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Feb 2005
SENSITIVE AND SELECTIVE INORGANIC ARSENIC DETERMINATION ON A VOLTAMMETRIC PLATFORM IN AQUATIC SAMPLES FROM SOLOMON ISLANDS AND FIJI

by

Wycliff Tupiti

A thesis submitted in fulfilment of the requirements for the degree of Master of Science

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School of Biological and Chemical Sciences
Faculty of Science, Technology and Environment
University of the South Pacific

December, 2016
DEDICATION

To my loving parents
DECLARATION

Statement by Author:

I hereby declare that the work presented in this thesis is the result of my own work and that any information cited from literature or otherwise has been duly and appropriately acknowledged and referenced.

Date: 2\textsuperscript{nd}/12/2016

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(ID: s11045515)

Statement by Supervisor:

The research described in this thesis was performed under our supervision and to our knowledge is the sole work of Wycliff Tupiti.

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Date: ........................

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Date: ........................

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### ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Ampere</td>
</tr>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectrometry</td>
</tr>
<tr>
<td>AdSV</td>
<td>Adsorptive Stripping Voltammetry</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AFS</td>
<td>Atomic Force Spectrometry</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminium</td>
</tr>
<tr>
<td>ANZECC</td>
<td>Australian and New Zealand Guidelines for Marine Water Quality</td>
</tr>
<tr>
<td>As</td>
<td>Arsenic</td>
</tr>
<tr>
<td>ASV</td>
<td>Anodic Stripping Voltammetry</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>Au NPs</td>
<td>Gold nanoparticles</td>
</tr>
<tr>
<td>Cd</td>
<td>Cadmium</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>CSV</td>
<td>Cathodic Stripping Voltammetry</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>DMAA</td>
<td>Dymethylarsinic acid</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved Oxygen</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
</tr>
<tr>
<td>E</td>
<td>Potential</td>
</tr>
<tr>
<td>EcHG</td>
<td>Electrochemical Hydride Generation</td>
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<tr>
<td>Fe</td>
<td>Iron</td>
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<tr>
<td>g</td>
<td>Gram</td>
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<td>h</td>
<td>Hour</td>
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<tr>
<td>HDME</td>
<td>Hanging Drop Mercury Electrode</td>
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<tr>
<td>HG</td>
<td>Hydride Generation</td>
</tr>
<tr>
<td>Hg</td>
<td>Mercury</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>i</td>
<td>Current</td>
</tr>
<tr>
<td>ICPMS</td>
<td>Inductively Coupled Plasma Mass Spectrometry</td>
</tr>
<tr>
<td>Ir</td>
<td>Iridium</td>
</tr>
<tr>
<td>km</td>
<td>Kilometer</td>
</tr>
<tr>
<td>kPa</td>
<td>Kilo pascal</td>
</tr>
<tr>
<td>L</td>
<td>Liter</td>
</tr>
<tr>
<td>LOD</td>
<td>Limit of Detection</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear Sweep Voltammetry</td>
</tr>
<tr>
<td>M</td>
<td>Molar (Moles per liter)</td>
</tr>
<tr>
<td>m</td>
<td>Meter</td>
</tr>
<tr>
<td>mg</td>
<td>Milligram</td>
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<tr>
<td>mg/L</td>
<td>Milligram per litre</td>
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<tr>
<td>μg/L</td>
<td>Microgram per litre</td>
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<tr>
<td>mL</td>
<td>Milliliter</td>
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<td>mM</td>
<td>Millimolar</td>
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<tr>
<td>mm</td>
<td>Millimeter</td>
</tr>
<tr>
<td>MMAA</td>
<td>Monomethylarsonic acid</td>
</tr>
<tr>
<td>Mn</td>
<td>Manganese</td>
</tr>
<tr>
<td>Mo</td>
<td>Molybdenum</td>
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<tr>
<td>mV</td>
<td>Millivolt</td>
</tr>
<tr>
<td>N</td>
<td>Number of replicates</td>
</tr>
<tr>
<td>n</td>
<td>Number of electrons</td>
</tr>
<tr>
<td>nA</td>
<td>Nanoampere</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>P</td>
<td>Phosphorous</td>
</tr>
<tr>
<td>pA</td>
<td>Picoampere</td>
</tr>
<tr>
<td>Pb</td>
<td>Lead</td>
</tr>
<tr>
<td>PC</td>
<td>Personal computer</td>
</tr>
<tr>
<td>PBS</td>
<td>Phosphate Buffered Saline</td>
</tr>
<tr>
<td>PICCAP</td>
<td>Pacific Islands Climate Change Assistance Programme</td>
</tr>
</tbody>
</table>
pM - Picomolar
Pt - Platinum
R - Correlation coefficient
r - Radius
RSD - Relative Standard Deviation
s - Second
Sb - Antimony
SCE - Saturated Calomel Electrode
SD - Standard Deviation
SEM - Scanning Electron Microscopy
SICFCS - Solomon Islands Coastal Marine Resources Consultancy Services
SIG - Solomon Islands Government
SIMS - Secondary Ion Mass spectrometry
SPC - Secretariat of the Pacific Community
SPREP - South Pacific Regional Environmental Programme
SWV - Square Wave Voltammetry
\( t \) - Time
Te - Tellurium
TEM - Transmission Electron Microscopy
USA - United States of America
UV - Ultraviolet
vs - Versus
W - Tungsten
WHO - World Health Organization
wt - Weight
XPS - X-ray Photoelectron Microscopy
Zn - Zinc
% - Percentage
\( \mu \) - Micro
\( ^\circ C \) - Degree Celsius
\( \Omega \) - Siemen
ABSTRACT

Speciation of inorganic As using linear sweep voltammetry (LSV) on a gold working electrode was successfully carried out in real water samples in this study. As(III) present in the sample was first detected using the LSV method. As(V) present in the sample was then reduced to As(III) by reaction with Na$_2$SO$_3$ and then detected as total As(III) using the same method. The precision and accuracy of the method was tested using 5 μg/L and 50 μg/L As(III) standards. For precision analysis RSD (N = 6) values of 2.7% and 5.3% were obtained for the two As(III) standards. For accuracy analysis, RSD (N = 3) values of 8% and 10% were obtained for the two As(III) standards. The limit of detection of the method was found to be 0.763 μg/L. Sensitivity of the method was determined from the standard calibration and found to be 224.7 nA/μM. The interference from Cu(II) was also evaluated, where the Cu(II) stripping peak with concentration up to 200 μg/L did not affect the As(III) stripping peak. The proposed method was applied to water samples from two mining regions, Gold Ridge mine in the Solomon Islands and Sabeto in Fiji. The method provided reproducible and accurate results for total inorganic As, As(III) and As(V). For Metapona River, the highest total inorganic As was found to be 72.7 ± 1.2 μg/L while at Sabeto River, the highest total inorganic As was found to be 67.0 ± 7.2 μg/L. These As concentrations occur at sites closest to the mine site and decrease at sites further away from the mine sites. Results from this study found that As concentrations at both study sites have exceeded the WHO guideline value of 10 μg/L. The toxic form of inorganic As, As(III) was also found to be present in elevated levels at both study sites.

Physically small carbon electrodes were also developed in this study by pyrolysing carbon in and on the shank of pulled quartz capillary. Fabricated electrodes were deposited with Au nanoparticles (Au NPs) using chronoamperometry by ramping the potential from 1 to 0 V for a period of 5 s. The characterization of electrodes in [Ru(NH$_3$)$_6$]$^{3+}$ and [Fe(CN)$_6$]$^{3-}$ showed sigmoidal shaped voltammograms before and after modification. The diffusion current was observed to increase by 68% (N = 5) in [Ru(NH$_3$)$_6$]$^{3+}$ and 75% (N = 5) in [Fe(CN)$_6$]$^{3-}$ in modified electrodes compared to bare carbon electrodes. Determination of electrode radius was performed in
[Ru(NH$_3$)$_6$]$^{3+}$ by chronoamperometry. Using the cotrell equation the electrode radius was estimated to be 6.9 μm (N = 6). The results from this study found that the waveslope was 143.5 mV/decade (N = 5) in [Ru(NH$_3$)$_6$]$^{3+}$ and 198.1 mV/decade (N = 5) in [Fe(CN)$_6$]$^{3-}$. The waveslope decreased by 49.5% and 37% in [Ru(NH$_3$)$_6$]$^{3+}$ and [Fe(CN)$_6$]$^{3-}$, respectively after deposition of Au NPs. The $E_{1/2}$ was found to be 214.0 mV (N = 5) and -149.0 mV (N = 5) in [Ru(NH$_3$)$_6$]$^{3+}$ and [Fe(CN)$_6$]$^{3-}$, respectively. $E_{1/2}$ determinations after deposition show that $E_{1/2}$ increased by 4.9% in [Ru(NH$_3$)$_6$]$^{3+}$ and decreased by 150% in [Fe(CN)$_6$]$^{3-}$. The shifts in $E_{1/2}$ in both redox markers proved that the electrode surfaces were modified. The modified electrodes were applied for the detection of As(III), however, As(III) stripping peaks were observed in only one modified electrode in As(III) standards.
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CHAPTER 1

GENERAL INTRODUCTION

1.0 Introduction

Since the industrial revolution, the quality of the natural environment has been deteriorating especially due to pollution which has existed as a serious problem ever since (Zevenhoven et al., 2007) and has raised increasing global concern over the public health impacts attributed to environmental pollution (Khan and Ghouri, 2011). With the ever increasing impacts of exponentially growing population and of industrializing society, the contamination of the physical environment including water has become a threat to humans and as well as plant and animal communities of various ecosystems (Larios et al., 2012, Grigoratos et al., 2014).

Access to clean water for consumption is essential for the well-being of all people (Clark, 2014). However, in many countries around the world, including Pacific Islands, pollutants including toxic heavy metals and metalloids have made their way into water supplies as a result of industrial activity, which has impacted on the health and economic status of the populations (Mosley and Singh, 2003). It is recognized that the Pacific Island Countries must have, or should develop, the capacity to regularly and accurately monitor their water quality in order to protect their populations from the health risks associated with the consumption and usage of contaminated water (Stephen et al., 2008).

In the South Pacific Countries, land is among the most important resources for the people as it is crucial for food security, shelter, community development and economic wealth. The potential for enhanced development and utilization of land based resources is considerable, particularly as the demand for resources increases with the increasing trend in industrialization (SPREP, 2012). Therefore, it is the responsibility of the people of the Pacific to undertake appropriate measures to safeguard this natural environment. Island nations such as Solomon Islands and Fiji
are generally characterized with small land masses surrounded by vast stretches of oceans.

The negative impact of human activities on a global scale is mainly evident in densely populated urban areas (Dupon and Morhange, 1993). The Pacific Islands, despite their relatively small populations have not escaped this trend. It is in the fast growing major towns and cities in the region that the environment has suffered the most severe damage, because of damaging factors, and the primarily coastal setting of urban areas. In the smaller Pacific Island nations (particularly in Micronesia and Polynesia), high urban populations along the coasts has significant detrimental effects on the environment (Dupon and Morhange, 1993). The population growth, and internal migration, has quickly worsened this damage on the atolls. This is worrying for their governments because some of these island nations have very high population densities in a fragile natural environment. Similarly, in the main high islands, the development of historic capitals around the major port has encouraged trade and industry which are also the main contributing factors to environmental pollution on these islands (SPREP, 2012).

Many of the polluting substances originating from land based sources are also of particular concern to the marine environment since they exhibit at the same time toxicity, persistence and bioaccumulation in the food chain once they end up in the marine environment (Gangaiya, 1994). This is a serious concern because people from the Pacific Islands depend on the marine environment for survival. With the increasing populations (Dupon and Morhange, 1993), changing land use patterns (SPREP, 2014) and increasing development, the amounts and types of substances that can be generated that could end up as pollutants are on the rise and becoming more complex (Gangaiya, 1994). Therefore, it is important to assess the amounts and types of these pollutants and to enable Pacific Islanders to devise proper management strategies for these substances.
1.1 General information on Solomon Islands and Fiji

1.1.1 Solomon Islands

Solomon Islands is an archipelago of volcanic origin, geographically located between latitudes 5° South and 12° South and longitudes 152° East and 163° East (SICFCS, 2002). The South Pacific Island nation has a land area of 28,370 square kilometres and a population of just over half a million (SIG, 2007). Approximately 16% of the population live in urban areas, while most Solomon Islanders live in rural communities based on traditional village structures and are dependent on subsistence agriculture supplemented by cash cropping, fishing and forest products (SPC, 2008b). The islands are rich in undeveloped mineral resources such as Pb, Zn, Ni and Au (SPC, 2008b).

1.1.1.1 Environmental situation in the Solomon Islands

The physical environment in the Solomon Islands remains largely intact due to the relatively low population density, short history of significant exploitation and high productivity of the seas, thus limiting the reliance of the populations on land resources alone (Paul and Sammy, 2010). However, with one of the highest population growth rates in the region, the demand for land has increased which has resulted in the intensification of land use activities including logging and mining which has already affected the natural environment especially water and land resources (SIG, 2007).

Mining is a growing industry in the Solomon Islands with the potential of boosting the country’s economy. It has gained momentum in recent years and is expected to play an increasingly important role in the economy (IMF, 2011). The Gold Ridge mine is the biggest mining company in the Solomon Islands which is located on Guadalcanal Island. Apart from this, gold prospecting works are currently underway in other parts of Guadalcanal. Furthermore, the government has also issued gold, nickel and bauxite mining leases to other mining companies and are currently on active prospecting on Guadalcanal and other islands in the country (Theonomi, 2015). These activities reflect how the Solomon Islands government is investing in the
mining sector. However, the environmental effects of such developments will also be a key consideration in ensuring environmental sustainability as well as overall national benefit (Paul and Sammy, 2010).

1.2 Fiji

Fiji is a South Pacific country located between longitudes 175° East and 178° West and latitudes 15° and 22° South, comprises of some 322 islands, with only 100 being inhabited (SPC, 2008a). The two largest islands are Viti Levu and Vanua Levu that are home to approximately 70% of the population. Both islands account for roughly 85% of Fiji’s total land area of 18,272 km². The larger islands are mainly of volcanic origin while the smaller islands are mainly coral formations (SPC, 2008a, PICCAP, 2005).

The country has one of the largest and the most developed economies in the Pacific region and has abundant natural resources which accounts for a significant component of the gross domestic income (SPC, 2008a).

Mineral industry activities in Fiji are mainly the production of cement, gold, silver and exploration for oil offshore (Lin, 2012). Mining is an integral part of Fiji’s economy, gold is one of the country’s most valuable export and the country had been a major regional gold producer for more than 80 years (Lin, 2012).

1.2.1.1 Environmental situation in Fiji

Fiji has an abundant supply of natural resources. Proper environmental management and sustainable use of these resources is critical for sustainable development of its largely natural resource base economy. The Department of Environment is responsible for better coordination, effective formulation and implementation of national environmental policies (PICCAP, 2005). Fiji faces some serious environmental problems that are intensified mainly by the ineffectiveness with which they are treated. Particular problems include degradation of land resources, increasing
risk of flooding, waste management problems, water pollution and environmental impacts of urbanization which undermines people’s quality of life (Tabaiwalu, 2010).

1.3 As contamination and mining

The predominant As species in natural waters include inorganic As, organic arsines as dimethylarsine and monomethylarsine. Inorganic As exists as As(III) and As(V) and As(III) is the highly toxic (Giacomino et al., 2011).

Mining activity is one industrial activity that leads to greater accumulation of As in soils and sediments which then reaches out to the natural aquatic system (Larios et al., 2012). Mining works generate tailings and leftover materials that may contain a great variety of As compounds. Specifically in gold mining areas, weathering of As-bearing phases in geochemical anomalies can be considered as a diffuse source of pollution into ground and surface waters (Smedley and Kinniburgh, 2002). As is initially present in sulphide deposits and As transfer to the aqueous reservoir may be influenced by various geochemical processes (Bossy et al., 2012). These include the formation of secondary phases (sulfates, Fe-, Mn- and Al-oxyhydroxides) which do not trap As from primary phase alteration and by the sorption on oxyhydroxides and clay minerals (Foster et al., 2011). All these phases are permanent or temporary sinks of As depending on their stability and their As retention capacity (Drahota et al., 2009). The mobility and bioavailability of As is influenced by environmental conditions (redox, ionic strength and pH) and microbial activities (Kim et al., 2014). As release can cause problems in drinking water supplies (Hopenhayn, 2006). It also induces ecosystem modifications depending on As concentrations, speciation, and toxicity towards living organisms (Casiot et al., 2009).

The guideline value for As in drinking water as indicated by the World Health Organization (WHO) is 10 μg/L (WHO, 2004). Many techniques have been proposed to determine such level of As. However, from the analytical point of view, development of sensitive and reliable techniques capable to determine very low levels of inorganic As is a challenge (Sun et al., 1997). An attractive and less expensive approach is represented by electrochemical techniques (Giacomino et al., 2011).
These techniques have been proven to be sensitive and selective for trace analysis of As (Rasul et al., 2002).

In this study, water samples were collected from rivers that drain two gold mining regions, Gold Ridge in the Solomon Islands and Sabeto in Viti Levu, Fiji. These rivers or streams are relied on by the populous for sustenance, thus any risk of As in such waters presents a real risk to the population of both acute and chronic As poisoning. Linear sweep anodic stripping voltammetry was employed to detect As(III) and As(V) in the μg/L levels. Thus, the work was initiated with the aims and objectives as detailed below.

1.4 Aims and objectives

This study is designed to evaluate the risks of As(III) and total dissolved As in Metapona River in the Solomon Islands, and Upper Sabeto River in western Viti Levu. As rivers and streams are important part of the daily lives of Pacific Islanders for important food and water sources (Polhemus et al., 2008), any risk of As in such waters presents a real risk to the population of both acute and chronic As poisoning. The results of the study would enable the identification of immediate risk (derived from consuming food or water from these rivers and streams) and similarly, any likely effect on the food security of the populous. Another expected outcome of this study is that it enabled the determination of prevailing concentrations of the element and a better understanding of the natural background/baseline levels to allow management and monitoring any changes caused by anthropogenic activities in the future. The environmental management of natural resources like water in a world with ever increasing industrial activities, urbanization and human population has been the focus of extensive research to protect and preserve them for future generations across the globe (Sultan et al., 2011). This, and the fact that the populations living within the study areas are mainly comprised of subsistence farmers relying on these rivers for their water needs and the surrounding areas for cultivation of their crops, this study may be of help to evaluate the likely risks to the livelihoods of these people in terms
of direct As contamination and through secondary effects arising from its mobilization.

For the assessment of water quality, guideline values or approved standard concentration regimes have been put in place by internationally recognised scientific bodies which have been used as guides. Guideline values to determine quality of drinking water were taken from WHO Guidelines for Drinking Water Quality (WHO, 2004). Concentrations exceeding the guideline values show that water is not safe for drinking. Similarly, guideline values (or sometimes referred to as trigger values) to determine the quality of freshwater were taken from the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC, 2000). Concentrations exceeding these values indicate a potential environmental problem and so trigger a management response. Thus, the objectives of the project were:

1. To determine the total concentration of As in the environmental water samples from selected sites in the Solomon Islands.
2. To determine the inorganic speciation of As in the water samples.
3. To identify any environmental risks associated with As levels in the aquatic areas studied.
4. To develop, characterize and evaluate physically small carbon electrodes modified with Au nano-particles. The modified electrodes were then applied towards the detection of inorganic As and compared their performance with that of Au working electrode.
2.0 Introduction

Arsenic (As) is a metalloid (semi-metal) with atomic number 33 in the periodic table of the elements. It is an environmentally significant element and thus, it has also been recognized as one of the world’s greatest environmental hazards (Ravenscroft, 2007). The average concentration of As in the continental crust is 1 – 2 mg/L (Taylor, 1972). However, elevated levels of this metalloid have been reported worldwide as a result of both natural and anthropogenic sources.

