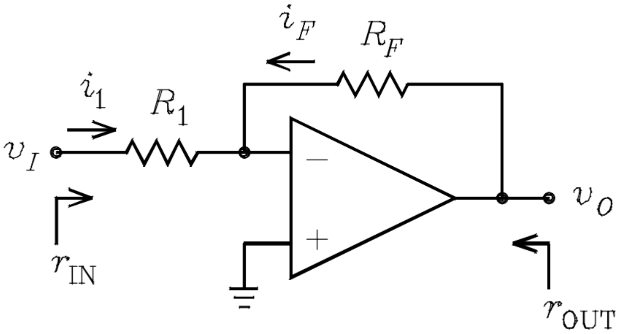


Figure 4.21 Inverting amplifer configuration

For the circuit, the voltage at the inverting input is given by $v_- = v_o/A$. If v_o is finite and $A \rightarrow \infty$, it follows that $v_- \rightarrow 0$. Even though the v_- input is not grounded, it is said to be a virtual ground because the voltage is zero. i.e., at ground potential. Because $i_- = 0$, the sum of the currents into the v- node through resistors R_1 and R_F must be zero, i.e., $i_1 + i_F = 0$, where $i_1 = v_I/R_1$ and $i_F = v_o/R_F$. Thus we can write

$$i_1 + i_F = 0 \text{ which implies, } \frac{v_I}{R_1} + \frac{v_o}{R_F} = 0$$

This can be solved for the voltage gain to obtain $\frac{v_o}{v_I} = -\frac{R_F}{R_1}$

The input resistance is given by $r_{IN} = \frac{v_I}{i_1}$, because $v_- = 0$, it follows that $r_{\mathrm{IN}} = R_1$.

4.5.3 The Voltage Follower

The voltage follower or unity-gain buffer is a non-inverting amplifier with unity gain. The circuit diagram is shown in Figure 4.22. Because the output node is connected directly to the inverting input, the circuit is said to have 100% feedback. Because $v_+ = v_-$, it follows that $v_o = v_I$. Therefore, the circuit has unity voltage gain. The voltage follower is often used to isolate a low-resistance load from a source having a high output resistance. That is, the voltage follower supplies the current to drive the load while drawing no current from the input circuit.

It is also used as a buffer in applications where it is desired to prevent the frequency response of a circuit from being a function of the output resistance of the source or a function of the load resistance.

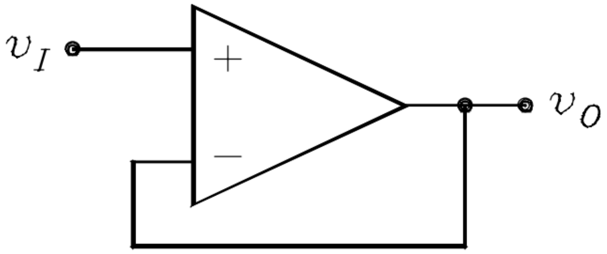


Figure 4.22 Voltage follower circuit

4.5.4 The Current-to-Voltage Converter

The circuit diagram of current-to-voltage converter is given in Figure 4.23. The circuit is a special case of an inverting amplifier where the input resistor is replaced with a short circuit. Because the v_- terminal is a virtual ground, the input resistance is zero. The output resistance is zero. Because $i_1 + i_F = 0$ it follows that $v_o = -\frac{i_F}{R_F}$. Therefore, output voltage is proportional to the input current, but is inverted.

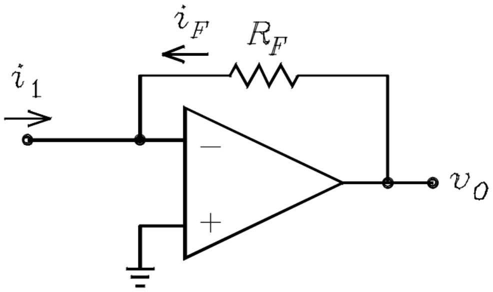


Figure 4.23 Current-to-voltage circuit

4.5.5 The Inverting Summer Circuit

The inverting summer circuit is a basic op-amp circuit that is used to sum two or more signal voltages, to sum a dc voltage with a signal voltage, etc. The circuit diagram of a four-input inverting summer is shown in Figure 4.24. If all inputs are grounded except the j^{th} input, where j = 1,2,3 or 4, then the circuit behaves similar to a simple non-inverting amplifier. It follows by superposition that the total output voltage is given by

$$v_0 = -\frac{R_F}{R_1}v_{I1} - \frac{R_F}{R_2}v_{I2} - \frac{R_F}{R_3}v_{I3} - \frac{R_F}{R_4}v_{I4}$$

The output resistance of the circuit is zero.

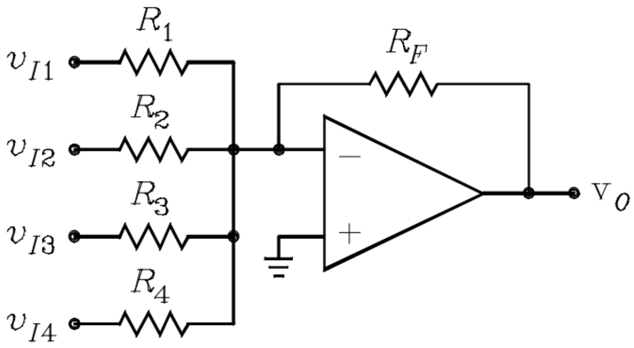


Figure 4.24 Inverter summer circuit

5 CONCLUSIONS AND FUTURE RECOMMENDATION

5.1 Conclusions

There are millions of tube-well water sources under use for drinking water, which contain alarming amounts of arsenic. A large section of population is at the risk of arsenic poisoning because of proper grading of water sources and people continue to consume water from contaminated sources. Such situation exists because present analytical techniques are restricted to laboratory and are very expensive. Most of the research for arsenic detection in drinking water is focused on development of novel electrodes to lower the detection limit or to detect with least interference from other elements. There is hardly any work reported that centered around reducing the equipment cost required for the analytical technique. This forms the motivation for the present research. The main objective of the work is to propose a solution that is economic, reproducible and portable that can accurately detect and estimate arsenic. In this regard, a novel hardware-software combination is proposed that is field deployable and is capable of successfully analyzing field samples for arsenic detection. The dissertation has chapters 3 and 4 as its major contribution whose highlights are presented below.

Experimentation With Arsenic Contaminated Water: Optimal parameter set for conducting ASV on simulated water samples using commercial potentiostat has been worked out. The optimal set ensures linear current response of the analysis across all concentrations of arsenite ranging from 5 ppb to 250 ppb. Experimental results have shown that the e-tongue employed is immune to any copper interference in the water samples analysed. Arsenite detection was successfully attempted with as much as 100 times copper across all arsenic concentrations in the range from 5 ppb to 250 ppb.

Design and Development of E-tongue: A low cost alternative to the expensive commercial potentiostat has been presented. The newly proposed e-tongue system consists of a data acquisition card interfaced with an in-house analog card that is connected to the electrochemical cell on one end, and an in-house developed software module implemented in C# (4.0). The hardware-software combination was successfully tested for arsenic detection across various concentrations ranging from 2 ppb to 250 ppb using SWASV. The experimental results have shown that the newly developed e-tongue system is also immune to any copper interference during arsenic detection showing similar trend as with commercial potentiostat. Finally, validation of the new e-tongue system was done by testing for arsenic in field samples collected from different sites in 24 paraganas district of West Bengal state, India. The results produced were validated against those produced by AAS. The newly proposed e-tongue system, therefore can be reliably deployed for in-situ analysis of field samples and has potential for large-scale deployment owing to its low cost and reliable results that could detect arsenic concentrations up to 2 ppb which is below WHO limit.

5.2 Future Recommendation

The proposed setup has great potential for large-scale deployment to test arsenic in drinking water. Another important application of the solution proposed can be foreseen in academics. The proposed hardware-software combination reduces the cost of potentiostat by 90% and hence it could be a strong encouraging factor for universities to offer the course of electrochemistry. The newly developed e-tongue system was extensively tested for the arsenic concentrations ranging from 2 ppb to 250 ppb by maintaining ambient temperature at 25^{o}C.

The following are few suggestions to take forward the present research:

i. **Miniaturisation:** Though the present solution is portable, it still depends on a PC/laptop. This can be further miniaturized by implementing a microcontroller based solution. Such solution would result in further cost reduction of the equipment.

ii. **Choice of electrode:** The research was carried out with a macro gold electrode as working electrode. The cost of the electrode can be further reduced by replacing it with inexpensive working electrodes such as gold nanoparticle coated electrodes, carbon nanotubes or screen-printed electrodes. CPEs may be a preferred choice for real sample analysis and would perform in situ measurements.

iii. **Remote Monitoring:** The solution could be connected to cloud via internet connectivity such that the field-analyzed data could be directly uploaded to a central server along with the location details of the site from where the sample was collected.

iv. **Extension to Other Analytes:** Though the present solution was developed for arsenic detection, the same could be deployed for testing other heavy metals such as chromium.

v. **Effect of Temperature:** A study of influence of variation in ambient temperature on the performance of the newly developed solution is desirable.

References

[1] B. Gordon, P. Callan, C. Vickers, WHO guidelines for drinking-water quality., WHO Chron. 38 (2008) 564. doi:10.1016/S1462-0758(00)00006-6.

[2] T. Bhattacharjee, M. Goswami, Heavy Metals (As , Cd & Pb) Toxicity & Detection of These Metals in Ground Water Sample : A Review on Different Techniques, 7 (2018) 12–21.

[3] A.H. Smith, E.O. Lingas, M. Rahman, Contamination of Drinking Water by Arsenic in Bangladesh : A Public Health Emergency . Bulletin of the World Health Organization 78 : Contamination of drinking-water by arsenic in Bangladesh : a public health emergency, 78 (2000).

[4] L. Rasmussen, K.J. Andersen, Environmental health and human exposure assessment, United Nations Synth. Rep. Arsen. Drink. Water. (2001).

[5] D. Chakraborti, M.M. Rahman, B. Das, B. Nayak, A. Pal, M.K. Sengupta, M.A. Hossain, S. Ahamed, M. Sahu, K.C. Saha, S.C. Mukherjee, S. Pati, R.N. Dutta, Q. Quamruzzaman, Groundwater arsenic contamination in Ganga-Meghna-Brahmaputra plain, its health effects and an approach for mitigation, Environ. Earth Sci. 70 (2013) 1993–2008. doi:10.1007/s12665-013-2699-y.

[6] K.W. Whitten, R.E. Davis, G.G. Stanley, Chemistry, 9th Editio, Brooks/Cole, Cengage Learning, 2010.