As is an essential trace element for some animals, including humans (Emsley, 2011). In small quantities it stimulates metabolism and boosts the formation of red blood cells (Conacher et al., 2012). Its deficiency in humans can lead to stomach, blood and heart disorders, intellectual impairment in children and foetal malformations. However conversely, high levels of As are carcinogenic and poisonous to humans, for instance, 100 mg/L or more in the tissue is lethal (Conacher et al., 2012).

Accordingly, a lot of research effort has been devoted towards As in the environment (Narayana et al., 2006, Ma et al., 2014, Chen et al., 2014). As particularly in the +3 oxidation state has long been considered a toxin (Gong et al., 2002, Giacomino et al., 2011). Thus, the occurrence of As(III) in our aquatic systems poses a significant health risk to humans especially if the levels exceed the recommended permissible contaminant levels (Mandal and Suzuki, 2002). Knowledge of speciation of As in natural water is extremely important because the bioavailability, physiological and toxicological effects of As all depends on its chemical form (Gong et al., 2002).

2.1 Background

As is an important metalloid with environment of biological, industrial, and toxicological significance. Even though As occurs in a number of oxidation states (+5,
+3, 0 and -3), the +5 (arsenate ion) and the +3 (arsenite ion) are the most common species in the natural environments (Ulusoy et al., 2011, Tyrovola and Nikolaidis, 2009). As is mostly produced as a by-product of refining the ores of other metals in the industrial processes involved in mining (Bossy et al., 2012).

Human exposure to As can be estimated by direct or indirect methods. The direct methods are based primarily on chemical analysis of the various matrices the species is commonly encountered in such as food, water and air. Indirect methods on the other hand include analysis of As in urine and hair which can serve as indicators of its presence (Xu et al., 1994).

As has been used as a medicine and poison as well since humans first became interested in chemistry (Gorby, 1994), throughout recorded history instances of poisoning with As compounds have occurred. On the other hand, medicinal effects of As were already documented as early as 460-357 B.C by Hippocrates and 384 - 324 B.C by Aristotle (Gorby, 1994). As poisoning in humans can occur by acute and/or chronic poisoning (Sofuoglu et al., 2014). Arsenic trioxide is the most commonly used poison among As compounds (Dubey et al., 2014). It is usually used as homicidal and suicidal poisoning. Adverse health effects of As depend strongly on the dose and duration of exposure (Kapaj et al., 2006). The toxicity of As to human health ranges from skin lesions to cancer of the brain, liver, kidney, and stomach (Chen et al., 2009).

2.1.1 As occurrence in the environment

As is widely distributed in the environment (soil, water, air and also in living matter) and exists in weathered rocks and soils (Ulusoy et al., 2011, Tiemann, 2008). It is the twentieth most abundant element in the earth’s crust (Larios et al., 2012b), the terrestrial abundance of As is around 1.5 – 3 mg/kg (Mandal and Suzuki, 2002).

The source of As in the environment includes both natural and anthropogenic (Mandal and Suzuki, 2002). Weathering of rocks is the major source of inorganic As, it occurs naturally as a sulphide mineral in pyrite rock or sulfide ores (Conacher et al., 2012),
depending on the biogeochemical conditions, the toxic inorganic forms can be released in groundwater (Cortés-Salazar et al., 2013). It most often exists with sulphide minerals because of its strong affinity for sulphur, but sometimes as an oxide (Dojlido and Best, 1993).

As is naturally occurring, however, anthropogenic extraction of natural resources releases As into the air water and soil, it can be also released from certain As containing pesticides, mining or smelting activities which can eventually result in the contamination of water and food sources (Cortés-Salazar et al., 2013). It can be also released into the natural environment as a result of industrial activities (e.g. emissions from coal fired power plants which were common in the past) (Istvan and Benton, 1997) and releases from its use as a wood preservative, in semi-conductors and paints, and from mining and agricultural activities (Tiemann, 2008). Mine wastes generated from mining activities are common sources for As in environment in the mining areas. These sources, in addition to runoff and metal-rich soil weathering, result in wide spread As contamination into the aquatic systems (Larios et al., 2012b, Omar et al., 2013). Considerable amounts of As containing gases, aerosols and particulate matters are also generated from ore processing in mines and these can be fixed by sediments, soils or biota (Larios et al., 2012b).

2.1.2 As in human health

As has been known to be toxic to humans (Cortés-Salazar et al., 2013). Chronic As exposure can lead to serious health effects including cancer of the skin, lungs, urinary bladder, and kidneys (Chen et al., 2010), diabetes, renal system effects and cardiovascular diseases (Cortés-Salazar et al., 2013). Human exposure to As can occur by consumption of groundwater containing elevated levels of inorganic As, food prepared with this water, and crops irrigated with high-As water sources (Kaszubkiewicz et al., 2014). The maximum permissible concentration of As in drinking water is 50 μg/L (Mandal and Suzuki, 2002) and the recommended value is 10 μg/L by World Health Organization (WHO) (Mays and Hussam, 2009, Cortés-Salazar et al., 2013, Dai et al., 2004). In countries like Bangladesh, where As
contamination is common, a threshold value of 50 μg/L is currently being employed (Cortés-Salazar et al., 2013). Similarly, Mexico has a maximum recommended level of 25 μg/L (Omar et al., 2013). In hotter climate countries where people drink several liters of water per day when working in the heat and inorganic As levels are high in their aquatic systems, there is a likelihood of widespread arsenicosis, in which the skin erupts in leprosy-like lesions, which after many years of exposure has been shown to eventually lead to cancerous growths (Emsley, 2011, Mays and Hussam, 2009).

### 2.1.3 Sources of dietary As and metabolism

Human exposure to many different forms of inorganic and organic As species (arsenicals) can be through food, water and other environmental media (Emsley, 2011). The study of the kinetics and metabolism of arsenicals in animals and humans is a complex subject because each of the forms of arsenic has different physiochemical properties and bioavailability (Mandal and Suzuki, 2002).

As levels are higher in rice than in most other foods because rice takes up this metalloid form both the water and the soil, and in the organic form (Emsley, 2011). The daily intake of As in a normal diet in humans can vary considerably, even being as high as 1 mg if certain foods are consumed (Emsley, 2011).

### 2.1.4 As toxicity

It is well known that the toxicity of As is highly dependent on its chemical forms and that the inorganic species of As are more toxic than its organic forms (Mays and Hussam, 2009, Ulusoy et al., 2011, Gibbon-Walsh et al., 2011). The inorganic form of this metalloid exists as As(III) and As(V) and it has been reported by numerous authors that As(III) is more toxic and mobile than As(V) (Larios et al., 2012a, Salaun et al., 2012, Gibbon-Walsh et al., 2010), while organic As is relatively safe (Emsley, 2011, García-Salgado et al., 2012, Gong et al., 2002). It has also been reported that
As(III) is 10 times more toxic than As(V) and 70 times more toxic than the monomethylarsine (MMA) and dimethylarsine (DMA) forms (Larios et al., 2012b). Depending on As concentrations, speciation, and toxicity towards living organisms also induces ecosystem modifications (Bossy et al., 2012). While As toxicity is mainly from drinking contaminated water, in parts of India, Nepal, and Bangladesh, burning of dried cow (which have been fed contaminated rice straw grown in high As level waters) pats which are often used as fuel for cooking, releases As as As$_2$O$_3$ putting those who are cooking in unventilated kitchens at risk (Emsley, 2011).

### 2.1.5 Industrial use of As

Compounds of As have been used since the earliest times, both as a pigment and as a poison for rodents and insects (Dojlido and Best, 1993). Therefore, As still has a wide range of industrial applications. For instance, it has been used in gunshot, embalming, taxidermy, weed control, rat killer, pyrotechnics, and cosmetics while in recent times, most of these no longer involve As, some still do (Emsley, 2011). Exploiting its toxicity, As and As containing compounds had been widely used in agriculture as pesticides, herbicides and soil sterilants in the past and thus, were also found in fairly high concentrations (0.2%) in some agricultural soils (Istvan and Benton, 1997, Dojlido and Best, 1993). More than 80% of As compounds are used in the manufacture of products for agricultural applications (Dubey et al., 2014). However, because of environmental factors and the availability of more ‘target specific’ organic compounds its usage in pesticidal formulations has been decreasing (Dojlido and Best, 1993).

In animal agriculture, As finds usage in piggery and poultry where it is added as feed to fatten the animals. However, the As containing manure from these which is used as fertilizers in farmland can break down to inorganic As. This raises its concentration in the crops thereafter, which then poses a threat on the human populations who eat these crops produce (Emsley, 2011).

The main As producers were China, USSR, France, Mexico, Germany, Peru, Namibia, Sweden and USA, and these countries accounted for about 90% of the world
production, and about 80% of the consumption of As were for agricultural purposes (Nelson, 1977). However, its usage in agriculture has also been declining due to its toxicity (Kaszubkiewicz et al., 2014).

2.1.6 As in the aquatic environment

The fate and mobility of As are mainly controlled by five processes in surface water and groundwater. These are redox reactions, adsorption and desorption, competitive adsorption (ion exchange), solid phase precipitation and dissolution, and biological activity (Cheng et al., 2009). These processes interact with each other and the mobility of As may be controlled by multiple processes under a given set of conditions. Many factors, such as redox potential (Eh), pH, chemical composition of the system (e.g., redox pairs) and reaction kinetics also play a major role in these processes (Cheng et al., 2009). While inorganic As exists as As(III) and As(V) in water, the predominant species in aerobic surface waters is As(V) while As(III) is found mainly in anaerobic waters (Omar et al., 2013). The major chemical form in which As appears to be thermodynamically stable however is arsenate ion (Mandal and Suzuki, 2002). In natural waters, As is found at low concentrations (Mandal and Suzuki, 2002). Its release into receiving streams is as a result of weathering of strata containing As and from volcanic activity (Dojlido and Best, 1993). As is present in the earth’s crust and discharged from geothermal systems mainly in the reduced form of As(III) which is then oxidized to As(V). This process is enhanced through microbial input during the ascension of geothermal hot waters and their mixing with shallow oxidized groundwaters, which can then be transported to surface and groundwaters causing contamination to the aquatic systems (Tyrovola and Nikolaidis, 2009). As exists primarily as an inorganic ion, arsenate in surface river waters, however, reduced As and methyl arsenicals [monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA)] are also occasionally present (Anderson and Bruland, 1991). As content in fresh water is 0.1 – 800 μg/L with 0.5 μg/L as the reference value (Istvan and Benton, 1997). The common chemical species of As occurring in the aquatic environment include HAsO₄²⁻, H₂AsO₄⁻, and possibly H₃AsO₄, AsO₄³⁻ or H₂AsO₃⁻ (Istvan and Benton, 1997). Elevated levels of As are found more frequently
in ground water than in surface water (Tiemann, 2008), thus the concentrations tend to be higher in well waters which are common in small communities compared to those sourced from surface waters that mostly supply the water needs of towns and cities. According to the Australian and New Zealand guidelines for fresh and marine water quality the trigger values for As(III) and As(V) are 24 μg/L and 13 μg/L respectively.

2.1.7 As and mining activities

The weathering of As bearing phases in geochemical anomalies can be considered as the diffuse source of pollution source into ground and surface waters especially in gold-mining sites (Smedley and Kinniburgh, 2002). As is initially present in sulfide deposits. Its transfer to the aqueous reservoirs may be influenced by the formation of secondary phases (sulfates, Fe-, Mn- and Al-oxyhydroxides) which do not trap all mobilized As from preliminary phase alteration, and the sorption on oxyhydroxides and clay minerals (Morin and Calas, 2006). All these phases act as permanent or temporary sinks of As depending on their stability and their As retention capacity (Paktunc et al., 2003). As mobility and bioavailability involving partial or solid phase dissolution or desorption can be influenced by environmental conditions (redox, ionic strength, and pH) and microbial activities (Bossy et al., 2012). A study by Bossy et al. (2012) on As sources on a high grade As geochemical anomaly also found that As mobility in the aqueous fraction depends mainly on Fe-oxyhydroxide stability, and observed that As levels were highest in surface waters when the groundwater flow rates from aquifers were low and the major process occurring was the dissolution of Fe-oxyhydroxides releasing As into the waters. Mining economic mineral deposits and the associated industrial processes involved, leads to the release of As which eventually ends up in the aquatic environment (Larios et al., 2012b). Its distribution is highly influenced by the extent of mining and ore processing and is associated mostly with Fe-oxyhydroxides and sulfide minerals (Bossy et al., 2012, Larios et al., 2012a, Larios et al., 2012b.). Remobilization of historic sources, such as mine drainage water can also lead to high levels of As in the surrounding aquatic systems (WHO, 2010).
2.1.8 Bioaccumulation of As

As is not highly mobile and therefore would not be expected to accumulate from its movement in the food chain. Its major source would be from physical deposition or from consuming products high in As, such as seafood (Istvan and Benton, 1997). As is predominantly present in the form of inorganic species in terrestrial plants, although organic species have been identified as well (Larios et al., 2012b). In plants, little is known about the mechanisms of uptake and distribution. It is generally assumed however, that roots are responsible for accumulating the most As with relatively slow and minimal translocation to the rest of the plant (Larios et al., 2012b). The degree of As levels varies with the crop species (Istvan and Benton, 1997). Some plants however, thrive on As, an example is the Chinese Ladder fern *Pteris vittata*, also known as the brake fern, grows rapidly and has the ability to absorb As to the extent of its making up 2% of its weight (Emsley, 2011). However, plants are generally considered phytotoxic if they contain As greater than 2 mg/kg dry weight. A study carried out by Larios et al. (2012b) on As speciation and bioaccumulation in different plant species at mining sites found that plants accumulated extremely high levels of As in their tissues and that the accumulation rates depend on extent of pollution of the site and the plant species itself. Inorganic As(V) was the predominant species found in most of the plants investigated while As(III) was also found in significant amounts in some (Larios et al., 2012b).

2.1.9 Need for As speciation in the aquatic environment

Understanding the speciation of elements is important in predicting their availability, lability and stability in the environment. This is also important in the designing of effective remediation strategies of industrial sites (Skya and Heather, 2011). As can exert unwanted toxic effects onto life forms and thus, high levels of As in the environment is worrying due to its toxic effects. However, the absolute level of most metalloids in the environment like As whilst useful does not always provide an accurate guide to toxicity. Therefore, As speciation information is required to understand its biogeochemical cycling and potential toxicity of waters (Larios et al.,
Species tend to behave differently in terms of mobility, bioavailability, toxicity and thus, their speciation is extremely important (Gibbon-Walsh et al., 2012).

2.1.10 Mining industry in the Solomon Islands and Fiji

2.1.10.1 Gold Ridge Mine, Solomon Islands

The mining industry is a major area of development and investment in the Solomon Islands (SPC, 2008). The country has an abundance of mineral reserves such as Au, Ni, Pb and Zn (Paul and Sammy, 2010) and bauxite, and there is a high probability of production operations commencing in the next few years (SPC, 2008). Gold Ridge Mine is located within the central part of Guadalcanal, Solomon Islands largest island. The gold deposits are concentrations of low-sulphidation intrusion related epithermal gold mineralization (Godfrey et al., 2011). As assays were normally used for estimating gold concentrations within the gold deposit areas. Gold concentrations were found to correlate with As content in the ore deposits. This is reflected in the analysis of assay data which showed that a higher proportion of As and Au mineralization occurs in high grade As areas (Godfrey et al., 2011).

The mine started its mining operations in 1998. It was later shut down in 2000 due to the ethnic crisis on the island and subsequently reopened in 2010 up until 2014. In 2014, severe flooding that affected most parts of Guadalcanal caused the mine’s closure (Solomon, 2014, Billy, 2013). Since then, landowners and especially those living downstream Metapona River are calling on the national government to allow the Australian company that operated the mine to come back and resume operations to deal with the tailings dam as there were reports that the dam has been overflowing following recent cyclone and rainy seasons (Eddie, 2014). This has caused immense concerns among the inhabitants and landowners of the area. Landowners are also calling on the government to urgently address the pollution caused to the Metapona River due to the mining activities as those living downstream can no longer use the river for washing and cooking anymore (Solomon, 2014).
2.1.10.2 Sabeto, Fiji

Mining has been an integral part of Fiji’s economy and the gold (Au) was the country’s second most valuable export (Lin, 2012). Au deposits were discovered in the upper reaches of Sabeto valley in 1987, since then exploration and drilling (surface and underground) activities have been undertaken. Mine developments carried out from 1996 to 2000 included various geochemical and geophysical surveys and drilling and underground mine developments. The mining work was suspended in 2000 due to low Au prices and resumed in 2001 till present (Wayne et al., 2010). The Tuvatu deposit in upper Sabeto is one of several epithermal gold systems in northeast Viti Levu, a number of Au deposits have been discovered around this region including the Vatukoula deposit which has produced some 7 million ounces of Au since 1937 (Wayne et al., 2010).

2.1.11 Environmental As status in the Solomon Islands

Developments that can potentially contribute to increase As levels in the environment in the Solomon Islands include mining (Larios et al., 2012a), and in the timber industry where As containing compounds are sometimes used in wood preservation (Ko et al., 2007).

A search of prevailing literature shows limited data on As speciation studies in the Solomon Islands, although total As measurements have been previously reported (Conacher et al., 2012). Previous reports on some of these rivers and streams in the Solomon Islands, particularly on Santa Isabel island showed total As levels were higher than the normal permissible and contaminant levels recommended by the Australian and New Zealand guidelines for fresh and marine water quality (ANZECC, 2000). These standards are some of the main guideline used in the Solomon Islands for characterizing water and sediment quality (Conacher et al., 2012). Geochemical work has also been carried out for Metapona River on Guadalcanal in the past mainly by geologists and geochemists (Yeo et al., 1996). However, analysis for As was not done in this study. An initial baseline study of sediment geochemistry of Metapona
River was carried out in 1992 (Qopoto et al., 1994). Analysis using atomic absorption spectroscopy (AAS) was carried out for metals and metalloid including As as it is commonly used as an indicator element in geochemical exploration for Au (Qopoto et al., 1994). The analysis showed As concentration decreasing exponentially with distance from Gold ridge from a maximum concentration of 467 mg/L at Gold Ridge to <5 mg/L near the coast which is more than 15 km from Gold Ridge. However, more detailed analysis is required to quantify the concentration of each species of As, thereby establishing immediate risk of toxicity, as toxicity is a function of the speciated form. The Gold Ridge mine has operated since 1998 to 2000 and from 2010 up until 2014, according to the Geology Division of the Government of Solomon Islands, no baseline studies for As has been carried out ever since (Billy, 2013) except that reported by Qopoto et al. (1994). The study also recommended further studies to be carried out in order to establish how these high As concentrations in sediments can interact and affect the wider local environment.