[7] F. Settle, Handbook Of Instrumental Techniques For Analytical CHemistry - Fran A.Settle.pdf, J. Liq. Chromatogr. Relat. Technol. 21 (1998) 3072–3076. doi:10.1080/10826079808006889.

[8] D. Harvey, Optimizing Chromatographic Separations, Mod. Anal. Chem. (2000) 556–562.

[9] G.M.S. Alves, J.M.C.S. Magalhães, P. Salaün, C.M.G. van den Berg, H.M.V.M. Soares, Simultaneous electrochemical determination of arsenic, copper, lead and mercury in unpolluted fresh waters using a vibrating gold microwire electrode, Anal. Chim. Acta. 703 (2011) 1–7. doi:10.1016/j.aca.2011.07.022.

[10] C.R. Sanger, O.F. Black, The Quantitative Determination of Arsenic by the Gutzeit Method Author (s): Charles Robert Sanger and Otis Fisher Black Source : Proceedings of the American Academy of Arts and Sciences , Vol . 43 , No . 8 (Oct ., Proc. Am. Acad. Arts Sci. 43 (1907) 297–324. http://www.jstor.org/stable/20022326.

[11] A. Cavicchioli, M.A. La-Scalea, I.G.R. Gutz, Analysis and speciation of traces of arsenic in environmental, food and industrial samples by voltammetry: A review, Electroanalysis. 16 (2004) 697–711. doi:10.1002/elan.200302936.

[12] M.M. Nearing, I. Koch, K.J. Reimer, Complementary arsenic speciation methods: A review, Spectrochim. Acta - Part B At. Spectrosc. 99 (2014) 150–162. doi:10.1016/j.sab.2014.07.001.

[13] Z.-G. Liu, X.-J. Huang, Voltammetric determination of inorganic arsenic, TrAC Trends Anal. Chem. 60 (2014) 25–35. doi:10.1016/j.trac.2014.04.014.

[14] L. Cui, J. Wu, H. Ju, Electrochemical sensing of heavy metal ions with inorganic, organic and bio-materials, Biosens. Bioelectron. 63 (2015) 276–286. doi:10.1016/j.bios.2014.07.052.

[15] Z. Guo, M. Yang, X.J. Huang, Recent developments in electrochemical determination

of arsenic, Curr. Opin. Electrochem. 3 (2017) 130–136. doi:10.1016/j.coelec.2017.08.002.

[16] B.K. Bansod, T. Kumar, R. Thakur, S. Rana, I. Singh, A review on various electrochemical techniques for heavy metal ions detection with different sensing platforms, Biosens. Bioelectron. 94 (2017) 443–455. doi:10.1016/j.bios.2017.03.031.

[17] N. Sankararamakrishnan, S. Mishra, Comprehensive Review on Various Analytical Methods for the Determination of Inorganic and Organic Arsenic in Environmental Samples, Environ. Contam. Energy, Environ. Sustain. (2018).

[18] E. Muñoz, S. Palmero, Analysis and speciation of arsenic by stripping potentiometry: A review, Talanta. 65 (2005) 613–620. doi:10.1016/j.talanta.2004.07.034.

[19] J. Tyson, The Determination of Arsenic Compounds: A Critical Review, ISRN Anal. Chem. 2013 (2013) 1–24. doi:10.1155/2013/835371.

[20] J.H.T. Luong, E. Majid, K.B. Male, Analytical Tools for Monitoring Arsenic in the Environment, Open Anal. Chem. J. . 1 (2007) 7–14. doi:10.2174/1874065000701017005.

[21] A.A.T.K.C.L.K. Riggs, Environmental Technology Verification Report - Nano-Band Explorer Portable Water Analyzer, U.S. Environ. Prot. Agency. (2002).

[22] E. Polshin, A. Rudnitskaya, D. Kirsanov, J. Lammertyn, B. Nicolaï, D. Saison, F.R. Delvaux, F. Delvaux, A. Legin, Measurement of beer taste attributes using an electronic tongue, AIP Conf. Proc. 1137 (2009) 259–262. doi:10.1063/1.3156520.

[23] M. Śliwińska, P. Wiśniewska, T. Dymerski, W. Wardencki, J. Namieśnik, Advances in Electronic Noses and Tongues for Food Authenticity Testing, Adv. Food Authent. Test. (2016) 201–225. doi:10.1016/B978-0-08-100220-9.00008-4.

[24] E. Methods, Chapter 11 Electrochemical Methods, Anal. Chem. 2.0. (1996) 1–115.

[25] D. Harvey, 11D: Voltammetric Methods - Chemwiki, Chemwiki. (2016) 1–23. http://chemwiki.ucdavis.edu/Core/Analytical_Chemistry/Analytical_Chemistry_2.0/11_Electrochemical_Methods/11D%3A_Voltammetric_Methods.

[26] D. Harris, Quantitative Chemical Analysis, 2015. doi:10.1017/CBO9781107415324.004.

[27] N. Elgrishi, K.J. Rountree, B.D. McCarthy, E.S. Rountree, T.T. Eisenhart, J.L. Dempsey, A Practical Beginner’s Guide to Cyclic Voltammetry, J. Chem. Educ. 95 (2018) 197–206. doi:10.1021/acs.jchemed.7b00361.

[28] F. Scholz, G. Inzelt, Z. Stojek, Seminal Publications in Electrochemistry and Electroanalysis, (2005).

[29] G. Forsberg, J.W. O’Laughlin, R.G. Megargle, S.R. Koirtyohann, Determination of Arsenic by Anodic Stripping Voltammetry and Differential Pulse Anodic Stripping Voltammetry, Anal. Chem. 47 (1975) 1586–1592. doi:10.1021/ac60359a057.

[30] A.O. Simm, C.E. Banks, R.G. Compton, The electrochemical detection of arsenic(III) at a silver electrode, Electroanalysis. 17 (2005) 1727–1733. doi:10.1002/elan.200503299.

[31] D.G. Williams, D.C. Johnson, Pulsed voltammetric detection of arsenic(III) at platinum electrodes in acidic media, Anal. Chem. 64 (1992) 1785–1789. doi:10.1021/ac00041a009.

[32] M. Del C. Aguirre, B.L. Rivas, L. Basáeza, C. Peña-Farfalc, Electrochemical detection of arsenite with silver electrodes in inorganic electrolyte and natural system mixtures, J. Braz. Chem. Soc. 22 (2011) 2362–2370. doi:10.1590/S0103-50532011001200018.

[33] A.O. Simm, O. Ordeig, J. Del Campo, F.X. Muñoz, R.G. Compton, Diffusional

protection of electrode surfaces using regular arrays of immobilised droplets: overcoming interferences in electroanalysis., Analyst. 131 (2006) 987–989. doi:10.1039/b607888e.

[34] D.E. Mays, A. Hussam, Voltammetric methods for determination and speciation of inorganic arsenic in the environment-A review, Anal. Chim. Acta. 646 (2009) 6–16. doi:10.1016/j.aca.2009.05.006.

[35] D.E. Mays, Voltammetric Stripping of Trace Arsenic in Flow Cells with Gold Wire as Working Electrode, (n.d.).

[36] G. Hignett, J.D. Wadhawan, N.S. Lawrence, D.Q. Hung, C. Prado, F. Marken, R.G. Compton, Electrochemical detection of as(III) via iodine electrogenerated at platinum, gold, diamond or carbon-based electrodes, Electroanalysis. 16 (2004) 897–903. doi:10.1002/elan.200302903.

[37] D. Yamada, T.A. Ivandini, M. Komatsu, A. Fujishima, Y. Einaga, Anodic stripping voltammetry of inorganic species of As3+ and As5+ at gold-modified boron doped diamond electrodes, J. Electroanal. Chem. 615 (2008) 145–153. doi:10.1016/j.jelechem.2007.12.004.

[38] G. March, T. Nguyen, B. Piro, Modified Electrodes Used for Electrochemical Detection of Metal Ions in Environmental Analysis, Biosensors. 5 (2015) 241–275. doi:10.3390/bios5020241.

[39] A.I. Kamenev, S.E. Orlov, A.B. Lyakhov, Electrochemical Preconcentration of Arsenic (III) in Its Determination by Stripping Voltammetry at Graphite Electrodes Modified with Gold and Copper, 56 (2001) 962–966.

[40] A.I. Kamenev, A.B. Lyakhov, S.E. Orlov, Determination of Arsenic (III) and Copper (II) by Stripping Voltammetry in a Mixed EDTA – Phosphoric Acid Supporting Electrolyte, Text. 60 (2005) 156–162.

[41] Y.C. Sun, J. Mierzwa, M.H. Yang, New method of gold-film electrode preparation for anodic stripping voltammetric determination of arsenic (III and V) in seawater, Talanta. 44 (1997) 1379–1387. doi:10.1016/S0039-9140(96)02197-2.

[42] S. Duangthong, A. Suwanin, P. Chooto, C. Innuphat, Flow injection-differential pulse anodic stripping voltammetry to measure As(III) and As(V) in natural water samples, ScienceAsia. 42 (2016) 266–274. doi:10.2306/scienceasia1513-1874.2016.42.266.

[43] T. Ndlovu, B.B. Mamba, S. Sampath, R.W. Krause, O.A. Arotiba, Voltammetric detection of arsenic on a bismuth modified exfoliated graphite electrode, Electrochim. Acta. 128 (2014) 48–53. doi:10.1016/j.electacta.2013.08.084.

[44] Y. Liu, W. Wei, Layer-by-layer assembled DNA functionalized single-walled carbon nanotube hybrids for arsenic(III) detection, Electrochem. Commun. 10 (2008) 872–875. doi:10.1016/j.elecom.2008.03.013.

[45] N.A. Yusof, N. Daud, T.W. Tee, A.H. Abdullah, Electrocatalytic Characteristic of Carbon Nanotubes / Glutamine / Nafion Modified Platinum Electrode in Development of Sensor for Determination of As (III), Int. J. Electrochem. Sci. 6 (2011) 2385–2397.

[46] G.G. Wildgoose, C.E. Banks, R.G. Compton, Metal nanoparticles and related materials supported on Carbon nanotubes: Methods and applications, Small. 2 (2006) 182–193. doi:10.1002/smll.200500324.

[47] S. Daniele, C. Bragato, From Macroelectrodes to Microelectrodes: Theory and Electrode Properties, (2015) 373–401. doi:https://doi.org/10.1007/978-1-4939-0676-5_15.

[48] C.S. Chapman, C.M.G. Van Den Berg, Anodic stripping voltammetry using a vibrating electrode, Electroanalysis. 19 (2007) 1347–1355. doi:10.1002/elan.200703873.

[49] P. Salaün, B. Planer-Friedrich, C.M.G. van den Berg, Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode, Anal. Chim. Acta. 585 (2007) 312–322. doi:10.1016/j.aca.2006.12.048.