The most recent study on water quality assessment downstream of Gold Ridge Mine was carried out in 2014 by Albert et al. (2014). The group did water quality assessment and analyzed for As and heavy metals in water and sediment samples at sites around the mine area to downstream Metapona River. As speciation studies were carried out for Metapona River samples, the As(III) levels were below detection limits, while As(V) levels ranged from 5 – 7 μg/L. Sample analysis was performed using National Association of Testing Authorities (NATA) accredited methods (NATA, 2013).

The current state of the Metapona River is murky and the river water is not clear at most areas (Figure 2.1 and 2.2). According to Kitoto (2014), a resident at the Metapona downstream area, the river used to be clear and free flowing, and the river mouth was a popular fishing spot in the past. However, that’s not the case now; there is obvious sedimentation at the lower reaches of the river which has also caused the river water to be stagnant at some areas. Fishing activities are not common now due to the changing appearance of the river waters.
Figure 2.1. Present day appearance of Metapona River (downstream).

Figure 2.2. Present day appearance of Metapona River (upstream).
2.1.12 Environmental As status in Fiji

Inorganic As levels in most sites around Fiji, particularly Viti Levu are relatively low except for Suva area, according to published reports (Mosley and Singh, 2003, Chand et al., 2011). Previous studies have shown that some hazardous metals and metalloids were present at concentrations above background levels particularly within the Lami estuary and Suva harbor (Chand et al., 2010, Maata and Singh, 2008). This was attributed to the industrial activities in Suva and Lami. As levels in marine surficial sediments reported by Chand et al. (2010) were as high as 334 mg/L in dry weight.

Trace metal studies in the Great Astrolabe Lagoon in Fiji by Morrison et al. (1997) showed that As levels were comparable to those reported for marine waters, averaging about 1.5 µg/L. This lagoon is located far from Suva and other industrial areas. The As result obtained in this study gave a clear evidence of the unpolluted nature of the lagoon.

These results show that As contamination in Fiji is not much of an environmental concern. Only the Suva harbor and Lami estuary recorded high levels of As in marine sediments which can be attributed to the industrial activities in that area (Maata and Singh, 2008).

Studies carried out by Matanitobua (2006) showed elevated inorganic As levels in surface waters in the Vatukoula/Tavua region. This region hosts the major Gold mine in Fiji (located 50 km northeast of Sabeto mine) and with mineralogy very similar to that of Sabeto. Total inorganic As levels in surface waters detected in this study from Vatukoula/Tavua region ranged from 50 to 2350 µg/L. As(III) concentrations were also particularly high ranging from <10 to 1750 µg/L while As(V) concentrations ranged from 50 µg/L to 1950 µg/L. These values are consistent with those of highly contaminated areas (Smedley and Kinniburgh, 2002, Bossy et al., 2012).
2.1.13 Analytical considerations for As determination in environmental water

A number of analytical methods have been reported for the determination of total inorganic As such as flow injection analysis (FIA) with hydride generation, atomic absorption spectroscopy (AAS), graphite furnace-atomic absorption spectroscopy (GF-AAS), induced coupled plasma-atomic absorption spectroscopy (ICP-AAS), neutron activation spectroscopy (NAS), etc. However, most of these methods also suffer from certain limitations such as interference by certain large number of ions, of low sensitivity, and need of extraction into organic solvents or heating (Narayana et al., 2006).

2.1.14 General analytical methods for inorganic As determination

Many laboratory based techniques have been used in recent years for the determination of total inorganic As. These include atomic fluorescence spectrometry (AFS) (Cai, 2000), inductively coupled plasma mass spectrometry (ICP-MS) (Álvarez-Llamas et al., 2005), electro spray mass spectrometry (ESMS) (Chassaigne et al., 2000), GFAAS (Santos and Jacob, 2009), hydride generation atomic absorption spectrometry (HGAAS) (Ulusoy et al., 2011, Zhang et al., 2011) and electrochemical analysis (Li et al., 2012a). These methods are discussed in detail in the following sections.

2.1.14.1 Hydride generation (HG)

One of the common analytical methods for measuring trace levels of As in the aquatic environment is hydride generation. This method involves the separation of As from the matrix by the formation of the volatile AsH₃, thus lowering the detection limit. As is then detected by atomic emission spectroscopy, graphite furnace atomic absorption or atomic fluorescence spectroscopy (Gibbon-Walsh et al., 2012, Ulusoy et al., 2011). The use of HG as an analytical technique is becoming increasingly popular because of its ability of differentiating different oxidation states of analytes by simple procedures.
However, one of the major drawbacks of HG is that several other interfering reactions can also occur both in the hydride generation and in the atomization process that affect the signal (Ulusoy et al., 2011). A suitable alternative to chemical generation techniques based on the tetrahydroborate-acid system is electrochemical hydride generation (EcHG). This technique coupled to AAS, EcHG-AAS, has been proven to be effective in the determination of As(III) and As(V). However, the elimination of interference from some transition elements needs further investigation (Li et al., 2006).

For instance, incorporating HG between HPLC and ICP-MS for As speciation in human urine has also been shown to improve sensitivity and specificity by Chen et al. (2010). The research group was able to quantitatively determine concentrations of As(III) and As(V) with detection limits in sub-microgram per liter range in human urine (0.032 μg/L for As(III) and 0.042 μg/L for As(V).

Determination of As(III) with a low detection limit (0.008 μg/L) in aqueous samples by HG-AAS after pre-concentration by cloud point extraction methodology has also been reported by Ulusoy et al. (2011).

The use of HG-AAS has also been successfully applied for the determination of inorganic As species in water as reported by Issa et al. (2011). The group was able to develop a simple and efficient method for the separation and determination of inorganic and organic As in environment water samples.

### 2.1.14.2 Electroanalytical stripping method

Electroanalytical stripping techniques for trace metal analysis have been known to chemists for more than 50 years (Mays and Hussam, 2009). These techniques are considered very powerful tools in electroanalysis due to their high selectivity, wide range of possible analytes, low cost equipment, versatility and portability (Herzog and Beni, 2013). Electrochemical stripping methods for As(III) determination involve cathodic stripping voltammetry (CSV), anodic stripping voltammetry (ASV) and adsorptive stripping voltammetry (AdSV) (Herzog and Beni, 2013, Dai et al., 2004).
2.1.14.3 Anodic stripping voltammetry (ASV)

Specific techniques employed to evaluate As concentrations vary (Mays and Hussam, 2009, Dai et al., 2004, Zhang et al., 2011). Electrochemical analysis particularly on a voltammetric platform such as ASV is one means of analytical measurement techniques for inorganic As in the +3 and +5 oxidation states in environmental water samples (Mays and Hussam, 2009, Gibbon-Walsh et al., 2010). ASV is a powerful tool among the various electroanalytical techniques for the determination of trace levels of As(III) owing to its high sensitivity, selectivity and low detection limit (Li et al., 2012b, Mays and Hussam, 2009, Sebez et al., 2013). This technique is the most widely used form of stripping analysis and involves the pre-concentration step whereby the metal analyte is electrodeposited onto the working electrode surface by cathodic deposition at a controlled time and potential. The potential is then scanned anodically, during which the metal analytes are re-oxidized or stripped out of the electrode (in an order that is a function of each metal standard potential), and an oxidation (stripping) current is flowing (Wang, 2006). The resulting voltammetric signal recorded during this process provides indication on the nature of the analyte (through the oxidation or reduction potential) and its concentration (current magnitude) (Herzog and Beni, 2013, Wang, 2006). A hanging mercury (Hg) electrode can be used in stripping analysis of As(III). However, due to the potential toxicity of Hg together with operational limitations, portable sensors utilizing Hg electrodes have been subsequently replaced by solid substrates (Dai et al., 2004).

Numerous studies on As determination have been carried out via ASV and have used various working electrode materials including Hg, Pt and Au (Dai et al., 2004), Ir, Ag and carbon based materials (Herzog and Beni, 2013). Reviewed literature can be classified based on the working material used as follows: bulk Au 46%, thin Au film deposited on carbon (glassy carbon, graphite) 20%, Hg (as hanging drop Hg electrode-HDME) 16%, Pt 12%, Cu 4% and boron doped diamond electrode 2% (Mays and Hussam, 2009). Au appears to give a more sensitive response toward As oxidation than the other electrode materials and has a higher hydrogen overvoltage than Pt. The As stripping peak appears as a shoulder on the oxidation waves of Hg and Ag, and for this reason, these metals are not suitable as electrodes for As
determination via ASV (Dai et al., 2004). Among the substrates used for working electrode, Au has been considered to be the most superior considered to date (Dai et al., 2004, Xiao et al., 2008, Dai and Compton, 2005, Dai and Compton, 2006, Liu and Huang, 2014). However, it has also been suggested that Au electrode should not be scanned beyond +0.7 V (vs. SCE) to prevent surface oxidation which could slow down the electron transfer kinetics (Mays and Hussam, 2009).

A variety of electrolytes can be used in ASV. A review by Mays and Hussam (2009) on selected papers shows that the majority of papers used minerals acids such as HCl (42.4%), H2SO4 (11.9%), HNO3 (11.9%), phosphate buffered saline (PBS) (5.1%), and H3PO4 (3.4%). In ASV, analyte ions reach the working electrode by diffusion and convection processes at which they are being reduced. Here, convective transport is mainly achieved by electrode rotation or solution stirring (Wang, 2006). In previous works, where Au microwire electrodes were used, the sensitivity was greatly improved when a vibrating electrode as opposed to stirring the solution was used as reported by Gibbon-Walsh et al. (2010). The authors used Au microwire electrode for the simultaneous determination of As, Cu, Pb and Hg in unpolluted fresh waters, which resulted in a very small, stable and reproducible diffusion layer (<1 μm). This greatly improved the sensitivity and the reproducibility of the results, allowing determinations with a very short deposition time (Gibbon-Walsh et al., 2010).

The presence of O2 interferes with the measurement of many reducible analytes because it undergoes stepwise reduction resulting in a large background current (Wang, 2006, Gibbon-Walsh et al., 2012). A variety of methods have been employed for the removal of oxygen, the most common of which is purging with an inert gas (pure N2) as has also been reported by numerous authors (Gibbon-Walsh et al., 2012, Dai et al., 2004, Rasul et al., 2002, Salaun et al., 2007). Some authors were able to perform stripping analysis without deoxygenation, this makes the stripping protocol more simple and allows for shorter measurement times (Alves et al., 2011). However, they carried out total As determinations in their study and most of the literatures cited carried out deoxygenation for As(III) determinations using ASV (Gibbon-Walsh et al., 2012, Dai et al., 2004, Rasul et al., 2002, Salaun et al., 2007).
Dai et al. (2004) have developed a simple novel method for As(III) detection at a gold nanoparticle-modified glassy carbon electrode. A high sensitivity of 95 μA/μM was obtained using square wave voltammetry (SWV), and a limit of detection (LOD) of 0.0096 μg/L (using linear sweep voltammetry) and 0.014 μg/L using SWV were achieved. This method was then successfully applied towards the detection As(III) in spiked river water samples.

Similar studies by Xiao et al. (2008) have used Au nanoparticles (Au NPs) deposited on multiwalled carbon nanotubes (CNTs) via in situ reduction of HAuCl₄ by NaBH₄. Electrochemical detection was then successfully carried out via ASV. The limit of detection obtained was 0.1 μg/L, and more importantly, a sensitivity of 1985 μA/μM was obtained with SWV.

Determination of total inorganic As by ASV can be carried out by a chemical reduction step. Since inorganic As consists of As(III) + As(V), the reduction step allows all the As(V) to be reduced to As(III). As(V) can then be determined as As(III) after the reduction step prior to the voltammetric detection of As(III) by ASV (Salaun et al., 2007). Thus, the total inorganic As can be determined after the reduction step. Several reducing agents have been used for the chemical reduction step, these include ascorbic acid, iodide, hydrazine hydrochloride, hydrazine sulphate, etc (Salaun et al., 2007). However, sodium sulfite has been proven to be more easier to implement, and thus is more often used (Rasul et al., 2002). The reducing agent reduces As(V) to As(III) with SO₂ gas produced insitu by the acid decomposition of Na₂SO₃, As(III) detected thus, gives the total inorganic As present in the sample.

2.1.14.3.1 Present status

With the advent of computer controlled electrochemical systems over the years, much better control of stripping voltammetry experiments including ASV is now possible (Mays and Hussam, 2009). It is therefore, now possible to achieve lower detection limits (in the μg/L range and even lower). These are comparable to that of very expensive spectroscopic techniques such as HG-AAS, provided by a signal-to-noise enhancement through the reduction in capacitance background. This is possible with
the introduction of new pulse voltammetric techniques such as differential pulse and SWV (Ahuja and Jesperen, 2007).

2.1.14.3.2 Electrode or substrate for inorganic As analysis

The choice for the working electrode depends on careful considerations for ideal characteristics which include reproducibility, selectivity, sensitivity, long term stability, portability, ease of use, and cost effectiveness (Gao and Huang, 2013). Various electrode types continue to be developed and used for the inorganic As such as glassy carbon electrode (Dai et al., 2004), diamond electrode (Song and Swain, 2007), graphite electrode and carbon paste electrode (Liu and Huang, 2014), screen printed electrode (Khairy et al., 2010), Ag electrode (Billon and Berg, 2004), Au electrode (Rasul et al., 2002), Pt electrode (Liu and Huang, 2014), and Hg electrode (Liu and Huang, 2014).

2.1.15 As stability and storage – analytical considerations for speciation studies

After collection of water samples for As speciation studies, filtration, pre-treatment and proper storage of the samples in appropriate storage containers ensures to maintain analyte stability. Pre-treatment is usually done using concentrated acid to lower the pH of the samples. In most of the papers on inorganic As speciation studies, the water samples were usually acidified to pH < 3 (Alves et al., 2011, Ulusoy et al., 2011, Sadana, 1983). However, depending on the type of electrode, there are published reports on inorganic As speciation studies in neutral media as well using mercaptoethylamine modified Au electrode via ASV (Li et al., 2012a) and Mn-coated Au microwire electrode for the determination of As(V) in seawater (Gibbon-Walsh et al., 2012).

Arsenic species in samples may undergo transformation before analysis due to the contact between samples with air or reduction caused by dissolved organic carbon (DOC) in the water samples (Bednar et al., 2002). Even slight transformations may
give rise to remarkable inaccuracies because the As concentrations in most samples generally remain very low. Thus, treated samples should ideally be stored at low temperatures (e.g. 4 °C) before analysis or immediate analysis of the samples is required (Huang and Ilgen, 2004, Issa et al., 2011).

Huang and Ilgen (2004) have reported that As released from plastic bottles (e.g. polyethylene and polycarbonate) and from most of the glassware remained undetected when Milli-Q water was used. However, in one particular case, small amounts of As were detected when the glassware was incubated with 10% HNO₃ acid. This means that the sources of As could be from leaching from glassware or the blank value originated from HNO₃ itself. Thus, the authors did not recommend the use of glassware and cleaning glassware with HNO₃ acid.

Analysis of samples should be carried out as soon as practical, since exposure of samples to air prior to analysis seems to oxidize As(III) into As(V) which can lead to a false impression of the true speciation within the sample (Siangproh et al., 2011). However, the signal can be stabilized by the addition of a reductant like hydrazine (Li and Smart, 1996, Sadana, 1983, Salaun et al., 2012), ascorbic acid (He et al., 2004) or by acidification; which is the most common method (Salaun et al., 2007, Polya et al., 2003, Lenoble et al., 2013). In addition, without pre-concentration, As(V) can be reduced to As(III) due to the presence of DOC (Huang and Ilgen, 2004).

As reviewed in multiple references ASV has been and continues to be one of the most common electrochemical methods for the determination of trace levels of As in water (Mays and Hussam, 2009). Although ASV provides a successful performance in the determination of trace levels of As(III) with a low detection limit, it also suffers from the interference from other metal ions especially Cu(II). This is because their standard electrode potentials appear close to each other, which could even lead to the overlapping of the As(III) peak if the concentration of the interference is high enough (Li et al., 2012b). Thus, metal interference studies should also be performed to evaluate any possible occurrence of overlaps. This can be done by spiking the water sample with an increased concentration of a possible interferent (Alves et al., 2011). Alves et al. (2011) further reported that, after successive scans using a vibrating Au microwire electrode and Ag|AgCl reference electrode the peak heights decreased
continuously indicating the possible build-up of interfering compounds at the Au electrode surface during the electrochemical determination of As. Li et al. (2012) also reported that this phenomenon may be attributed to chlorine being generated at the auxiliary electrode during the As deposition step using a bare Au electrode and a Ag|AgCl reference electrode via ASV. Whilst trace level As(III) detection using Au electrodes is still prone to interferences, particularly from Cu ions and organic matter in real samples, a variety of methods to overcome this method have been developed (Alves et al., 2011). These include the development of commercially available water testing kits for the in-field determination of As in real water samples which use Au electrodes and the use of nanoparticulate Au, supported on carbon substrates (Xiao et al., 2008). In addition, UV digestion of samples removes organic surface active substances which may interfere with the direct determination of total As in natural waters (Alves et al., 2011).

2.1.16 Inorganic As [As(III) and As(V)] – standards and samples

For the electrochemical analysis of inorganic As speciation via linear sweep voltammetry (LSV), standard addition method is the most common method used for this determination (Dai et al., 2004).

Issa et al. (2011) reported collecting and filtering water samples through a 0.45 μm membrane filter, following which, the samples were acidified to pH less than 2 with HNO₃ (1:1) and stored in refrigerator at 4 °C in polyethylene bottles. The As(III) working stock solution was prepared by dissolving sodium arsenite (4.95 g As₂O₃ + 1.30 g NaOH) in 1 L volumetric flask and refrigerated in an amber bottle which was found to be stable for at least one year. The group prepared As(V) working stock solution by dissolving 4.16 g Na₂HAsO₃·CH₃·7H₂O in 1 L of deionized water (1000.0 mg/L stock solution) which was preserved in 0.5% HNO₃.

This study was designed to evaluate the risks of As contamination in Metapona River in Guadalcanal, Solomon Islands and also in the upper Sabeto River, Viti Levu. More specifically the objectives were to carry out a standardized analytical method that can be applied towards the speciation analysis of inorganic As in environmental water
samples from the two sites and to identify any environmental risks associated with As levels in the aquatic areas studied. As is a known toxic metalloid particularly in the III oxidation state. Hence, it is important to quantify the levels of this species in our natural environment. The two study sites are gold mining areas in the Solomon Islands and Fiji. The results will be used to compare with the recommended levels of As(III) contamination in the aquatic system and then to identify any environmental risks associated with As levels in the aquatic areas studied.
CHAPTER 3

MATERIALS AND METHOD

3.0 Method

Samples were collected from two sampling sites at the Metapona River in the Solomon Islands and Sabeto River in Viti Levu, Fiji. Quantitative analysis on the samples for the determination of As(III), As(V) and total inorganic As was carried out using linear sweep anodic stripping voltammetry (LSASV). The following section details the methodologies carried out in the analyses.

3.1 Reagents

All chemicals and reagents used were of analytical grade and used without further purification. Ultrapure (Milli-Q) water, with resistivity of not less than 18.2 MΩ.cm, was used to prepare all solutions. Analytical grade HCl acid, H₂SO₄ acid and arsenic(III) oxide (As₂O₃) were obtained from Acros Organics (USA), while NaOH was acquired from Lobachemie (India).