[50] M. Yang, T.J. Jiang, Y. Wang, J.H. Liu, L.N. Li, X. Chen, X.J. Huang, Enhanced electrochemical sensing arsenic(III) with excellent anti-interference using amino-functionalized graphene oxide decorated gold microelectrode: XPS and XANES evidence, Sensors Actuators, B Chem. 245 (2017) 230–237. doi:10.1016/j.snb.2017.01.139.

[51] D.X.O. Jaramillo, A. Sukeri, L.P.H. Saravia, P.J. Espinoza-Montero, M. Bertotti, Nanoporous Gold Microelectrode: A Novel Sensing Platform for Highly Sensitive and Selective Determination of Arsenic (III) using Anodic Stripping Voltammetry, Electroanalysis. 29 (2017) 2316–2322. doi:10.1002/elan.201700301.

[52] R. Touilloux, M.-L. Tercier-Waeber, E. Bakker, Antifouling membrane integrated renewable gold microelectrode for in situ detection of As(<scp>iii</scp>), Anal. Methods. 7 (2015) 7503–7510. doi:10.1039/C5AY01941A.

[53] C. Zhou, M. Yang, S.S. Li, T.J. Jiang, J.H. Liu, X.J. Huang, X. Chen, Electrochemically etched gold wire microelectrode for the determination of inorganic arsenic, Electrochim. Acta. 231 (2017) 238–246. doi:10.1016/j.electacta.2017.01.184.

[54] E.A. Zakharova, G.N. Noskova, A.S. Kabakaev, N. V. Rees, R.G. Compton, Gold microelectrode ensembles: Cheap, reusable and stable electrodes for the determination of arsenic (V) under aerobic conditions, Int. J. Environ. Anal. Chem. 93 (2013) 1105–1115. doi:10.1080/03067319.2012.690151.

[55] M. Yang, X. Chen, T.-J. Jiang, Z. Guo, J.-H. Liu, X.-J. Huang, Electrochemical Detection of Trace Arsenic(III) by Nanocomposite of Nanorod-Like α-MnO $_2$ Decorated with ∼5 nm Au Nanoparticles: Considering the Change of Arsenic Speciation, Anal. Chem. 88 (2016) 9720–9728. doi:10.1021/acs.analchem.6b02629.

[56] L. Xiao, G.G. Wildgoose, R.G. Compton, Sensitive electrochemical detection of arsenic (III) using gold nanoparticle modified carbon nanotubes via anodic stripping voltammetry, Anal. Chim. Acta. 620 (2008) 44–49. doi:10.1016/j.aca.2008.05.015.

[57] A.K. Sakira, I.T. Somé, E. Ziemons, B. Dejaegher, D. Mertens, P. Hubert, J.M. Kauffmann, Determination of Arsenic(III) at a Nanogold Modified Solid Carbon Paste Electrode, Electroanalysis. 27 (2015) 309–316. doi:10.1002/elan.201400485.

[58] J.C.M. Gamboa, L. Cornejo, J.A. Squella, Vibrating screen printed electrode of gold nanoparticle-modified carbon nanotubes for the determination of arsenic(III), J. Appl. Electrochem. 44 (2014) 1255–1260. doi:10.1007/s10800-014-0727-6.

[59] S. Kempahanumakkagari, A. Deep, K.H. Kim, S. Kumar Kailasa, H.O. Yoon, Nanomaterial-based electrochemical sensors for arsenic - A review, Biosens. Bioelectron. 95 (2017) 106–116. doi:10.1016/j.bios.2017.04.013.

[60] M.G. Trachioti, A.E. Karantzalis, J. Hrbac, M.I. Prodromidis, Low-cost screen-printed sensors on-demand: Instantly prepared sparked gold nanoparticles from eutectic Au/Si alloy for the determination of arsenic at the sub-ppb level, Sensors Actuators, B Chem. 281 (2019) 273–280. doi:10.1016/j.snb.2018.10.112.

[61] M. Khairy, D.K. Kampouris, R.O. Kadara, C.E. Banks, Gold Nanoparticle Modified Screen Printed Electrodes for the Trace Sensing of Arsenic(III) in the Presence of

Copper(II), Electroanalysis. 22 (2010) 2496–2501. doi:10.1002/elan.201000226.

[62] S.S. Hassan, Sirajuddin, A.R. Solangi, T.G. Kazi, M.S. Kalhoro, Y. Junejo, Z.A. Tagar, N.H. Kalwar, Nafion stabilized ibuprofen-gold nanostructures modified screen printed electrode as arsenic(III) sensor, J. Electroanal. Chem. 682 (2012) 77–82. doi:10.1016/j.jelechem.2012.07.006.

[63] M. Rajkumar, S. Thiagarajan, S.M. Chen, Electrochemical detection of arsenic in various water samples, Int. J. Electrochem. Sci. 6 (2011) 3164–3177.

[64] P. Devi, C. Sharma, P. Kumar, M. Kumar, B.K.S. Bansod, M.K. Nayak, M.L. Singla, Selective electrochemical sensing for arsenite using rGO/Fe3O4 nanocomposites, J. Hazard. Mater. 322 (2017) 85–94. doi:10.1016/j.jhazmat.2016.02.066.

[65] D. Li, J. Li, X. Jia, Y. Han, E. Wang, Electrochemical determination of arsenic(III) on mercaptoethylamine modified Au electrode in neutral media, Anal. Chim. Acta. 733 (2012) 23–27. doi:10.1016/j.aca.2012.04.030.

[66] X. Dai, R.G. Compton, Determination of Copper in the Presence of Various Amounts of Arsenic withL-Cysteine Modified Gold Electrodes, Electroanalysis. 17 (2005) 1835–1840. doi:10.1002/elan.200503310.

[67] Z.G. Liu, X. Chen, J.H. Liu, X.J. Huang, Robust electrochemical analysis of As(III) integrating with interference tests: A case study in groundwater, J. Hazard. Mater. 278 (2014) 66. doi:10.1016/j.jhazmat.2014.05.094.

[68] A. Giacomino, O. Abollino, M. Lazzara, M. Malandrino, E. Mentasti, Determination of As(III) by anodic stripping voltammetry using a lateral gold electrode: Experimental conditions, electron transfer and monitoring of electrode surface, Talanta. 83 (2011) 1428–1435. doi:10.1016/j.talanta.2010.11.033.

[69] X. Dai, R.G. Compton, Gold nanoparticle modified electrodes show a reduced interference by Cu(II) in the detection of As(III) using anodic stripping voltammetry, Electroanalysis. 17 (2005) 1325–1330. doi:10.1002/elan.200403246.

[70] T. Gu, L. Bu, Z. Huang, Y. Liu, Z. Tang, Y. Liu, S. Huang, Q. Xie, S. Yao, X. Tu, X. Luo, S. Luo, Dual-signal anodic stripping voltammetric determination of trace arsenic(III) at a glassy carbon electrode modified with internal-electrolysis deposited gold nanoparticles, Electrochem. Commun. 33 (2013) 43–46. doi:10.1016/j.elecom.2013.04.019.

[71] X. Dai, R.G. Compton, Detection of As(III) via oxidation to As(V) using platinum nanoparticle modified glassy carbon electrodes: arsenic detection without interference from copper., Analyst. 131 (2006) 516–521. doi:10.1039/b513686e.

[72] F.J. Pereira, M.D. Vázquez, L. Debán, A.J. Aller, Inorganic arsenic speciation by differential pulse anodic stripping voltammetry using thoria nanoparticles-carbon paste electrodes, Talanta. 152 (2016) 211–218. doi:10.1016/j.talanta.2016.02.011.

[73] A.A. Ensafi, A.C. Ring, I. Fritsch, Highly sensitive voltammetric speciation and determination of inorganic arsenic in water and alloy samples using ammonium 2-amino-1-cyclopentene-1-dithiocarboxylate, Electroanalysis. 22 (2010) 1175–1185. doi:10.1002/elan.200900347.

[74] S. Sanllorente-Méndez, O. Domínguez-Renedo, M. Julia Arcos-Martínez, Immobilization of acetylcholinesterase on screen-printed electrodes. Application to the determination of arsenic(III), Sensors. 10 (2010) 2119–2128. doi:10.3390/s100302119.

[75] L. Rassaei, M. Sillanpää, R.W. French, R.G. Compton, F. Markenc, Arsenite determination in phosphate media at electroaggregated gold nanoparticle deposits,

Electroanalysis. 20 (2008) 1286–1292. doi:10.1002/elan.200804226.

[76] H. Huang, P.K. Dasgupta, A field-deployable instrument for the measurement and speciation of arsenic in potable water, Anal. Chim. Acta. 380 (1999) 27–37. doi:10.1016/S0003-2670(98)00649-7.

[77] R. Prakash, R.C. Srivastava, P.K. Seth, Direct estimation of total arsenic using a novel metal side disk rotating electrode, Electroanalysis. 15 (2003) 1410–1414. doi:10.1002/elan.200302658.

[78] A.J. Bard, L.R. Faulkner, N. York, C. @bullet, W. Brisbane, S.E. Toronto, Electrochemical Methods - Fundamentals and Applications, 1944. doi:10.1016/B978-0-12-381373-2.00056-9.

[79] B. Šljukić, G.G. Wildgoose, A. Crossley, J.H. Jones, L. Jiang, T.G.J. Jones, R.G. Compton, The thermodynamics of sequestration of toxic copper(ii) metal ion pollutants from aqueous media by l-cysteine methyl ester modified glassy carbon spheres, J. Mater. Chem. 16 (2006) 970. doi:10.1039/b514819g.

[80] G. Lauer, R. Abel, F.C. Anson, Electrochemical Data Acquisition, 360 (1966).

[81] R.W. Shideler, U. Bertocci, A low-noise potentiostat for the study of small amplitude signals in electrochemistry, J. Res. Natl. Bur. Stand. (1934). 85 (1980) 211. doi:10.6028/jres.085.012.

[82] R.F.B. Turner, D.J. Harrison, H.P. Baltes, A CMOS potentiostat for amperometric chemical sensors, IEEE J. Solid-State Circuits. 22 (1987) 473–478. doi:10.1109/JSSC.1987.1052753.

[83] R. a. Cottis, A Low Cost Computer-Controlled Electrochemical Measurement System for Education and Research, Mater. Sci. Forum. 44–45 (1989) 123–138. doi:10.4028/www.scientific.net/MSF.44-45.123.

[84] T. Fang, Development of a computer controlled multichannel potentiostat for applications with flowing solution analysis, (1994).

[85] M.D. Steinberg, A micropower amperometric potentiostat, Sensors Actuators, B Chem. 97 (2004) 284–289. doi:10.1016/j.snb.2003.09.002.