3.2 Standards

1000 mg/L As(III) standard solution was prepared by dissolving 0.1320 g of As₂O₃ in minimum amount (10 mL) of 1 M NaOH. The pH was then adjusted to 3.0 with 1 M HCl and the solution diluted to 100 mL with ultra-pure water. This solution was prepared daily during As(III) detection analysis. Subsequent dilutions from the stock solution were then carried out to prepare the calibration standards in the range 0 – 80 μg/L. All standards were purged with N₂ gas prior to any analysis to remove any oxygen presence.
3.3 Instrumentation and apparatus

Electrochemical measurements involving linear sweep stripping were performed using a potentiostat (eDAQ Pty Ltd., Sydney, Australia) computer controlled having a EChem version 2.1.15 software. A single compartment, three electrode glass cell containing the gold working electrode, a platinum counter electrode and a Ag/AgCl reference electrode was used. All measurements were carried out at controlled room temperature (25 °C). The instrumentation set up is shown in Figure 3.1.

![Figure 3.1](image)

**Figure 3.1.** Schematic of instrumentation set up. Electrochemical measurements were performed using a potentiostat (1) which was operated using EChem software using a PC (2). All analyses were carried out in a Faraday cage (3) which houses the three electrode cell (4) mounted on a magnetic stirrer (5).

3.4 Water sampling

3.4.1 Sampling method

Polyethene sampling bottles were used for sample collection. The bottles were first cleaned with detergent and then soaked in 5% HCl for at least 24 h. The bottles were then rinsed several times with distilled water and then stored in sealed plastic bags. At the sampling site, onsite filtration was carried out using a syringe filter equipped with a 0.45 μm filter. The sampling bottles were first rinsed three times with the filtered
sample prior to filling with the filtered sample. After filling, the sample was acidified to pH 2 using concentrated HCl before being capped and returned to plastic bag. Nitrile disposable hand gloves were worn during sample collection. Sample collection was done in duplicates for all the sites. Physical parameters such as pH, temperature, turbidity, dissolved oxygen, conductivity, total dissolved solids, salinity and geographical location were also recorded for all the sites. All samples were kept in ice until they reached the USP laboratory where they were transferred to a freezer and stored at 4 °C. All laboratory analyses were carried out within 2 weeks of sampling. Speciation analysis of inorganic As in pre-concentrated and refrigerated environmental water samples within 2 weeks of sampling has been reported by (Rasul et al., 2002). The authors reported that the method was effective in retaining As(III) and As(V) and the 2 weeks storage did not affect the analysis. Similarly, in this study, analysis was not affected as a result of storage of samples within 2 weeks.

3.5 Sampling areas

3.5.1 Metapona River

Metapona River is located on Guadalcanal Island, the largest island in the Solomon Islands. The river drains the Gold Ridge mine, The Gold Ridge gold deposits are located at the head waters of the Metapona River (Godfrey et al., 2011). The river delta, located on the Guadalcanal plains, lies 26 km east of Honiara, capital of Solomon Islands. Intense agriculture activities are common at the lower Metapona floodplain especially commercial oil palm plantations. There is also considerable traditional gardening as many people live along the river, most of whom are traditional subsistence farmers.

The Guadalcanal plain was formed by a combination of vertical aggradation of meandering river deposits and delta propagation by the seven large rivers draining north from the Guadalcanal highlands. The seven rivers crossing Guadalcanal plain drain 33% of the island, the Metapona is the central one of these rivers (Roy, 1990, Yeo et al., 1996). The Metapona River is characterized by narrow, steep sided, meandering channels and a sediment load that is fine grained. Present day appearance
of the river is murky and is highly turbid with increased sediment loads visible along the banks.

Samples were collected from eight different sites along the river commencing from downstream to upstream. Figure 3.2 shows the sampling sites along the Metapona River. Site 1 is located downstream of the Metapona River while the final sampling Site 8 is located upstream. Gold Ridge Mine is located close to the head waters of the Metapona River further upstream. Most villages are concentrated downstream and further downstream of the river, while few villages are located up stream. Vast stretches of grassland and vegetation line the river banks. Food gardens are also common along the river banks. Oil palm plantations are also common on the lower Metapona plains.

### 3.5.2 Upper Sabeto River

Sabeto River is located 24 km Northeast of Nadi Town in Fiji’s main island Viti Levu. This river drains an area that hosts the Tuvatu deposits which is one of several gold prospects known from the Sabeto area of North Western Viti Levu (Wayne et al., 2010).

Samples were collected from five different sites along upper Sabeto River and Qalibua River and these sites are shown in Figure 3.3. Site 1 is located upstream of Sabeto River. Site 2 is located close to the entrance to the old mine adit and is located along the Qalibua River which is a tributary that flows into the Sabeto River. Site 3 is located further upstream of the Qalibua River and the old mine site. Site 4 is located at the confluence between Sabeto and Qalibua River, moving away from the old mine site towards downstream. Site 5 is located close to the mine camp site which is furthest away from the old mine site.
Figure 3.2. Map showing location of water sampling sites along Metapona River with map of Solomon Islands inset (Source: Google maps).
Figure 3.3. Map showing the location of water sampling sites at the upper Sabeto River with map of Fiji Islands inset (Source: Google maps).
3.6 Validation

3.6.1 Precision and accuracy

The repeatability of the proposed method was determined using two As(III) standards with concentrations within the linear calibration range. A 5 μg/L was chosen for the lower concentration range while a 50 μg/L standard was chosen for the higher range. Six replicates of each of the two standards were prepared and analyzed within one day throughout the course of the analysis (Miller and Miller, 2005). Thus, the accuracy of the method was tested by ASV analysis of As(III) standards with known concentrations of 5 μg/L and 50 μg/L using standard addition technique.

3.6.2 Replicate analysis

All analyses were carried out in triplicate to ensure reliability of the data.

3.6.3 Method detection limit

The detection limit is the smallest quantity of analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero (Miller and Miller, 2005). The procedure for the detection limit was adapted from that reported by Harris (2010). This was done by first identifying the lowest possible concentration standard with current signal that is significantly different from that of the blank. Using this method a 5 μg/L As(III) standard was identified and eight replicates of this standard were prepared and analysed by ASV. The standard deviation of the mean was then calculated. The detection limit was obtained by multiplying the standard deviation by 3 and dividing by the slope of the standard calibration plot.
3.7 Procedure for determination of As(III) by ASV

As(III) determination in the environmental water samples was carried out using the standard addition method. Using this technique, known quantities of the As(III) standard were added to the unknown sample. From the increase in signal, the amount of As(III) standard in the original unknown sample was deduced. A linear response to As(III) standard is required in this method (Harris, 2010).

For the determination of As(III) in the environmental water samples, 10 mL of the filtered water sample was pipetted into a vial and spiked simultaneously with 200 μL additions of 1 mg/L As(III) standard at increasing concentration levels. For each of the samples, analysis was carried out in triplicates.

The procedure for As(III) detection in this study was adapted from that reported by Dai et al. (2004) with some adjustments. As(III) measurements with the solid Au electrode was performed via a pre-concentration and then a stripping step. Firstly, a deposition step was carried out at -344 mV (versus Ag|AgCl) for 300 s to preconcentrate the As(III) with constant stirring using magnetic stirrer. A linear sweep voltammetric anodic scan (stripping step) follows from -344 mV to 500 mV at a scan rate of 20 mV/s. An electrochemical cleaning step was then carried out at 500 mV for 30 s. The cleaning step was carried out at more positive potential to make sure that all As(III) ions are oxidized back into the solution and subsequently the electrode is ready for the next analysis. Since the method has been demonstrated to be specific for As(III), the analysis for As(III) was carried out directly using the recommended procedure against a blank prepared similarly.

3.7.1 Electrode pre-treatment and conditioning

Prior to the analysis, the solid Au electrode was cleaned by polishing in 0.05 μm polishing grade alumina on a fine polishing pad to a mirror finish, distilled de-ionized water was then used to rinse off adhering alumina particles (Giacomino et al., 2011, Alam, 2008).
After polishing and rinsing of the electrode, electrode conditioning was carried out using 0.5 M H₂SO₄. Cyclic voltammetry profiles of the electrode in 0.5 M H₂SO₄ were then recorded in the potential range from 0 mV to 1500 mV (vs Ag/AgCl) at a scan rate of 100 mV/s. This was repeated for 20 cycles until a stable voltammogram was achieved. This indicates the completing cleaning of the Au surface and verification of activation of the electrode surface (Liu et al., 2010, Giacomino et al., 2011, Kopanica and Novotný, 1998).

### 3.8 Procedure for the determination of total inorganic As [As(III) + As(V)]

The procedure for the determination of total inorganic As [As(III) + As(V)] was adapted from Rasul et al. (2002). The determination of total inorganic As was done by reducing As(V) to As(III) with Na₂SO₃ according to the following reactions.

\[
Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2SO_4
\]

\[
H_3AsO_4 + H_2SO_3 \rightarrow H_3AsO_3 + H_2SO_4
\]

To a solution of 5 mL of water sample + 5 mL 9 M HCl, 0.2 g anhydrous Na₂SO₃ was added. The solution was then heated at 50 °C for 30 min with constant stirring. The solution was left to cool to room temperature and analysis carried out as described in section 3.7 for the determination of As(III), the concentration of As(III) detected is the total inorganic As concentration.

### 3.9 Data treatment

Using the method of standard additions (as described in section 3.7), the analytical detection was carried out using linear sweep anodic stripping voltammetry (LSASV). All results obtained were fitted according to Gaussian method using Origin graphing software (version 8.6). For each of the scans, the analytical signal was obtained after subtracting the background scan to obtain the background corrected scan which was used for quantification (Dai et al., 2004).
Statistical analysis of data in this study was performed using SPSS statistics software (version 21). All values reported and error bars shown in graphical representation are within 95% confidence interval unless stated otherwise.
CHAPTER 4

RESULTS AND DISCUSSION

4.0 Precision and accuracy

The repeatability of the proposed method was determined using two concentrations within the linear range: 5 μg/L and 50 μg/L As(III) standards. Six standard solutions for each concentration were prepared and analyzed within one day. The results are shown in Table 4.1. The relative standard deviations (RSD) obtained from the repeated analysis of the two standards are: 2.7% for the 5 μg/L standard and 5.3% for the 50 μg/L standard. These RSD values were quite satisfactory which means that the method has good precision in the detection of As(III) in the water samples. The RSD values found in this study are lower compared to other studies performed for As (III) detection by ASV using Au electrode such as that reported by Kopanica and Novotný (1998) (16.1%), Rasul et al. (2002) (10%) and Yamada et al. (2008) (7.5%).

Table 4.1. Current precision test using a 5 μg/L and 50 μg/L As(III) standards (N = 6).

<table>
<thead>
<tr>
<th>Replicate No.</th>
<th>Current signal (× 10⁻⁸ A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 μg/L</td>
</tr>
<tr>
<td>1</td>
<td>3.2</td>
</tr>
<tr>
<td>2</td>
<td>3.3</td>
</tr>
<tr>
<td>3</td>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
<td>3.3</td>
</tr>
<tr>
<td>5</td>
<td>3.2</td>
</tr>
<tr>
<td>6</td>
<td>3.2</td>
</tr>
<tr>
<td>Mean Current (× 10⁻⁸)A</td>
<td>3.3</td>
</tr>
<tr>
<td>Standard deviation (SD)</td>
<td>0.9</td>
</tr>
<tr>
<td>RSD%</td>
<td>2.7</td>
</tr>
</tbody>
</table>

RSD = Relative standard deviation
The accuracy of the method was tested by linear sweep ASV (LSASV) analysis of As(III) standards with known concentration of 5 μg/L and 50 μg/L using standard addition technique. The concentrations found were 5 ± 0.4 μg/L (N = 3) and 50 ± 5 μg/L (N = 3). Therefore the accuracy of the method was considered to be quite good.

4.1 Replicate analysis

All analyses were carried out in triplicates to ensure reliability of results. Satisfactory results were obtained with all replicate analysis. The triplicates are reflected in the reported results as shown in Table 4.2 and Table 4.3 for the Metapona and Sabeto results, respectively. For each sample the mean of triplicate runs was recorded as the As(III) or total inorganic As concentration ± the standard error of the mean.

Table 4.2. As(III), As(V) and total inorganic As levels at each of the sites at Metapona River (N = 3 for each site). Also included are the Field parameters. (DO: Dissolved O₂).

<table>
<thead>
<tr>
<th>Site</th>
<th>Mean [As(III)] (μg/L)</th>
<th>Mean [As(V)] (μg/L)</th>
<th>Mean total inorganic [As] (μg/L)</th>
<th>Field parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>pH</td>
</tr>
<tr>
<td>1</td>
<td>1.4 ± 0.1</td>
<td>20.3 ± 0.4</td>
<td>21.7 ± 0.5</td>
<td>7.9</td>
</tr>
<tr>
<td>2</td>
<td>16.3 ± 2.9</td>
<td>14.3 ± 1.9</td>
<td>30.6 ± 4.7</td>
<td>6.1</td>
</tr>
<tr>
<td>3</td>
<td>15.9 ± 0.5</td>
<td>10.1 ± 4.7</td>
<td>26.0 ± 4.2</td>
<td>6.4</td>
</tr>
<tr>
<td>4</td>
<td>5.8 ± 0.4</td>
<td>25.7 ± 2.6</td>
<td>31.5 ± 2.2</td>
<td>7.4</td>
</tr>
<tr>
<td>5</td>
<td>10.0 ± 2.2</td>
<td>26.0 ± 2.3</td>
<td>36.0 ± 2.5</td>
<td>7.4</td>
</tr>
<tr>
<td>6</td>
<td>11.9 ± 0.7</td>
<td>28.0 ± 1.0</td>
<td>39.9 ± 0.9</td>
<td>7.2</td>
</tr>
<tr>
<td>7</td>
<td>15.6 ± 0.2</td>
<td>22.2 ± 2.1</td>
<td>37.8 ± 2.2</td>
<td>6.6</td>
</tr>
<tr>
<td>8</td>
<td>20.7 ± 0.7</td>
<td>52.0 ± 0.9</td>
<td>72.7 ± 1.2</td>
<td>7.1</td>
</tr>
</tbody>
</table>
Table 4.3. As(III), As(V) and total inorganic As levels at each of the sites at Sabeto River (N = 3 for each site). Also included are the field parameters. (DO: Dissolved O₂).

<table>
<thead>
<tr>
<th>Site</th>
<th>Mean [As(III)] (μg/L)</th>
<th>Mean [As(V)] (μg/L)</th>
<th>Mean total inorganic [As] (μg/L)</th>
<th>Field parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>pH</td>
</tr>
<tr>
<td>1</td>
<td>7.3 ± 0.8</td>
<td>19.5 ± 5.8</td>
<td>26.9 ± 5.1</td>
<td>7.9</td>
</tr>
<tr>
<td>2</td>
<td>55.2 ± 6.9</td>
<td>11.8 ± 2.1</td>
<td>67.0 ± 7.2</td>
<td>5.7</td>
</tr>
<tr>
<td>3</td>
<td>49.7 ± 1.3</td>
<td>14.0 ± 2.5</td>
<td>63.7 ± 2.8</td>
<td>6.2</td>
</tr>
<tr>
<td>4</td>
<td>30.4 ± 3.7</td>
<td>11.3 ± 2.5</td>
<td>41.6 ± 6.0</td>
<td>6.5</td>
</tr>
<tr>
<td>5</td>
<td>16.0 ± 4.5</td>
<td>26.9 ± 3.2</td>
<td>42.9 ± 5.1</td>
<td>7.5</td>
</tr>
</tbody>
</table>

4.2 Treatments and cyclic voltammetry study of the Au surface

The importance of the pre-treatment and conditioning/activation steps of the active surface of Au electrodes, in order to maintain the electrode surface active and reproducible, is well known (Giacomino et al., 2011, Profumo et al., 2005, Wang, 2006). Electrode conditioning was essential to enhance the quality and reproducibility of the As signal (Giacomino et al., 2011, Salaun et al., 2007, Kopanica and Novotný, 1998). Figure 4.1 depicts the cyclic voltammograms (20 cycles) of the electrode in 0.5 M H₂SO₄. The oxidation peaks at 1200 – 1400 mV are due to the oxidation of Au oxides at the electrode surface, while the reduction peaks at 900 V are attributed to the reduction of these Au oxides (Dai et al., 2004, Giacomino et al., 2011). During the activation step, stable voltammograms were obtained after cycling 20 times in 0.5 M H₂SO₄ which suggests a clean Au surface electrode. The voltammogram obtained by cyclic voltammetry during the activation step was also used for the daily monitoring of the electrode surface.
Figure 4.1. Cyclic voltammogram curves in 0.5 M H$_2$SO$_4$ for Au electrode with a clean surface.

4.3 Analysis of As(III) standards and linearity

Analysis of As(III) standards was carried out using LSASV in 1.0 M HCl supporting electrolyte. The current signal was observed to increase with increasing As(III) standard concentrations for As(III) standards from 10 to 80 μg/L. Using this method the As stripping peak was seen between 100 mV and 150 mV which is shown in Figure 4.2.
Figure 4.2. Linear sweep voltammetry curves of As(III) in 1 M HCl. Pre-deposition at -344 mV vs Ag|AgCl for 300 s, potential scan rate: 20 mV/s. Graph with voltammetric curves with potentials from 0 – 250 mV is shown inset.

By scanning As(III) standards within various concentration regimes, the linear calibration range was found to occur from 0.763 to 80.0 μg/L for the Au electrode. Therefore, this As(III) concentration range deemed as optimum was used for the standard calibration plot. Spiked samples giving current signals corresponding to As(III) concentrations higher than 80 μg/L were diluted prior to analysis. The current signals from the linear scans were deduced for each of the standards and plotted against the increasing concentrations of the standards. A linear relationship was observed which is graphically illustrated in Figure 4.3.
From the calibration plot above (Figure 2.8), the sensitivity of this method was obtained. This is based on the slope of the calibration plot, and yielded a value of 224.7 nA/μM.

It was observed that there was a gradual decrease in sensitivity with concentrations greater than 80 μg/L. The reason for this diminished sensitivity has been previously attributed to the saturation of the Au electrode surface with the deposited As(0) which is non-conductive (Khairy et al., 2010, Salaun et al., 2007). This effect causes the electrode to be fouled which is a common problem in electrochemical analyses. Electrode saturation occurs at high concentrations of analytes in the solution media, or after continuous usage of working electrode without cleaning or surface renewal. It has been proposed by Yang et al. (2012) that the mechanism in which electrode fouling occurs is by diffusion through pinholes, electron tunnelling or mass permeation through the fouling layer.
4.4 Method detection limit

To determine the limit of detection, the procedure reported by Harris (2010) was followed. Eight replicates of 5 μg/L As(III) standard were prepared and analysed. The standard deviation of the mean was then calculated. The detection limit was obtained by multiplying the standard deviation by 3 and dividing by the slope of the standard calibration plot. Using this method the detection limit was found to be 0.763 μg/L which is lower than the maximum contaminant level of 10 μg/L recommended by WHO. The LOD obtained in this study is lower than some LODs reported for other electrochemical methods for inorganic As speciation studies. For instance (Yamada et al., 2008) did ASV using Au modified Boron doped diamond electrode for As(III) detection and reported a LOD of 5 μg/L. As(III) detection carried out by (Adeloju et al., 1999) using cathodic stripping voltammetry on a mercury film electrode yielded a LOD of 2 μg/L. As speciation studies was also performed by Rupasinghe et al. (2009) using pervaporation flow injection which used on-line hydride generation for separation of As(III) from sample matrix and detection using amperometry. The group reported a LOD of 1 μg/L in their study.