[86] C.-Y. Chun-Yueb Huang, H.-Y. Huan-Yu Lin, Y.-C. Yu-Chien Wang, W.-Y. Wei-Yin Liao, T.-C. Tse-Chuan Chou, A portable and wireless data transmission potentiostat, 2004 IEEE Asia-Pacific Conf. Circuits Syst. 2004. Proceedings. 2 (2004) 633–636. doi:10.1109/APCCAS.2004.1412957.

[87] D. Melamed, Monitoring arsenic in the environment: A review of science and technologies with the potential for field measurements, Anal. Chim. Acta. 532 (2005) 1–13. doi:10.1016/j.aca.2004.10.047.

[88] E.M. Avdikos, M.I. Prodromidis, C.E. Efstathiou, Construction and analytical applications of a palm-sized microcontroller-based amperometric analyzer, Sensors Actuators, B Chem. 107 (2005) 372–378. doi:10.1016/j.snb.2004.10.029.

[89] A.V. Gopinath, D. Russell, An Inexpensive Field-Portable Programmable Potentiostat, Chem. Educ. 6 (2005) 1–6. doi:10.1333/s00897050972a.

[90] V. Beni, V.I. Ogurtsov, N. V. Bakunin, D.W.M. Arrigan, M. Hill, Development of a portable electroanalytical system for the stripping voltammetry of metals: Determination of copper in acetic acid soil extracts, Anal. Chim. Acta. 552 (2005) 190–200. doi:10.1016/j.aca.2005.07.058.

[91] S. Kwakye, A. Baeumner, An embedded system for portable electrochemical detection, Sensors Actuators, B Chem. 123 (2007) 336–343. doi:10.1016/j.snb.2006.08.032.

[92] K. Christidis, K. Gow, P. Robertson, P. Pollard, Intelligent potentiostat for identification of heavy metals in situ, Rev. Sci. Instrum. 77 (2006) 1–4. doi:10.1063/1.2165570.

[93] S.M.R. Hasan, Stability Analysis and Novel Compensation of a CMOS Current-Feedback Potentiostat Circuit for Electrochemical Sensors, IEEE Sens. J. 7 (2007) 814–824. doi:10.1109/JSEN.2007.893236.

[94] M.H. Nazari, R. Genov, A fully differential CMOS potentiostat, Proc. - IEEE Int. Symp. Circuits Syst. (2009) 2177–2180. doi:10.1109/ISCAS.2009.5118228.

[95] S.M. Martin, F.H. Gebara, T.D. Strong, R.B. Brown, A fully differential potentiostat, IEEE Sens. J. 9 (2009) 135–142. doi:10.1109/JSEN.2008.2011085.

[96] M.M. Ahmadi, G.A. Jullien, Current-mirror-based potentiostats for three-electrode amperometric electrochemical sensors, IEEE Trans. Circuits Syst. I Regul. Pap. 56 (2009) 1339–1348. doi:10.1109/TCSI.2008.2005927.

[97] T. Sensors, SGX Sensortech. Electrochemical Sensors Application Note 2 Design of Electronics for Electrochemical Gas Sensors, (2016) 1–7. https://www.sgxsensortech.com/content/uploads/2014/08/A1A-EC_SENSORS_AN2-Design-of-Electronics-for-EC-Sensors-V4.pdf.

[98] A.A. Rowe, A.J. Bonham, R.J. White, M.P. Zimmer, R.J. Yadgar, T.M. Hobza, J.W. Honea, I. Ben-Yaacov, K.W. Plaxco, Cheapstat: An open-source, “do-it-yourself” potentiostat for analytical and educational applications, PLoS One. 6 (2011). doi:10.1371/journal.pone.0023783.

[99] M. Roknsharifi, B.J. Blalock, J. Holleman, M. Mahfouz, A Low-Power, Highly Stabilized Three-Electrode Potentiostat Using Subthreshold Techniques, (2012). http://trace.tennessee.edu/utk_graddiss/1557.

[100] E.S. Friedman, M.A. Rosenbaum, A.W. Lee, D.A. Lipson, B.R. Land, L.T. Angenent, A cost-effective and field-ready potentiostat that poises subsurface electrodes to monitor bacterial respiration, Biosens. Bioelectron. 32 (2012) 309–313. doi:10.1016/j.bios.2011.12.013.

[101] D.G.S. Jenna R. Mott, Paul J. Munson, Rodney A. Kreuter, Balwant S. Chohan, Design, Development, and Characterization of an Inexpensive Portable Cyclic Voltammeter, J. Chem. Educ. 91 (2014) 1028–1036. http://www.newyorker.com/tech/elements/werner-herzog-talks-virtual-reality.

[102] E. Friedman, A. Hartoto, Low-Cost Portable Potentiostat for Biosensing Applications, (2014) 1–10.

[103] B. Aremo, M. Oyebamiji Adeoye, I.B. Obioh, O.A. Adeboye, A Simplified Microcontroller Based Potentiostat for Low-Resource Applications, Open J. Met. 05 (2015) 37–46. doi:10.4236/ojmetal.2015.54005.

[104] L. Zuo;, I. Mahbub, A Low-Power 1-V Potentiostat for Glucose Sensors, IEEE Trans. Circuits Syst. 62 (2015) 204–208. doi:10.1109/TCSII.2014.2387691.

[105] M.D. Steinberg, P. Kassal, I. Kereković, I.M. Steinberg, A wireless potentiostat for mobile chemical sensing and biosensing, Talanta. 143 (2015) 178–183. doi:10.1016/j.talanta.2015.05.028.

[106] K. Ngamchuea, P. Hurst, C. Batchelor-McAuley, R.G. Compton, Handheld electrochemical device for the determination of the strength of garlic, Sensors Actuators, B Chem. 232 (2016) 138–142. doi:10.1016/j.snb.2016.03.057.

[107] P. Wu, G. Vazquez, N. Mikstas, S. Krishnan, U. Kim, Aquasift: A low-cost, hand-held potentiostat for point-of-use electrochemical detection of contaminants in drinking

water, GHTC 2017 - IEEE Glob. Humanit. Technol. Conf. Proc. 2017–Janua (2017) 1–4. doi:10.1109/GHTC.2017.8239306.

[108] P. Linhardt, S. Kührer, G. Ball, M. V. Biezma, Design of a multichannel potentiostat and its application to corrosion testing of a nickel-aluminum bronze, Mater. Corros. 69 (2018) 358–364. doi:10.1002/maco.201709781.

[109] C. Cheng, K. Zor, J. Wang, K. Sanger, W. Wang, A.M. Capria, A. Boisen, K. Huang, E. Hwu, Wireless , Smartphone Controlled Potentiostat Integrated With Lab-on-Disc Platform, 21st Int. Conf. Miniaturized Syst. Chem. Life Sci. Savannah, United States. (2017) 629–630.

[110] G.N. Meloni, Building a microcontroller based potentiostat: A inexpensive and versatile platform for teaching electrochemistry and instrumentation, J. Chem. Educ. 93 (2016) 1320–1322. doi:10.1021/acs.jchemed.5b00961.

[111] S.N.H. Umar, E.A. Bakar, N.M. Kamaruddin, N. Uchiyama, A low cost potentiostat device for monitoring aqueous solution, MATEC Web Conf. 04001 (2018) 8. doi:https://doi.org/10.1051/matecconf/201821704001.

[112] A.I. Muñoz-Martínez, O.I.G. Peña, J. Colomer-Farrarons, J.M. Rodríguez-Delgado, A. Ávila-Ortega, G. Dieck-Assad, Electrochemical Instrumentation of an Embedded Potentiostat System (EPS) for a Programmable-System-On-a-Chip, Sensors. 18 (2018) 4490. doi:10.3390/s18124490.

[113] W.W. Goldsworthy, R.G. Clem, A Digital Potentiostat, Anal. Chem. 43 (1971) 1718–1720. doi:10.1021/ac60306a025.

[114] J.C. Chou, R.T. Chen, Y.H. Liao, J.S. Chen, M.S. Huang, H.T. Chou, Dynamic and Wireless Sensing Measurements of Potentiometric Glucose Biosensor Based on Graphene and Magnetic Beads, IEEE Sens. J. 15 (2015) 5718–5725. doi:10.1109/JSEN.2015.2449906.

[115] G. Denuault, Electrochemical techniques and sensors for ocean research, Ocean Sci. 5 (2009) 697–710. doi:10.5194/os-5-697-2009.

[116] J.T. Stock, A simple low-current potentiostat coulometric analysis, J. Chem. Educ. 45 (1968) 736. doi:10.1021/ed045p736.

[117] C. Fan, K.W. Plaxco, A.J. Heeger, Electrochemical interrogation of conformational changes as a reagentless method for the sequence-specific detection of DNA, Proc. Natl. Acad. Sci. 100 (2003) 9134–9137. doi:10.1073/pnas.1633515100.

[118] S.W. Lee, J.C. Méranger, Determination of total arsenic species by anodic stripping voltammetry, Anal. Chem. 53 (1981) 130–131. doi:10.1021/ac00224a036.

[119] L.M. Fischer, M. Tenje, A.R. Heiskanen, N. Masuda, J. Castillo, A. Bentien, J. Émneus, M.H. Jakobsen, A. Boisen, Gold cleaning methods for electrochemical detection applications, Microelectron. Eng. 86 (2009) 1282–1285. doi:10.1016/j.mee.2008.11.045.

[120] G. Scarponi, Optimization of square wave anodic stripping voltammetry (SWASV) for the simultaneous determination of Cd, Pb, and Cu in seawater and comparison with differential pulse anodic stripping voltammetry (DPASV)., (2002). http://citeweb.info/20020474074.

[121] E. Security, T.C. Program, Environmental Security Technology Certification Program (ESTCP) Cost and Performance Report Field Validation of Real Time Airborne Lead Analyzer January 2002, (2002).

[122] S. Wilbur, Agilent Technologies, A Comparison of the Relative Cost and Productivity

of Traditional Metals Analysis Techniques Versus ICP-MS in High Throughput Commercial Laboratories Application, (2005) 1–6.

[123] J.M. Spear, Y.M. Zhou, C.A. Cole, Y.F. Xie, Evaluation of arsenic field test kits for drinking water analysis, J. / Am. Water Work. Assoc. 98 (2006) 97–105.

Dissemination

1. **S. K. Agir**, M. Kundu, Detection and quantification of arsenic in water using electronic tongue, in: 2016 IEEE 1st Int. Conf. Control. Meas. Instrumentation, C. 2016, 2016. doi:10.1109/CMI.2016.7413783.

2. **S. K. Agir**, M. Kundu, An electronic tongue based arsenic quantifier, Indian patent application No. 201831020756, filed June 4, 2018.