4.5 Effect of interference from Cu(II)

A common interfering species in the detection of As(III) by ASV using Au electrode is Cu(II) (Feeney and Kounaves, 2002, Punrat et al., 2013). Its effects on the determination of As(III) have also been widely discussed in the literature (Giacomino et al., 2011, Sun et al., 1997, Feeney and Kounaves, 2002, Khairy et al., 2010b). In fact, it is well known that Cu(II) forms as intermetallic compound with As (Sun et al., 1997, Dai et al., 2004) which causes the decrease of the As(III) analytical signal. It is also known that Cu(II) can be easily co-deposited with As(III) with little separation between their respective stripping peaks (Du et al., 2009). Therefore, if the concentration of Cu(II) is sufficiently high, the stripping peak of As(III) will be partly or even totally obscured by that of Cu(II). The presence of Cu(II) has also shown to cause a shift in the As(III) stripping peak potential to a higher potential (Punrat et al., 2013, Song and Swain, 2007). In this study, the interfering effect of Cu(II) on the
As(III) signal was evaluated using a 50 μg/L As(III) standard in the presence on 0, 150 and 200 μg/L Cu(II) respectively. The voltammograms are shown in Figure 4.4. In the presence of 0 to 200 μg/L Cu(II), the anodic stripping current of As(III) did not show any significant change. However, there was a slight shift to a higher potential [from 106 mV with no added Cu(II) to 110 mV (with added Cu(II))]. This slight positive potential shift of 4 mV is similar to a previous study by Song and Swain (2007) where a positive shift of 8 mV was observed using differential pulse ASV on Au coated diamond electrode. The group attributed the slight shift in potential to the presence of Cu(II). Furthermore, in the presence of 150 μg/L Cu(II) another peak started to appear at ~340 mV, which increased in height when the Cu(II) was increased to 200 μg/L. This new peak is attributed to the oxidation of Cu metal deposited on the surface of the Au electrode (Song and Swain, 2007). The potential at which this peak occurs is consistent with previous findings using Au electrode, which occurs around ~300 – 400 mV (Salaun et al., 2012, Punrat et al., 2013, Song and Swain, 2007).

**Figure 4.4.** Linear sweep anodic stripping voltammograms of a solution containing 50 μg/L As(III) in 1 M HCl and in the presence of 0, 150 and 200 μg/L Cu(II) respectively.
The Cu(II) stripping peak and the As(III) stripping peak occur at close potentials. However, the Cu(II) stripping peak with concentration up to 200 μg/L does not affect the integration of the As(III) stripping height as the peaks occur at two discrete potentials. This is shown in the fitted voltammograms in Figure 4.5.

![Fitted voltammograms of 50 μg/L As(III) in the presence of 0, 150 and 200 μg/L Cu(II).](image)

**Figure 4.5.** Fitted voltammograms of 50 μg/L As(III) in the presence of 0, 150 and 200 μg/L Cu(II).

### 4.6 Effect of deposition time

The effect of deposition time was studied by varying the deposition time in the range 30 – 720 s, this is shown in Figure 4.6. The stripping current was observed to increase with increasing deposition time. This is because with increasing deposition time, more As(0) were deposited on the electrode surface. This resulted in more As(0) being oxidized and stripped into the solution which subsequently resulted in increased current signals. However, at deposition times greater than 300 s, the slope reduces and
the plot started to be curved which may be attributed to the saturation of the electrode surface. A deposition time of 300 s was therefore chosen as a good compromise between sensitivity and analysis time.

**Figure 4.6.** Effect of varying deposition potential on a 50 μg/L As(III) standard.

### 4.7 As(III) and total inorganic As detection

Analytical detection of As(III) was carried out by method of standard addition as described in section 3.7. This analytical technique involves the addition of known quantities of As(III) standard to the unknown. From the increasing signal, the amount of As(III) in the original unknown samples is deduced. This method is especially appropriate when the sample composition is unknown or complex and can affect the analytical signal (Harris, 2010). This technique involving low spike volumes which ensures that matrix effects are minimized.
The voltammetric responses of standard additions of As(III) to the water sample is shown in Figure 4.7. Originally, the increase in background current was also accompanied by a migratory–baseline away from the horizontal with increasing concentrations. This was addressed by fitting the waveforms according to the Gaussian model, and the fitted results are presented in Figure 4.7 (inset) together with the unfitted results. The current signals were obtained from the fitted waveforms. The stripping peak seen between 100 – 200 mV in the voltammogram is due to the electrochemical stripping of As(0) to As(III). With increasing spike volume added, the current signal showed a subsequent increase. However, in the spiked samples at higher As(III) concentrations (>100 μg/L), there was a reduction in corresponding rate of current increase in As(III) stripping peaks. This can be attributed to saturation effects on the surface of the Au electrode causing a coating on the electrode surface with the deposited As(0) which is non-conductive (Khairy et al., 2010, Giacomino et al., 2011) as aforementioned. Quantitative responses of As(III) stripping peaks were obtained using this method. With increasing As(III) concentration, a slight increase in background currents was observed, quite likely due to background reactions particularly those associated with the double layer charging around the electrode (Sokol and Evans, 1981, Wang, 2006).
Figure 4.7. Voltammetric responses of spiked As(III) to water sample with the fitted waveforms (inset). Pre-deposition at -344 mV vs Ag|AgCl for 300 s, potential scan rate: 20 mV/s.

The current signals obtained for corresponding concentrations after spiking were plotted against the As(III) concentration in the sample which yielded a linear response as shown in Figure 4.8. The y-axis confidence interval at 95% confidence level for each point is also included. The concentration of As(III) in the sample was then deduced directly from the graph.
Total inorganic As determination was carried out after the reduction step that enables the conversion of As(V) ions to As(III). As(V) concentrations were obtained by subtracting As(III) from total inorganic As, since As(III) + As(V) equals total inorganic As (Song and Swain, 2007).

### 4.8 Environmental guideline values

The data collected in this study, and discussed in the sections that follow were compared against known guideline values for the assessment of inorganic As in the Metapona River and Sabeto River. These are international water quality guidelines used worldwide for the assessment of the quality of the environmental and its constituents. As there are no established regional or national guidelines in the South Pacific region so Australian and New Zealand guiding parameters were adopted for comparison.

**Figure 4.8.** Standard addition plot for the measurement of As(III) in the water sample.
4.8.1 As guideline values in environmental waters

The percentage level of protection is a method of categorization that assigns a certain percentage value that corresponds to the conditions that an ecosystem is likely to be in. The levels of ecosystem conditions are proposed by the Australian and New Zealand guidelines for fresh and marine water quality as a basis for applying the guidelines (ANZECC, 2000). The four different percentage protection levels are 99%, 95%, 90% and 80%. Here the protection level signifies the percentage of biological species expected to be protected. The highest protection level (99%) corresponds to ecosystems with high conservation value. On the other hand, 80% protection level corresponds to ecosystems that are severely disturbed. In this study, the percentage level of protection was estimated to be at 95% for both; Metapona River and Sabeto River which corresponds to a moderately to highly disturbed ecosystem.

Methods for deriving the physical and chemical water quality guidelines for ecosystem management are known as “guideline trigger values” (ANZECC, 2000). These values were modified into regional, local or site specific guidelines by taking into account various environmental factors and conditions. They also provide a contextual level for analytes considered to represent ‘good’ water quality (ANZECC, 2000). While exceedances of the guideline values can indicate a potential environmental, problem, they do not necessarily indicate water pollution. For instance, some analytes may be naturally present in elevated levels above the guideline values because of natural sources. In such a case, exceedances of these guideline values ‘trigger’ management response e.g., further investigation and subsequent refinement of the guidelines according to local conditions. Table 4.4 shows the trigger values for As(III) and As(V) at 95% protection level.

<table>
<thead>
<tr>
<th>As species</th>
<th>Trigger values in freshwater (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td>24</td>
</tr>
<tr>
<td>As(V)</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 4.4. Trigger values for inorganic As at 95% levels of protection (% species).
4.9 As(III), As(V) and total inorganic As levels in Metapona water samples

The following section discusses the concentrations of inorganic As at the eight sites along the Metapona river. The sites are numbered starting from site 1 onwards until site 8 which is located upstream. These sites are shown in Figure 3.2 and represented in tabular form in Table 4.2 along with the determined concentration of As(III), As(V), total inorganic As and other parameters.

Gold mining regions are well known sources for anthropogenic inputs of As into the natural environment as its distribution is highly influenced by the extent of mining and ore processing (Larios et al., 2012a) and can also be in surrounding areas (Moreno-Jiménez et al., 2010, Grosbois et al., 2011). This may primarily be due to weathering and dissolution of As containing minerals which are accelerated due to mining activities. This metalloid is present in several minerals such as sulphides, arsenates, arsenides, oxides, and arsenites which often form ore deposits in association with transition metals and Cd, Pb, Ag, Au, Sb, P, W and Mo (Barats et al., 2014). However, arsenopyrite (FeAsS) and arsenian pyrite (Fe(S,As) are believed to be the most abundant in mineral ores (Smedley and Kinniburgh, 2002, Nordstrom, 2002).

4.9.1 Total inorganic As

The results from this study show that total inorganic As is present in high concentrations in the Metapona River. Site 8, as shown in Table 4.2 has the highest concentrations of total inorganic As as 72.7 ± 1.2 μg/L. This site which is located upstream is also the closest to the Gold Ridge mine. Generally, total inorganic As levels showed a continuing decrease in concentrations moving towards downstream. This describes that the probable source could be further upstream of Site 8. This decreasing trend in total inorganic As levels has been documented in previous studies which have shown that total inorganic As levels progressively decreased with distance of at sites from the mine site (Qopoto et al., 1994). Based on these findings, it is quite
likely that the As detected in the Metapona River could also be from the Gold Ridge mine. In such a scenario, the decrease in concentrations further downstream from the mine could arise from dilution effects of the river water.

Au deposit at Gold Ridge mine appears to be present as electrum in association with pyrite and in quartz-carbonate veins particularly where base metal sulphides are present (Godfrey et al., 2011). Sulphide mineralogy is dominated by pyrite-marcasite and includes arsenopyrite, sphalerite, galena and chalcopyrite. Arsenite and arsenate in aquatic systems can then be mobilized from arsenopyrite. This can occur by reaction of arsenopyrite with sulfide in the presence of O₂ through sulfide-arsenide exchange as shown below (Zhu et al., 2008).

\[
\text{FeAsS}^{\text{aq}} + \text{HS}^{-} + \frac{5}{4} \text{O}_2^{\text{aq}} + \frac{1}{2} \text{H}_2\text{O}^{\text{aq}} \rightarrow \text{FeS}_2^{\text{aq}} + \text{As(OH)}_3^{\text{aq}}
\]

Other processes include oxidation of arsenopyrite and sulfide complexation of dissolved As. For arsenopyrite oxidation the first products are As(III) and Fe(II) as shown in the following equation (Salzsauler et al., 2005).

\[
\text{FeAsS}^{\text{aq}} + \frac{11}{4} \text{O}_2^{\text{aq}} + \frac{3}{2} \text{H}_2\text{O}^{\text{aq}} \rightarrow \text{Fe}^{2+} + \text{H}_3\text{AsO}_3^{\text{aq}} + \text{SO}_4^{2-}
\]

After release into solution, As(III) is then oxidized to As(V) as shown in the following equation below (for species in solution at near neutral pH).

\[
\text{H}_2\text{AsO}_3^{\text{aq}} + \text{H}_2\text{O}^{\text{aq}} \rightarrow \text{HAsO}_4^{2-} + 4\text{H}^+ + 2\text{e}^{-}
\]

Previous reports have shown that geochemical analysis of ore deposits at Gold Ridge found that As is present mainly as arsenopyrite in the deposits (Godfrey et al., 2011). Therefore, the mechanism involving mobilization of arsenopyrite to As(III) and As(V), as explained above, could be a contributing factor to the high levels of inorganic As in the Metapona River.
4.9.2 Inorganic As speciation

As(III) and As(V) levels vary for all the site along the Metapona River, as shown in Table 4.2. Figure 4.9 shows the relationship between As(III), As(V) and total inorganic As for the eight sites. The results show that site 1 recorded the lowest As(III) level. However, moving upstream from site 1 the As(III) level increases in sites 2 and 3 with site 3 showing the highest As(III) level. As(III) levels then decrease for site 4 before slowly increasing at sites 5, 6 and 7 before showing a decrease at site 8 upstream.

Site 1, which is located downstream compared to all the sites recorded the least As(III) concentration and also showed the lowest total inorganic As concentration. This can be due to dilution effects of the river. As(III) is present at relatively high levels in sites 2 and 3 as 16.3 μg/L and 15.9 μg/L respectively, these two sites also recorded the lowest As(V) levels of 14.3 μg/L for site 2 and 10.2 μg/L for site 3. Site observation for sites 2 and 3 during sample collection shows that these 2 sites were predominantly muddy sites rich in organic matter. According to Drahota et al. (2009), in surface waters high As(III) levels and low As(V) levels occur in areas rich in organic matter. This is likely due to the presence of organic substances such as humic and fulvic acids, which are important electron donors for the reduction of elements (Dobran and Zagury, 2006).

As(III) levels showed decrease at sites 4, 5 and 6 while As(V) levels remained relatively high. This can be attributed to the slight increase in pH around (or just above) neutral (Table 4.2).
Figure 4.9. Relationship between As(III), As(V) and total inorganic As in Metapona River.

4.9.3 Comparison of total inorganic As levels in the Metapona River with levels determined from previous studies

An Environment Impact Assessment report was carried out by Mining Company in 1990 prior to mine development (Fletcher, 1998). Here, inorganic As determined in the Metapona River ranged from 1 – 3 μg/L. This study also showed As concentrations in stream sediments ranging from 7.42 – 53.6 mg/L which, far in of the threshold levels of >20 mg/L (ANZECC, 2000). Analysis of aquatic fauna in the river also showed elevated levels of As in the geochemical survey carried out in 1990 (Fanning, 1990). Speciation studies, however, were not carried out in these studies. These historical data show that the Gold Ridge and the surrounding areas are naturally enriched in As due to the geochemistry of the gold bearing ores within the area (Albert et al., 2014).

An initial baseline study was carried out in 1992 by Qopoto et al. (1994). However, this study was based primarily on the sediment geochemistry in the Metapona River.
The study also shows elevated total inorganic As levels in stream sediments (more than 40 mg/kg) for about 12 km downstream of Gold Ridge mine. The study also recommended further investigation to be undertaken to evaluate the implications the high As concentrations can have on the wider local environment. These historical data show that the Gold Ridge and the surrounding areas are naturally enriched in As due to the geochemistry of the gold bearing ores within the area (Albert et al., 2014).

A baseline study on sediment and water chemistry, water quality and ecology of the Metapona delta was carried out in 1995 by Yeo et al. (1996). For water analysis, sampling was done at the Metapona River mouth only. Total inorganic As levels ranged from <1 to 2.8 μg/L in this survey. In the present study, only site 1 is located within the study area sampled by Yeo et al. (1996) which was located further downstream. This site recorded the lowest total inorganic As in this study, the concentration determined was 21.7 μg/L. This shows that As levels have increased in the Metapona River over the years the Gold Ridge mine was in operation. These historical data show that the Gold Ridge and the surrounding areas are naturally enriched in As due to the geochemistry of the gold bearing ores within the area (Albert et al., 2014).

Previous studies have shown that total As levels in sediments were particularly high in concentration ranging from 10 to 40 mg/L, with a suggestion that the elevated As levels can be due to sediments carried by mine runoff transported from the Gold Ridge site upstream (Albert et al., 2014). This provides a notable link that the high inorganic As levels can be from the Gold Ridge mine (Albert et al., 2014).

A comparison of data from this study and those from previous works demonstrates an increase in total inorganic As levels in the Metapona River over the years. An Environmental Assessment Report carried out when the mine initially started operations shows ore and waste rock from the Gold Ridge project having As concentrations ranging from 96 – 920 mg/L (Mining, 1998). These wastes were then stored in tailings dams which are still present today.

Weathering of these exposed ores and waste rocks is likely responsible for the high levels of inorganic As in the Metapona River. Percolation of rainwater through waste rocks and soil heap materials is known to mobilize and transport mineral particles
downstream (Larios et al., 2012a). This causes the accumulation of As in waterways at these sites. The Gold Ridge mining operations also generated loads of sediments that are still visible along the banks of Metapona River. This has also caused a river blockade, subsequently causing diversion of the river further downstream. It is highly likely that various trace elements including As could be adsorbed to these sediments being eroded by physical processes and were carried down into the waterways and eventually into the Metapona River. In addition, studies have shown that river flooding also causes the release of As from soils and sediments which can eventually end up in river systems (Smedley and Kinniburgh, 2002, De Vitre et al., 1991). This release can be mainly associated with the dissolution of Al-/Fe-oxyhydroxides and clay minerals, which released both their adsorbed and incorporated As loads into the river system (Tabelin et al., 2014, Guo et al., 1997). Al-/Fe-oxyhydroxides and clay minerals are mineral phases that incorporated and/or adsorbed trace elements such as As. Dissolution and/or desorption of these mineral phases will result in the release of these trace elements into the river system. According to Tabelin et al. (2014), the dissolution and desorption of As from Al-/Fe-oxyhydroxides and clay minerals in sedimentary rocks in streams is pH-dependent. The release of As is intensified in acidic and alkaline conditions compared to near neutral pH conditions. From this, it means that for Metapona River, As mobility in the river water associated with this mechanism is not the dominant factor responsible for the high levels of inorganic As. This is because of the pH range from sites 1 to 8 is near or around neutral.

Total inorganic As occurrence in natural water bodies is very much dependent on the pH and redox conditions of the solution, oxidation state, and sorption or exchange reactions (Cheng et al., 2009). The relationship between As species and pH and Eh is shown in the pourbaix diagram in Figure 4.10. This diagram shows a visual representation of the zones of dominance for the various oxidations states in which As can exist in the aqueous media. As can be seen in the diagram, thermodynamically, at low pH and Eh, As(III) is the predominant species, which exists as H$_3$AsO$_3$.

The pH values from site 1 to 8 remained close to neutral i.e. 7.0 ± 0.6 when the sampling was carried out (Table 4.2). As(V) was the predominant species present. According to the pourbaix diagram in Figure 4.10, it is likely As(V) could exist as H$_2$AsO$_4^-$ and HAsO$_4^{2-}$ in the near neutral pH range for the Metapona River.
To better understand the statistical relationship between variables, correlation analysis was carried out using the Pearson Correlation method in this study. This method measures the strength of the linear relationship between two variables and has values (denoted ‘R’) ranging from +1 to -1 (Benesty et al., 2009). A value of +1 denotes total positive correlation, 0 denotes no correlation while -1 denotes total negative correlation.

The correlation between pH and As(III)/As(V) ratio is shown in Table 4.5. A strong negative correlation (-0.874) can be observed between the two variables. This means as pH increases As(V) becomes the predominant inorganic As species present in the water while As(III), while the reverse applies at lower pH. This is in agreement with
published reports that arsenite predominates at reducing conditions (low pH) while arsenate is associated with oxidizing conditions (high pH) (Cheng et al., 2009, Casiot et al., 2009).

Table 4.5. Correlation relationship between pH and As(III)/As(V) ratio at Metapona River (N= Number of samples, Sig. = Significance).

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>As(III)/As(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Pearson Correlation</td>
<td>-0.874**</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>8</td>
</tr>
<tr>
<td>As(III)/As(V)</td>
<td>Pearson Correlation</td>
<td>-0.874**</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>8</td>
</tr>
</tbody>
</table>

**Correlation is significant at the 0.01 level (2-tailed).

4.9.4 Effect of dissolved O\_2 (DO) content

The correlation between DO content and As(III)/As(V) ratio is shown in Table 4.6. A strong negative correlation ($r = -0.838$) can be also observed between the two variables. This means as DO content increases As(V) becomes the predominant inorganic As species present in the water due to oxic conditions while As(III) becomes the predominant species at lower DO content levels. Other researchers have arrived at similar conclusions, due to As(III) predominates at anoxic conditions while As(V) predominates at oxic conditions (Omar et al., 2013, Hasegawa et al., 2010). However, this does not mean DO is the main constituent controlling the ratio between the As(III) and As(V), as other constituents or processes might be involved also (Baeyens et al., 2007). Based on results, As present in the Metapona River is predominantly in the oxidized As(V) form. DO content is also a factor that controls the speciation of inorganic As in water systems (Panagiotaras et al., 2012). DO content is highly dependent on temperature, salinity, biological processes and rate of transfer from the atmosphere (WHO, 2004, ANZECC, 2000). The 1992 ANZECC
guidelines have recommended that dissolved oxygen should be at 6 mg/L or 80 – 90% saturation (ANZECC, 1992), below which conditions may become stressful to many biological species (Koehn and O'Connor, 1990).

Table 4.6. Correlation relationship between DO content and As(III)/As(V) ratio (N= Number of samples, Sig. = Significance).

<table>
<thead>
<tr>
<th>DO Content</th>
<th>Pearson Correlation Sig. (2-tailed)</th>
<th>DO Content</th>
<th>As(III)/As(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)/</td>
<td>-0.838**</td>
<td>-0.838**</td>
<td></td>
</tr>
<tr>
<td>As(V)</td>
<td></td>
<td>0.009</td>
<td></td>
</tr>
</tbody>
</table>

**Correlation is significant at the 0.01 level (2-tailed).**

DO levels were present in relatively low levels in the Metapona River ranging from 6.1 – 6.61 mg/L for all the sites. According to Stumm and Morgan (1996), the DO content in water depends on the balance between the flux of bioavailable organic carbon and the rate at which heterotrophic bacteria uses up O₂ in decomposition. It also depends on the amount of O₂ diffused from the atmosphere and photosynthesis. The low DO in Metapona River was also further evidenced by the very little sightings of biological species such as fish in the river.

The concentrations of As(III), As(V) and total inorganic As vary for all the sites. Table 4.7 shows the Pearson’s correlation coefficient analysis results. These results show that positive correlations exist between As(III), As(V) and total inorganic As. A moderate positive correlation coefficient value of 0.632 can be seen between As(III) and total inorganic As. A weak positive correlation (r = 0.190) exists between As(III) and As(V) while a strong positive correlation coefficient (r = 0.920) is observed between As(V) and total inorganic As.
Table 4.7. Correlation coefficients between As(III), As(V) and total inorganic As for the Metapona sites (For each correlation, N = 24, Sig. = Significance).

<table>
<thead>
<tr>
<th></th>
<th>As(III)</th>
<th>As(V)</th>
<th>Total inorganic As</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td>Pearson Correlation</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As(V)</td>
<td>Pearson Correlation</td>
<td>0.277</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0.190</td>
<td></td>
</tr>
<tr>
<td>Total inorganic As</td>
<td>Pearson Correlation</td>
<td>0.632**</td>
<td>0.920**</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0.001</td>
<td>0.000</td>
</tr>
</tbody>
</table>

**Correlation is significant at the 0.01 level (2-tailed).**

4.9.5 Relationship of As in sediments and water

In sediments, the majority of minerals binding As (as both arsenite and arsenate) are metal oxides, particularly those of Fe, Al and Mn (De Vitre et al., 1991). This can be also due to the strong adsorption affinity of oxide/hydroxide minerals, especially Fe oxides/hydroxides, for As under oxidizing, neutral to mildly acidic conditions (Smedley and Kinniburgh, 2002, Casiot et al., 2009). The equation below shows the adsorption of As on to the surface of Fe oxides/hydroxides (Panagiotaras et al., 2012).

\[
\text{FeOH}^{+}(\text{aq}) + \text{As}^{3+}(\text{aq}) \rightarrow \text{FeOAs}^{2+}(\text{aq}) + \text{H}^{+}(\text{aq})
\]

The river systems downstream of Gold Ridge mine including Metapona have been influenced by increased loads of sediments and metals as a result of mining operations over the last 15 years (Albert et al., 2014). Substantial erosion and sedimentation are associated with high rainfall events that are typical of Guadalcanal where Gold Ridge mine is located. Analysis for inorganic As in these sediments carried out by Albert et al. (2014) showed As levels up to 25.2 mg/kg, which exceed the trigger level of 20 mg/L set by the Australian and New Zealand Guidelines for fresh and marine water quality (ANZECC, 2000). This is already indicative of a potential environmental problem for Metapona River. As is strongly adsorbed to the sediments (Smedley and Kinniburgh, 2002). However, dissolution or desorption of only a small amount of this
solid As can trigger high levels of inorganic As in the river water that can also cause a serious environmental issue (BGS and DPHE, 2001).

The inorganic As levels obtained in the present study are present at elevated levels. These high levels are consistent with similar finding in the Metapona river sediments in previous studies (Qopoto et al., 1994, Mining, 1998). It is strongly likely that the high levels of As in the Metapona River may be from the Gold Ridge mine.

4.10 As(III), As(V) and total inorganic As levels in Sabeto water samples

The following section discusses the concentrations of inorganic As at the five sites along the Sabeto River and Qalibua River. These sites are shown in the map in Figure 3.3. The results are tabulated in Table 4.3.

The Au mineralizations within the Sabeto area are collectively known as the Tuvatu deposit and has been characterized as a low sulphidation epithermal deposit similar to the Gold Ridge deposit (Wayne et al., 2010). This deposit is the second largest in Viti Levu and also in Fiji after the Emperor deposit in Vatukoula which is located about 50 km northeast from the Tuvatu deposit in Sabeto (Scherbarth and Spry, 2006). Mineralization in Tuvatu occurs as Au and Ag rich Tellurides and Vanadium minerals with inclusions of pyrites. It has been reported that As concentrations in pyrite determined secondary ion mass spectrometry (SIMS) range from 0.01 to 11.06 wt.% while Au and Te make up the (Spry et al., 2004). As exists primarily as arsenopyrite in the Tuvatu deposit (Naden and Henney, 1995).

4.10.1 Total inorganic As levels

The results in Table 4.3 show that site 1 which is located upstream of Sabeto River recorded the lowest total inorganic As concentration of 26.9 μg/L. This can be possibly due to dilution effects of the river. This site is located further away from Qalibua River which is the tributary along which the mine is located. Site 2 has the highest concentration (67.0 μg/L) of total inorganic As. This site is located close to
the entrance to the mine adit. A small stream runoff runs from the mine adit and into the Qalibua River. The sample was collected from this stream which is closest to the mine operations site. The high level of inorganic As at this site can be attributed to the weathering of exposed ores and waste rocks generated during the mining operations inside the mine.

Site 3 also has high levels of total inorganic As (63.7 μg/L). This site is located further upstream along the Qalibua River relative to the mine site and mine works. Therefore, mineralization around this area might be responsible for this high concentration. The Sabeto Mine and the surrounding region sit on a natural Au mineralized zone, Au mineralization is also known to be associated with high As levels. Therefore, the high inorganic As levels in site 3 could be largely due to the natural geology of the area.

Sites 4 and 5 are located downstream relative to the mine site where site 2 is located and are located further away from the mine site. The total inorganic As concentrations were 41.6 μg/L and 42.9 μg/L at sites 4 and 5, respectively. The fairly low total inorganic As levels at these sites (compared to sites 2 and 3) may be due to the decreasing proximity from the mine site and dilution effects of the Sabeto River.

The inorganic As levels obtained at the five sites are considerably high compared to the natural levels for freshwater systems and are consistent with those of other mining regions around the world (Drahota et al., 2009, Haffert and Craw, 2008). Similar studies have shown that total inorganic As levels are highest at sites close to the mine sites or Au mineralized zones (Grosbois et al., 2011, Haffert and Craw, 2008, Fletcher, 1998). This occurs particularly when the inorganic As source is the mine area. This shows that there is increasing likelihood that the high inorganic As levels in the Sabeto River are due to the anthropogenic input from the mining activities occurring at the upstream Qalibua River. This can be due to Au bearing As containing sulphide minerals which are the main components in the Au deposits in the Sabeto area. Several Au mineralizations occur within the Sabeto area, this may account for the high levels of inorganic As in all the five sites. The Au deposit located at the upper Qalibua–Sabeto area is an epithermal Au deposit (Wayne et al., 2010). High As anomalies are associated with this type of deposit (Bossy et al., 2012). Thus, it is also
possible that the elevated levels of total inorganic As reflects the geology of the locality. In addition, the exposure of ore deposits (which can be seen close to site 2) through drilling and excavations that have been continuing in the area can be a huge contributing factor to the high levels of total inorganic As around the area.

4.10.2 Inorganic As speciation

The relationship between As(III), As(V) and total inorganic As levels determined for each of the five sites at Sabeto River is shown in Figure 4.11.

The results show that As(III) levels are particularly high in Sabeto River. Sites 2, 3 and 4, with higher As(III) concentrations, have shown to exceed the trigger value of 24 μg/L (ANZECC, 2000) which indicates a potential environmental problem. Inorganic As levels at these three sites existed predominantly in the reduced form, As(III). High levels of arsenite at the Sabeto River sites indicate increased rates or occurrence of reduction of the inorganic arsenate species. Another contributing factor could be the desorption of As from Fe oxides, and the reductive dissolution of the oxides themselves (Smedley and Kinniburgh, 2002). The reduction of arsenates to arsenites is mostly common under reducing conditions such as low pH.

The concentrations then decrease away from the mine site in the same fashion as that of total inorganic As. The lowest arsenite concentration was found at site 1 (7.3 μg/L). This low concentration may be because this site does not drain the Au enriched Qalibua deposit. On the other hand, As(V) concentrations showed little variation for all the sites.
Figure 4.11. Relationship between As(III), As(V) and total inorganic As in Sabeto River water samples.

4.10.3 Pearson correlation studies

Correlation effect analysis (Table 4.8) shows that a weak negative correlation can be seen between As(V) and total inorganic As. However, the R value of 0.622 was determined to be statistically insignificant. This means that the actual relationship between As(V) and total inorganic As for the Sabeto River sites is not distinct. Similarly, a moderate negative correlation exists between As(V) and As(III). Sites 1 and 5 which are the two sites furthest from the mine site recorded the highest concentrations of As(V). Figure 4.11 further shows that As(V) was lowest at the mine site (site 2) followed by site 4 and then site 3.

As(III) concentrations at the Sabeto River sites show a strong positive correlation with total inorganic As levels (R = 0.920) as shown in Table 4.8. The highest concentrations of As(III) were found in site 2 which is at the mine adit.
Table 4.8. Correlation coefficient for As(III), As(V) and total inorganic As at each of the sites at Sabeto River. (For each correlation, N = 15).

<table>
<thead>
<tr>
<th></th>
<th>As(III)</th>
<th>As(V)</th>
<th>Total_inorganic As</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td>Pearson Correlation</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As(V)</td>
<td>Pearson Correlation</td>
<td>-0.515*</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0.050</td>
<td></td>
</tr>
<tr>
<td>Total_inorganic As</td>
<td>Pearson Correlation</td>
<td>0.920**</td>
<td>-0.139</td>
</tr>
<tr>
<td></td>
<td>Sig. (2-tailed)</td>
<td>0.000</td>
<td>0.622</td>
</tr>
</tbody>
</table>

*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).

4.10.4 Effect of dissolved O₂

The DO levels ranging from 7.3 - 8.84 mg/L (Table 4.3) in the Sabeto River suggest the river is well oxygenated for the five sites studied. This indicates that As(V) is likely to predominate over As(III) in the river water, since As(V) is the predominate species in oxic conditions, as mentioned earlier. However, the results showed that As(III) levels were actually higher than As(V). This shows that there might be other processes that are involved in the distribution of inorganic As in the Sabeto River. The predominance of As(III) over As(V) [with the As(III)/As(V) ratio as high as 10] in highly oxygenated surface waters has also been reported in a previous study by Seyler and Martin (1989). These authors concluded that there are other processes such as sorption, adsorption, precipitation, and biological mediation besides oxidizing versus reducing conditions playing a role in distributions of inorganic As in natural waters. Thus, the occurrence of higher levels of As(III) compared to As(V) in the well oxygenated Sabeto River suggests that oxidizing and reducing conditions play a minor role in the distribution of inorganic As. This argument is in agreement with the findings of previous researchers who have mentioned that there are many processes that control the distribution and speciation of inorganic As in natural waters (Smedley and Kinniburgh, 2002, Hasegawa et al., 2010). According to Moreno-Jiménez et al. (2010), while As(V) tends to be the more water soluble and predominant species in
natural waters, there is an increasing body of evidence that As(III) is more prevalent than often anticipated (Cheng et al., 2009). This is supported by the fact that there are many natural processes that can effectively scavenge As(V) from the water systems which may not be as effective for As(III) (Cheng et al., 2009). However, the predominance of As(III) over As(V) at sites 2, 3 and 4 could indicate that reduced As(III) is released from anoxic soils below the groundwater level and from stream sediments in the hyporheic zone (Drahota et al., 2009). This is evident on the fact that the Qalibua–Sabeto area is a mineralized area enriched with various minerals including arsenopyrite and pyrite (Pals and Spry, 2003). As(III) levels decreased while As(V) levels showed increase with increasing distances from the mine, this is because the As(III) is being oxidized to the more stable As(V) after being released into the water.

4.11 General discussion on Metapona and Sabeto results

Results of the speciation studies for the Sabeto samples show that As(III) levels were actually higher than As(V) at the 3 sites closest to the mine. Comparing the As levels from around Fiji (Mosley and Singh, 2003, Maata and Singh, 2008, Chand et al., 2011) with the levels at Sabeto River, total inorganic As in Sabeto River water is present in elevated levels. These high As levels may pose a threat to the environment and the inhabitants.

The current drinking water standard guideline for As set by WHO is 10 μg/L (WHO, 2004), particularly as total inorganic As and does not differentiate between arsenite and arsenate. Most studies on As determinations report As concentrations as inorganic As to relate to the health issues associated with it. The International Agency for Research on Cancer has concluded that there is sufficient evidence in humans that high levels of As is carcinogenic (IARC, 2004).

The results for Metapona and Sabeto Rivers show that the total inorganic As levels at these two areas were well above the WHO guideline value of 10 μg/L. Furthermore, the highest concentration of total inorganic As found for both Metapona and Sabeto samples was about seven times the guideline value set by WHO. The results also
show that concentration become elevated at sites closer to mine sites in the respective study areas. Also noteworthy is the fact that As(III) levels were found to be particularly high for both Metapona and Sabeto Rivers sampling locations which has been suspected to be toxic to humans.

While epidemiological studies show that elevated risks to cancer and other adverse health effects are not demonstrable at As concentrations around 10 μg/L (Mazumder et al., 1998, Baastrup et al., 2008, Celik et al., 2008, Chen et al., 2009, Smith and Steinmaus, 2009), it has been demonstrated that a range of adverse health effects may result at higher As level exposure (>50 μg/L or 100 μg/L) (Mazumder et al., 2009, Smith and Steinmaus, 2009). These include skin, lung and bladder cancer, skin lesions, diseases of the lung, liver and cardiovascular systems and diabetes. In Fiji and Solomon Islands, health complications due to consumption of drinking water with elevated levels of As have not been reported so far. Health complications due to drinking water with high levels of As are commonly reported however in India, Bangladesh or Asian rural areas (Alam, 2008, Rasul et al., 2002, Smith et al., 2000).

4.12 Conclusion

The aim of this study was to determine total inorganic As and also the inorganic speciation of As in water samples from two mining regions, in Solomon Islands and Fiji. A gold working electrode was successfully used for the detection and speciation of inorganic As in surface waters from Metapona River in the Solomons and Sabeto River in Viti Levu, Fiji. As(III) and total inorganic As were successfully detected using anodic stripping voltammetry. Inorganic As detection was carried out after a chemical reduction step with anhydrous Na₂SO₃. The results showed that total inorganic As and As(III) levels were particularly high in both Metapona and Sabeto rivers. For Metapona River total inorganic As concentrations ranged from 21.7 to 72.7 μg/L. Similarly, total inorganic As concentrations for Sabeto River ranged from 26.9 to 67 μg/L. The Total inorganic As levels exceeded the World Health Organization guideline value of 10 μg/L for water quality for all the sites studied. This demonstrates that the river water at the study sites is no longer safe for human
consumption due to the potential health risks associated with exposure to high concentrations of this toxic element particularly in the As(III) form. The elevated levels of As(III) in these two sites (Metapona and Sabeto Rivers) studied is a cause of concern. It is thus important to monitor their potential sources to manage their input into the river systems that are normally used by humans for various purposes so that concentrations do not reach toxic levels. Total inorganic As levels at both Metapona and Sabeto River were found to be at higher concentrations at sites closer to the mine site and decreased at increasing distances from the mine. Therefore, the increased levels of inorganic As in both Metapona River and Sabeto River were concluded to be from Gold Ridge mine and Sabeto mine respectively.
5.0 Introduction

One of the main challenges in analytical chemistry is the development of methods to perform rapid analysis and monitoring of analytes of interest outside the laboratory that are sensitive and accurate. Electrochemical sensors are ideally suited for these applications, due to their high sensitivity and selectivity, portable size, rapid response time and relatively low cost (Sekretaryova, 2014).

Nanotechnology, based on the design, synthesis, characterization, and application of materials and devices whose smallest functional organization in at least one dimension is on the nanometer scale is receiving increasingly great attention recently in the field of nanotechnology, biotechnology and bioanalytical chemistry (Agrawal and Prajapati, 2012). Electrodes of nanometer size dimensions have evoked growing interest due to their intrinsic characteristics, and whose development leads to various scientific applications including environmental protection (Ji et al., 2004, Ligler et al., 2003), food safety (Ligler et al., 2003), biotechnology (Chandra et al., 2013), medicine and physiology (Agrawal and Prajapati, 2012), and drug screening (Ho and Leclerc, 2004, Agrawal and Prajapati, 2012).

In combination with nanomaterials, recent development in electrochemistry have been significant and include great efforts that have been made in designing and fabricating chemically modified electrodes for various electrochemical applications (Liu and Huang, 2014, Chandra et al., 2013, Chen and Kucernak, 2002, Liu et al., 2010). Fabrication and characterization of nanoelectrodes continues to gain widespread and growing interest due to various novel applications of such ultrasmall devices and the unique electrochemistry involved at the interface between a single nanoelectrode and the electrolyte (Chen and Kucernak, 2002, Billon and Berg, 2004).

Metal nanoparticles (NPs) also offer discretely unique properties (enhanced mass transport, high surface area and improved signal to noise ratio) that can often be
advantageous in electroanalytical techniques (Campbell and Compton, 2010). In the last decade, the advent of gold nanoparticles (Au NPs) as a sensory element has provided a broad spectrum of innovative approaches for the detection of metal ions, small molecules, proteins, nucleic acids, malignant cells, etc. in a rapid and effective manner (Wilson, 2008, Saha et al., 2012). Electrodes modified with Au NPs can provide mechanistic information on electrochemical processes (Khairy et al., 2010a).

5.1 Detection on electrochemical platforms – voltammetry

5.1.1 Fast scan cyclic voltammetry

Fast scan cyclic voltammetry is one of the voltammetric techniques widely used for real time measurements of various analytes and for acquiring qualitative information about electrochemical reactions (Keithley et al., 2011, Robinson et al., 2003, Wang, 2006). This technique involves scanning the potential of a stationary working electrode linearly in an unstirred solution (Wang, 2006). The direction of the potential scan is reversed (at switch potential) at the end of the linear scan, usually stopping at the initial potential. The resulting current-potential plot is termed a cyclic voltammogram (Monk, 2001, Budai and Mészáros, 2010). The voltage limits are chosen such that the oxidation and reduction of the analyte of interest lies within the potential window. This technique allows for measurements in the millisecond (ms) time scale, however, the fast scan rates can often cause a large background charging current due to double layer charging at the electrode (Nguyen and Venton, 2015). This background current is stable over time and can be subtracted out from the blank signal (Zestos et al., 2014). The resultant cyclic voltammogram is the voltammogram of the analyte.

5.1.2 Modified electrodes

The working electrode is at the heart of electrochemistry and the most important component in an electrochemical cell. The performance of the voltammetric procedure is strongly influenced by the working electrode material. In any
voltammetric technique, the working electrode should provide a high signal to noise characteristics, as well as a reproducible response (Wang, 2006). Electrode modification provides an easy and simple method for the development of sensors suitable for various types of electrochemical sensing. Examples include, high catalytic activity towards electrooxidation of nitric oxide (NO) upon modification of nanostructured indium tin oxide (SnO₂) surface with Au NPs (Zhang and Oyama, 2005). Faster electron transfer rates also been reported as a result of modification of anthraquinone surface with Au NPs, which can be useful in the development of biosensors (Razzaq et al., 2014). Hydrogenated carbon surfaces have also shown to exhibit minimal fouling effect compared to conventional carbon surfaces when applied in vivo towards neurotransmitter detection (Chandra and Wong, 2009). Electrode modification techniques vary, however, most of these techniques are less time consuming, simple and inexpensive (Goyal and Bishnoi, 2012, Khairy et al., 2010b). A modern approach to electrode systems is the use of chemically modified electrodes in electrochemical analysis. Modification of electrode surfaces can thus meet the needs of many electroanalytical problems. The performance of modified electrodes has been found to be enhanced compared to other approaches involving solid, unmodified electrode surfaces that has been common in the past (Li et al., 2012). These performance attributes include higher selectivity, sensitivity, or stability on electrochemical devices and faster electron transfer kinetics. Thus, such surface development provides a pathway which generally form the basis for new analytical applications and different sensing devices (Wang, 2006). These analytical applications and improvements have extensively been reviewed in the literature (Wang, 2006, Fedorczyk et al., 2014, Campbell and Compton, 2010, Hanrahan et al., 2004). Various materials have been used for electrode modification for various electrochemical applications. These include organic and biological molecules, enzymes and conducting polymers, metal nanoparticles (Saha et al., 2012).

5.1.2.1 Au nanoparticle-modified electrodes

Au nanoparticles feature excellent conductivity, high surface area and catalytic properties making them excellent materials for electrochemical sensing (Saha et al.,
The Fabrication of electrodes with Au NPs can be done by electrodeposition (Gu et al., 2013, Zakharova et al., 2012), coating (Khairy et al., 2010b, Dai and Compton, 2006) and self assembly (Liu and Huang, 2014).

A significant volume of research attention has been devoted to the use of electroanalysis in sensitive and selective determinations of a wide variety of analytes in foods and the physical environments which includes the detection of toxic elements as well. The study of nanoscale materials has been increasing in recent years, particularly with respect to metallic NPs which is becoming one of the most active areas in environmental analysis. This is mainly due to unique capabilities such as high active surface area, increased mass transport, low detection limit, and better signal to noise ratio (Bernalte et al., 2012).

5.1.2.1.1 Characterization of modified electrode

Characterization of any modified electrode is important as it verifies the nature of the surface of the electrode as well as provides important information such as its functioning. There are various techniques that can be used for characterization of modified electrodes which include Scanning Electron Microscopy (SEM) which is one of the best tools for this purpose due to its excellent resolution (Gonzalez et al., 2006, Bernalte et al., 2012), Atomic Force Microscopy (AFM) (Dai et al., 2004), Transmission Electron Microscopy (TEM) (Xiao et al., 2008) and Cyclic Voltammetry (Bernalte et al., 2012, Dai et al., 2004, Xiao et al., 2008).

For instance, in the characterization of Au NPs on screen printed carbon electrodes, Bernalte et al. (2012) have reported using SEM, X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry. Quantitative analysis on the purity of the Au NPs was performed using XPS by the same authors. Using cyclic voltammetry, the group was able to show that Au NPs on screen printed electrode allow a potential window limited to the potential of Au oxidation (+800 mV) and the potential of hydrogen reduction (-100 mV).
Characterization of Au NPs deposition on glassy carbon was carried out by Dai et al (2004). The group used AFM which involves scanning the surfaces of the bare glassy carbon and the Au NPs modified glassy carbon electrode. Using this technique, the group was able to view the images of Au NPs being deposited on the glassy carbon electrode using different experimental conditions. Based on this, and the voltammograms from cyclic voltammogram characterization, they were able to identify the optimum experimental conditions that can get as many Au NPs deposited as possible while avoiding the formation of a continuous gold film. The optimum conditions determined for Au NPs deposition was 15 s deposition time using 0.1 mM AuCl₄⁻ in 0.5 M H₂SO₄. Cyclic voltammetry profiles of the electrodes under various formation conditions were next recorded to get the surface information about the electrodeposited Au NPs on the glassy carbon. Based on these, the real surface area of the Au NPs loading on the glassy carbon was estimated to be 7.4 × 10⁻³ cm².

The [Fe(CN)₆]³⁻/⁴⁻ and [Ru(NH₃)₆]³⁺/²⁺ redox systems are two known redox markers that have been used by numerous authors for characterization of electrodes by cyclic voltammetry (Chen and Kucernak, 2002, Wang et al., 2005, Chandra et al., 2013, Gao et al., 2013). [Ru(NH₃)₆]³⁺/²⁺ helps identify functionality as it is insensitive to the electrode surface. [Fe(CN)₆]³⁻/⁴⁻ on the other hand, helps identify electrode surface kinetics, particularly prior to and following modification. The sigmoidal shaped voltammograms obtained is associated with the physically small size of these electrodes. In addition, the presence or absence of gaps between the forward and the reverse scans in the sigmoidal voltamograms gives an indication of the integrity of the electrode seal. Furthermore, characterization using these redox markers before and after modification makes it possible to determine the reversibility of the redox process at the electrodes, in these markers.

Electrode conditioning or activation is an important step to carry out before actually performing the analytical experiments to activate the electrode surface (Oesch and Janata, 1983). This prepares the electrode surface for analysis. For Au NPs modified electrodes this is usually done by cycling several times in H₂SO₄ until a stable cyclic voltammogram is obtained (Salaun et al., 2007, Dai et al., 2004, Giacomino et al., 2011).
5.1.3 Physically small electrodes

Miniaturization is a growing trend in the field of analytical chemistry particularly for the obvious practical advantages that it offers. Particularly for microelectrodes, these include; enhanced mass transfer rates and decreased ohmic drop (Kokkinos et al., 2012). These characteristics result in greater sensitivity, improved response time and increased signal to noise ratio in analytical applications.

This has also created some fundamentally new possibilities (Ramamoorthy et al., 2003), such as detection of analytes at very low levels (Billon and Berg, 2004) and as sensing devices in human brain for medical purposes (Fofonoff et al., 2004, Patrick, 2010). Such dimensions offer obvious analytical advantages, including the exploration of microscopic domains, measurements of local concentration profiles, detection in microflow systems, and analysis of very small (microliter) sample volumes (Wang, 2006).

Billon and Berg (2004) have developed micro-wire electrodes from Au and Ag wires with diameter of 25 μm and length of 3 – 21 mm. The Au electrodes were coated with Hg before use, while the Ag wires were used without coating. The group performed comparative measurements between the micro-wire electrodes and macro-disk electrodes. From the analysis they found that the micro-wire electrodes demonstrated higher sensitivity and a much (10 – 100×) lower detection limit, than micro-disk electrodes. Using a Au micro-electrode of 21 mm length and a deposition time of 300 s the limit of detection was 0.07 nM in seawater of natural pH, compared to a limit of detection of 10 nM Pb (more than 100× greater) using a Au micro-disk electrode of the same diameter. Using the Ag micro-wire electrode the limit of detection was improved by a factor of 10 in the analysis of Pb in acidified seawater. This shows the potential that micro-electrodes can lead to successful in situ detection of metals in natural waters due to improved sensitivity.
Physically small carbon electrodes have been developed by various methods reported in the literature. Chen and Kucernak (2002) have developed a method for producing insulated nanometer-sized carbon electrodes by electrochemical etching of carbon fibers. Repeated deposition of electrophoretic paint through cyclic voltammetry at these electrodes was then undertaken, followed by heat application to expose the tip of the electrode and also to effectively control the size of nanoelectrodes. The effective radius of electrodes developed in this manner was estimated to be 1 nM.

Wang et al. (2005) have also reported developing nanometer-sized carbon electrodes using the same method described above. The effective radius of the nanoelectrodes prepared ranged from tens to hundreds of nanometers. The fabricated electrodes showed ideal steady-state voltammetric behavior from which the effective areas of nanoelectrodes were determined. As the current approached the steady state behavior, a sigmoidal shaped voltammogram was observed.

Similarly, physically small carbon electrodes have been developed by Chandra et al. (2013). The group fabricated conical-tip carbon electrodes from pulled quartz capillary tubes by thermally pyrolysing acetylene gas at the tip and on the shank of the electrodes. The average radius of these electrodes was estimated to be 2.1 μm with an average axial length 0.1 μm (Britz et al., 2010). The electrodes were successfully used in the detection of dopamine after being modified with p-phenylacetate and demonstrated to show similarity in performance to bare carbon electrodes as 541 pM and 543 pM limits of detection, respectively and 16 pA/nM and 19 pA/nM sensitivity correspondingly.

The aim of this study was to develop and evaluate physically small carbon electrodes modified with Au NPs by electrochemical means. The modified electrodes developed in this study were then applied for the detection of As(III) in environmental water samples. Their performance towards As(III) detection using ASV were evaluated and compared with that of Au electrode. The electrodes were prepared and developed by thermally pyrolysing acetylene gas in and on the shank of quartz capillary already pulled down to a fine tip. Following pyrolysis, the electrodes were modified by
depositing Au NPs on the electrode surface. The modified electrodes were applied towards As(III) detection using ASV. This chapter presents a thorough method for the development, characterization and performance evaluation of the modified electrodes.

5.2 Experimental

5.2.1 Reagents

All reagents and chemicals used were of analytical grade and used without further purification. Preparation of all solutions was carried out using ultrapure (Mill-Q) water with resistivity of not less than 18 MΩ.cm. HCl and H2SO4 acids, KCl, K3[Fe(CN)]6, AuCl3.3H2O and graphite powder were purchased from Sigma Aldrich (USA). [Ru(NH3)6]Cl3 was sourced from Stremm Chemicals (Newport, USA) and Ultra high purity acetylene and nitrogen gases were purchased from BOC gases (Fiji). All redox solutions and supporting electrolytes were prepared daily and purged with nitrogen gas for 5 min prior to analysis.

5.2.2 Instrumentation and apparatus

A model P-2000 Sutter Puller (Sutter instrument Co.) was used to pull quartz capillaries to a fine tapered end, the size specifications of the quartz capillary are: 1 mm outside diameter, 0.5 mm inside diameter and 75 mm length. The electrochemical measurements involving cyclic voltammetry were carried out using a dual picostat that is capable of measuring very small currents in the range (2 pA – 10 μA eDAQ Pty Ltd., Sydney, Australia). This picostat was operated using an EChem version 2.1.5 software on a PC via an E-corder interface (eDAQ Pty Ltd.). The electrochemical analyses were carried out using a 50 mL three electrode glass cell consisting of a Ag/AgCl electrode as reference and a platinum wire as counter electrode. All measurements were performed in a Faraday cage at room temperature (25°C) within 3 h of sealing the electrodes.
5.2.3 Fabrication of conical tip carbon electrodes

Quartz capillaries (1 mm outside diameter, 0.5 mm inside diameter and 75 mm length, Sutter Instruments, Novato, CA) were pulled to a fine tip using a model P-2000 Sutter puller. This instrument is equipped with various parameters that control the heating and the pulling processes in the micropipette puller. These parameters are heat, filament, velocity, delay and pull. The procedure for the fabrication of the small carbon electrodes was adapted from that reported by Chandra et al. (2013). Electrodes of relatively low taper length and high diameter tip were required in this study which enabled the generation of electrodes of negligible resistance. Because of the low taper length, electrodes generated were physically more robust, this allowed the electrode to be used in smaller environments without causing damage to the tip. Once pulled, the capillary was left inside the puller to cool for a period of 20 - 30 s before it was taken out for further usage and to allow for the next capillary to be pulled. The pulled capillaries were then brought to the pyrolysis assembly set up and acetylene gas was used to thermally pyrolyse carbon in and on the shank of the capillaries. Bunsen flame was used as the heat source. All the gas tubings used in the pyrolysis assembly involved stainless steel and rubber. Copper containing components were not used in this set up as the formation of copper acetylide upon contact with acetylene gas is imminent which is explosive (Chandra et al., 2013).

During pyrolysis, the pulled quartz capillary was housed in a quartz NMR tube with internal diameter of 5 cm and 7 cm length and with both ends hollow. One end of the quartz NMR tube was firmly placed against the opening of the tee-piece. The quartz capillary was then allowed to protrude horizontally into the small opening of the tee-piece where it meets the oncoming rubber on the other side of the tee-piece which supplies the acetylene gas. The outer diameter of the rubber tubing was slightly larger than the inner diameter of the pulled capillary, this ensured a gas tight seal when the capillary was fitted into the rubber tubing. The other end of the quartz NMR tube was connected to a nitrogen gas tube that counter flows the direction of the acetylene gas flow. In the quartz NMR tube, the capillary sits horizontally with its base on the tee-piece while the pulled end of the capillary faces the incoming N\textsubscript{2} flow without touching the sides of the NMR tube to avoid damage to the tip. N\textsubscript{2} gas (60 mL/min
flow rate) counter flows acetylene gas (50 kPa pressure) which allowed the acetylene gas to be blown backward as it effused from the pulled capillary tip. This enabled acetylene to be pyrolysed depositing carbon at the tip and on the shank of the capillary. When heating the quartz NMR tube with the capillary housed inside, it was necessary to start heating the far end of the NMR quartz tube away from the tip at the beginning of the pyrolysis, and then slowly moving towards the region housing the capillary tip. This was to avoid thermal shock to the capillary which could lead to tip fracture. The pyrolysis time was 2 ½ minutes, time monitoring was started after the capillary tip started to glow red when thermally heated. Following pyrolysis, the capillary was left to cool for at least 20 sec before being carefully removed from the assembly and rinsed with distilled water to remove any possible carbon particles that may have adhered to the tip during pyrolysis. The pyrolysis set up is shown in Figure 5.1.

![Figure 5.1. Pyrolysis set up for fabrication of conical tip carbon electrodes.](image)

Graphite powder was then packed into the larger opening of the capillary tube. Following the packing with graphite, a thin conducting wire was then inserted into the capillary. The wire also allowed the packed graphite to be pushed to the tip, with the other end protruding out of the capillary opening for electrical connections. The wire
was then sealed with epoxy and left to dry out for at least 2 hours before commencing with electrochemical analyses. Figure 5.2 illustrates an electrode fabricated in this manner.

![Diagram of a fabricated carbon electrode]

**Figure 5.2.** Schematic depiction of a fabricated carbon electrode.

### 5.2.4 Electrochemical detection

After fabrication of the electrodes, the electrodes were characterized in known redox markers to determine the success of fabrication. To perform this, cyclic voltammetry of 1.0 mM solution of $[\text{Ru(NH}_3)_6]^{3+}$ in 1.0 M KCl as supporting electrolyte was carried out. Electrodes demonstrated to be functioning showed sigmoidal shaped behavior and without gaps which arise from a well-sealed small electrode. These were further characterized in 1.0 mM $[\text{Fe(CN)}_6]^{3-}$ in 1.0 M KCl. Prior to analysis, all the solutions were purged with N$_2$ gas to remove O$_2$ as being electroactive it can affect the electrochemical process.

### 5.2.5 Determination of electrode radius

The procedure for the determination of electrode dimensions was adapted from that reported by Chandra et al. (2013) in which chronoamperometry was employed for these determinations. This involves ramping a pulse on a resting potential applied to the working electrode in a redox system. The pulse applied should be beyond the
oxidation/reduction potential of the redox system which cause a change in the redox status of the species. \([\text{Ru(NH}_3\text{)}_6]^{3+/2+}\) redox system was used in this study, prior to chronoamperometric experiments, the reduction potential was determined by cyclic voltammetry. Based on this, a pulse of -600 mV was applied for 5.0 s to the electrode at a resting potential of 400 mV in a solution of 1.0 mM \([\text{Ru(NH}_3\text{)}_6]^{3+}\) in 1.0 KCl. The decaying current was then measured as a function of time, and using the Cottrell equation, the electrode tip radius was determined. The equation is as shown below and is further explained in section 5.3.3 where \(n\) = Number of electrons transferred, \(F\) =Faraday constant (96,485 C/mol), \(A\) = Electrochemical area (cm\(^2\)), \(D\) = Diffusion coefficient \((5.3 \times 10^{-6} \text{ cm}^2/\text{s})\), \(C\) = Concentration of redox species (mol/cm\(^3\)) and \(r\) = electrode radius (cm).

\[
i = \frac{nFADC}{r} \left[ 0.5 + \frac{r}{\sqrt{\pi Dt}} \right]
\]

5.2.6 Deposition of Au nanoparticles

Electrochemical deposition of Au NPs at the tip and on the shank of the carbon electrodes was carried out by chronoamperometry of 1.0 mM AuCl\(_4^-\) in 0.1 M HCl. In the chronoamperometry experiment, a pulse of -100 mV (from 100 to 0 mV) was applied for 5 s. The electrodes were then rinsed with distilled deionized water and stored for analysis.
5.3 Results and discussion

5.3.1 Characterization of physically small carbon electrodes in known redox markers

5.3.1.1 Characterization in $[\text{Ru(NH}_3\text{)}_6]^{3+/2+}$ redox system

Electrodes were fabricated in the manner as described in section 5.2.3. After fabrication, the electrodes were characterized using the $[\text{Ru(NH}_3\text{)}_6]^{3+/2+}$ redox system which is based on the reduction of $[\text{Ru(NH}_3\text{)}_6]^{3+}$ to $[\text{Ru(NH}_3\text{)}_6]^{2+}$.

$$[\text{Ru(NH}_3\text{)}_6]^{3+} + e^- \rightarrow [\text{Ru(NH}_3\text{)}_6]^{2+}$$

This is an outer sphere redox system which is insensitive to surface modifications or surface functional groups but only to the electronic structure of the carbon (Chen and McCreery, 1996, Davies et al., 2004). The resultant cyclic voltammograms obtained at a physically small carbon electrode before and after modification using $[\text{Ru(NH}_3\text{)}_6]^{3+}$ are shown in Figure 5.3. The voltammograms were obtained by cyclic scanning from +400 to -400 mV and return. For each voltammogram, as the potential was initially scanned from +400 mV, $[\text{Ru(NH}_3\text{)}_6]^{3+}$ started diffusing towards the surface of the electrode and then eventually gets reduced. This reduction generated a rapid increase in reduction current which can be observed between 300 V and 100 mV in the voltammograms in Figure 5.3. The scan was then switched at -400 mV. From -400 to +100 mV, $[\text{Ru(NH}_3\text{)}_6]^{2+}$ was present in the bulk solution which was then oxidized to $[\text{Ru(NH}_3\text{)}_6]^{3+}$ resulting in the oxidation current between 100 to 300 mV. The current plateau observed between 300 to 400 mV arises due to maximum diffusion of molecules to the electrode surface. For functioning electrodes, two features were observed as can be seen in Figure 5.3. These are sigmoidal shaped voltammogram arising from both linear and nonlinear diffusion around the electrode which is characteristic of a physically small electrode with a small surface area. The absence of gap in the voltammogram between the forward and the reverse scans suggests a well-sealed electrode (Zoski, 2002). Sigmoidal-shaped voltammogram corresponds to current limited by the rate of diffusion of analyte molecules to the electrode surface (Monk, 2001). Figure 5.3 shows that the shape of the
voltammogram remained sigmoidal after Au NPs deposition. This indicates that the features of the microelectrode were maintained after the deposition of Au NPs. The limiting current was observed to increase by 68% (with a standard deviation of 24%) at the Au NPs deposited electrode compared to the bare carbon electrode (N = 5). The increase in limiting current is attributed to the increase in surface area upon modification (Jia et al., 2007).

Figure 5.3. Cyclic voltammetry of 1.0 mM [Ru(NH₃)₆]³⁺ in 1.0 M KCl before (dashed line) and after (solid line) deposition of Au NPs. Scan rate: 100 mV/s.

5.3.1.2 Characterization in [Fe(CN)₆]³⁻/⁴⁻ redox system

Electrodes with voltammogram that showed sigmoidal shape behavior in [Ru(NH₃)₆]³⁺ were further characterized in 1.0 mM [Fe(CN)₆]³⁻ by cyclic voltammetry. This reaction is based on the reduction of [Fe(CN)₆]³⁻ to [Fe(CN)₆]⁴⁻ as
shown below where the scanning parameters were the same as that using 1.0 mM [Ru(NH₃)₆]³⁺.

\[
[\text{Fe(CN)}₆]^{3-} + e^- \rightarrow [\text{Fe(CN)}₆]^{4-}
\]

Figure 5.4 shows the voltammetric signal of 1.0 mM [Fe(CN)₆]³⁻ in 1.0 M KCl before and after deposition of Au NPs. The limiting current was observed to increase by 75% (with a standard deviation of 16%) at the Au NPs deposited electrode compared to the bare carbon electrode (N = 5).

**Figure 5.4.** Cyclic voltammetry of 1.0 mM [Fe(CN)₆]³⁻ in 1.0 M KCl before and after deposition of Au NPs with scan rate: 100 mV/s.

In both [Ru(NH₃)₆]³⁺ and [Fe(CN)₆]³⁻ redox markers (Figure 5.3 and Figure 5.4), the diffusion current increased after the deposition of Au NPs which is due to the increased surface area upon the deposition of Au NPs (Dai et al., 2004, Jia et al., 2007). This increased surface area results in the increased electrochemical activity observed. It has been reported that Au NPs modified electrodes can be considered as behaving as random arrays of microelectrodes (Zakharova et al., 2012). It provides advantages with the enhanced mass transfer, efficient catalysis, large surface area and
controllable microenvironment (Khairy et al., 2010a). Au has large degree of compatibility with various electrode surfaces. Its photosensitive visual uniqueness has proven to be useful tool in various industrial and medicinal applications (Budai and Mészáros, 2010, Saha et al., 2012). These properties enable the Au NPs to be coupled onto the electrode surface (Sivanesan and John, 2009).

Microelectrodes demonstrate several attractive and important properties that have expanded the possibilities of electrochemistry. The current responses from these small electrodes are very small, this makes it possible to work in highly resistive solutions that would develop small ohmic ($iR$) drop (Bruckenstein, 1987, Barnes et al., 2013). The decreased ohmic distortions allow electrochemical measurements to be performed on new and unique chemical environment (which are not amenable to macroscopic electrodes) (Wang, 2006). Due to their small area, these electrodes demonstrated to greatly reduce double layer capacitance. This allows high speed voltammetric experiments to be performed at millisecond (and even lower) timescale and hence to probe the kinetics of very fast electron transfer and coupling chemical reactions (Budai and Mészáros, 2010).

### 5.3.2 Waveslope and halfwave potential

The electrochemical behavior of electrodes including diffusion at the electrode solution interface depends on electrode dimensions and the diffusion layer. The total diffusion limited current ($i_{total}$) is composed of the planar ($i_{planar}$) and radial ($i_{radial}$) components as shown in the following equation (Wang, 2006).

$$i_{total} = i_{planar} + i_{radial}$$

For both planar and radial components, the relationship between electrode dimensions and the diffusion layer can be expressed by the dimensionless parameter $Dt/r_0^2$ where $D =$ diffusion coefficient, $t =$ electrolysis time and $r_0 =$ smallest dimension of the electrode.

Radial diffusion dominates at large ($>1$) $Dt/r_0^2$ values which corresponds to when the diffusion layer exceeds the electrode size. Voltammetric cycling under this
condition shows that the current approaching steady state and a sigmoidal voltammogram results. This situation can be observed with microelectrodes such as the ones developed in this study.

In contrast, when the electrode size exceeds the diffusion layer \((D t/r_0^2 < 1)\), planar diffusion dominates. This mostly occurs in redox analyses involving macro-sized electrodes. Under this condition a peak shaped behavior is observed for the voltammogram. From the separation in potentials between the oxidation and the reduction peaks, the reversibility of the redox system can be calculated. A peak separation value of 59/n mV corresponds to a reversible system (Wang, 2006).

In microelectrodes with sigmoidal shaped voltammograms, the reversibility of the redox system could not be determined in the same manner as described above due to the absence of redox peaks. The reversibility was determined however, from the waveslope obtained from the plot of potential \((E)\) vs \(\log_{10}[(i_{\text{lim}} - i)/i]\) which is derived from the equation as shown below where \(i\) denotes current and \(i_{\text{lim}}\) the limiting current on the voltammogram.

\[
E = E_{1/2}^1 + \frac{0.059}{n} \log_{10} \left( \frac{i_{\text{lim}} - i}{i} \right)
\]

The plot yields a linear relationship with the slope corresponding to the waveslope and the intercept on the potential axis gives the halfwave potential \((E_{1/2})\). The results of the waveslope and \(E_{1/2}\) measurements at the electrodes before and after deposition of Au NPs for \([\text{Fe(CN)}_6]^{3+/4-}\) and \([\text{Ru(NH}_3)_6]^{3+/2+}\) redox systems are summarized in Table 5.1.
Table 5.1. Waveslope and $E_{1/2}$ of electrodes in $[\text{Ru(NH}_3)_6]^{3+}$ and $[\text{Fe(CN)}_6]^{3-}$ redox media before and after deposition of Au NPs.

<table>
<thead>
<tr>
<th>Redox system</th>
<th>Waveslope/ mV/decade</th>
<th>N</th>
<th>Half wave potential ($E_{1/2}$/mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru(NH}_3)_6]^{3+}$ Before deposition</td>
<td>143.5 ± 14.2</td>
<td>5</td>
<td>214.0 ± 5.5</td>
</tr>
<tr>
<td>After deposition</td>
<td>72.4 ± 9.2</td>
<td>5</td>
<td>224.5 ± 16.2</td>
</tr>
<tr>
<td>$[\text{Fe(CN)}_6]^{3-}$ Before deposition</td>
<td>198.1 ± 68.5</td>
<td>5</td>
<td>-149.0 ± 60.7</td>
</tr>
<tr>
<td>After deposition</td>
<td>124.8 ± 41.6</td>
<td>5</td>
<td>75.5 ± 54.9</td>
</tr>
</tbody>
</table>

The waveslope and $E_{1/2}$ determined in this study are shown in Table 5.1. For a reversible reaction at the surface of the electrode, the waveslope value is $59/n$ mV/decade. Results in Table 5.1 show that the waveslope before modification in $[\text{Ru(NH}_3)_6]^{3+}$ is 143.5 mV/decade and 198.1 mV/decade in $[\text{Fe(CN)}_6]^{3-}$. Based on this, it is assumed that the electrodes developed in this study showed irreversible behavior in both redox systems. The electron transfer reactivity of carbon electrodes on electrode surface in both $[\text{Fe(CN)}_6]^{3-}$ and $[\text{Ru(NH}_3)_6]^{3+}$ has been discussed by previous researchers in the literature (Cline et al., 1994, Ji et al., 2006, Banks and Compton, 2006). The redox couple $[\text{Ru(NH}_3)_6]^{3+}$, is known to be insensitive to surface structures (Chen and McCreery, 1996). However, the bare carbon electrode displayed an irreversible behavior in this redox couple and then a slight shift towards a reversible behavior after modification. Upon modification, despite the deposition of Au NPs on the carbon surface, much of the carbon surface is also left exposed that is not covered by the NPs. The $[\text{Ru(NH}_3)_6]^{3+}$ redox couple will still be insensitive to this exposed carbon surface. Therefore, the shift in reversibility is likely due to the
altered kinetics caused by the deposited Au NPs. $[\text{Fe(CN)}_6]^{3-}$, on the other hand is very sensitive to surface structures, which is likely to be responsible for its irreversible behavior. After modification with Au NPs the waveslope decreased in both redox markers. A decrease of 49.5% was observed in $[\text{Ru(NH}_3)_6]^{3+}$ while in $[\text{Fe(CN)}_6]^{3-}$ the decrease was 37%. These demonstrated that the irreversible behaviour decreases in both redox markers after modification with Au NPs.

In carbon surfaces, the basal plane is the surface layer that lies parallel to the graphite surface while the edge plane is the layer that lies perpendicular to the graphite layer (Banks and Compton, 2006). Due to the nature of the chemical bonding in graphite, the two planes exhibit completely different electrochemical properties. Edge planes show considerably faster electron kinetics than basal planes for a range of redox couples (Davies et al., 2004). The low reactivity of the basal planes can be attributed to its low density of electronic states and to the lack of functional groups and adsorption sites (Chen and McCreery, 1996). This means an electrode with more edge planes will show a nearly reversible voltammogram while an electrode consisting mainly of basal planes will display irreversible voltammogram depending highly on the amount of edge present (Banks and Compton, 2006). Since both $[\text{Ru(NH}_3)_6]^{3+}$ and $[\text{Fe(CN)}_6]^{3-}$ redox systems displayed irreversible behavior, it was assumed that the electrodes developed in this study consist mainly of basal plane on the surface. Upon modification with Au NPs, the density of electronic states at the electrode surface increases. The increase in electronic states is expected to result in faster electron transfer and adsorption for a range of redox couples (Chen and McCreery, 1996). During the electrodeposition step, Au NPs were generated by a nucleation and growth process on the carbon surface and were dispersed on the surface of the bare carbon electrode (Finot et al., 1999, Xiao et al., 2008). This alters the electrode surface to some extent while much of the carbon surface is still left. As a result, there is increasing likelihood that some of the basal and edge planes were also covered with the Au NPs. This means that the electrodeposited Au NPs were likely responsible for the improvement in the reversible behavior after modification in both redox markers.

The $E_{1/2}$ determined in $[\text{Ru(NH}_3)_6]^{3+}$ and $[\text{Fe(CN)}_6]^{3-}$ were found to be 214.0 mV and -149.0 mV respectively. A slight increase of 4.9% in $E_{1/2}$ was observed in
[Ru(NH₃)₆]³⁺ after modification with Au NPs. However, in [Fe(CN)₆]³⁻, the $E_{1/2}$ showed a dramatic decrease of 150.7%. Based on a 49.5% decrease in waveslope and a 4.9% increase in $E_{1/2}$, the Au NPs appeared to show some effects on the electrochemical reversibility of [Ru(NH₃)₆]³⁺ reduction at the Au NPs modified electrode relative to the bare carbon electrodes. On the other hand, the 37% decrease in waveslope and 150.7% decrease in $E_{1/2}$ exhibit a larger effect on the electrochemical reversibility of [Fe(CN)₆]³⁻ reduction at the Au NPs modified electrode relative to the bare carbon electrodes. The $E_{1/2}$ shifts observed for the modified electrodes show that the electrode surfaces were altered upon the deposition of Au NPs.

### 5.3.3 Determination of electrode radius

Determination of electrode radius (for electrodes demonstrated to be functioning) was carried out experimentally by chronoamperometry and then estimated using the Cottrell equation. This is based on the assumption that the geometry of the electrode tip is cylindrical, consisting of a carbon disc at the tip and a carbon film on the shank. For cylindrical electrode geometry, the faradaic current of a redox species, $i$, under a constant potential can be expressed as follows where $n =$ Number of electrons transferred, $F =$ Faraday constant (96,485 C/mol), $A =$ Electrochemical area (cm²), $D =$ Diffusion coefficient (5.3 x 10⁻⁶ cm²/s), $C =$ Concentration of redox species (mol/cm³) and $r =$ radius of electrode (cm).

$$i = \frac{nFADC}{r} \left[ 0.5 + \frac{r}{\sqrt{\pi Dr}} \right]$$

A plot of $i$ versus $1/\sqrt{t}$ yields a straight line with both the slope and intercept used to estimate $A$ and $r$ (Britz et al., 2010). Chronoamperometry of 1.0 mM [Ru(NH₃)₆]³⁺ was conducted at a carbon electrode in 1.0 M supporting electrolyte. Figure 5.3 depicts the cyclic voltammograms of 1.0 mM [Ru(NH₃)₆]³⁺ in 1.0 M KCl before and after modification. Based on this, a resting potential of 400 mV was selected and a pulse of -600 mV was applied in the chronoamperometric experiment. The resulting
chronoamperogram is shown in Figure 5.5. The limiting current that is the subject of the modified Cottrell equation is obtained from the chronoamperometric experiment and substituted into the Cottrell equation to estimate \( r \). Using this approach, the current between 0 and 0.5 s in the chronoamperogram was selected and substituted into the Cottrell equation and \( r \) was estimated to be 6.9 \( \mu \)m with 2 \( \mu \)m standard deviation (\( N = 6 \)).

\[ \text{Figure 5.5. Current vs time chronoamperogram of 1.0 mM } [\text{Ru(NH}_3)_6]^{3+} \text{ in 1.0 M KCl at a carbon electrode.} \]

**5.3.4 Au nanoparticle deposition**

Deposition of Au NPs was performed using chronoamperometry. Potential was ramped from 100 to 0 mV for duration of 5.0 s. This potential range was chosen as the reduction potential of Au(III) to Au(0) lies within this potential range (Finot et al., 1999, Dai et al., 2004).
Before the potential was stepped from 1000 mV, the electrode was surrounded by only Au(III) ions, the concentration of which was same throughout the solution. When the potential was stepped to 0 mV, the Au(III) ions reduced to Au(0) and were deposited on the surface of the electrode, according to the reaction as shown below (Gotti et al., 2014).

\[
\text{AuCl}_4^{-} + 3e^- \rightarrow \text{Au} + 4\text{Cl}^{-}
\]

The potential step results in the rapid increase in current at 0 s observed in the chronoamperogram in Figure 5.6 which is attributed to the charging of the double layer (Finot et al., 1999). This is the region in the solution where the electrode is surrounded by the analytes (Monk, 2001). A current decay is then observed indicating a diffusion regime. This develops due to the overlap of hemispherical diffusion layers which initially provide mass transport for nanocrystal growth (Finot et al., 1999). A change in background current was also observed in the chronoamperogram when the potential step was applied. This indicates that the electrode surface has been modified to some extent resulting in altered kinetics on the electrode surface.
Figure 5.6. Current responses to a potential step from 1000 mV to 0 mV for a carbon microelectrode in 1.0 mM AuCl$_4^-$ in 0.1 M HCl.

5.3.5 As(III) detection

The modified electrodes were applied on the detection of As(III) in both As(III) standards and real water samples using ASV and deposition at -344 mV. The method of standard addition was used to detect As(III) in real water samples. However, the results showed that the modified electrodes were unable to detect As(III).

Using As(III) standards, the modified electrodes were unable to detect As(III) at concentrations from 0.01 μg/L to 1 mg/L at deposition times of 60 s, 120 s and 180 s. Supporting electrolytes of 0.1 M and 1.0 M HCl were used. As(III) detection was unsuccessful in both supporting electrolytes.
Physically small carbon electrodes (radii < 10 μm) were fabricated in this study by thermally pyrolysing acetylene gas in and on the shank of pulled quartz capillaries. The bare carbon electrodes were modified by deposition of Au NPs on the electrode surface. The electrodes were characterized in $[\text{Ru(NH}_3)_6]^{3+}$ and $[\text{Fe(CN)}_6]^{3-}$ redox markers to determine their performance before and after modification. Electrochemical analysis of the electrodes showed that they consist mainly of basal planes at the surface.

When characterized in $[\text{Ru(NH}_3)_6]^{3+}$ and $[\text{Fe(CN)}_6]^{3-}$, the electrodes displayed increase in limiting currents, 75% increase in $[\text{Fe(CN)}_6]^{3-}$ and 68% in $[\text{Ru(NH}_3)_6]^{3+}$. This is attributed to the increase in surface area upon modification. The electrodes developed in this study showed irreversible behavior in both redox systems.

The modified electrodes were applied on the detection of As(III) in As(III) standards and real water samples. However, As(III) stripping peaks were observed in only one modified electrode under the experimental conditions used in the analyses when detection was carried out in As(III) standards. When applied towards As(III) detection in real water samples, the electrodes were unable to detect As(III). This shows that further investigation need be carried out to evaluate the performance of these electrodes towards As(III) detection in both standards and real water samples.
CHAPTER 6

GENERAL DISCUSSION, CONCLUSION AND FUTURE DIRECTIONS

6.0 General conclusion

The detection of inorganic As in the environment is an active area of research owing to the toxicity of As(III). The primary goal of this research was to use existing instrumentation and also to develop methodologies for the measurement of inorganic As in river water samples.

Voltammetric speciation of inorganic As in Metapona River and Sabeto River was successfully carried out in this study using the Au working electrode. The ASV method carried out for the speciation of inorganic As proved to be simple, sensitive and selective and allows rapid detections and determination of inorganic As in real water samples. The method is suitable for the detection and determination of the levels of As(III), As(V) and total inorganic As in river water samples.

As(III), As(V) and total inorganic As were determined to exist in elevated levels in both river systems studied. The high levels of inorganic As in this waters could be attributed to the mining activities occurring in these areas.

Small carbon electrodes were also fabricated in this study by pyrolysis of acetylene gas in and on the shank of pulled quartz capillaries and then modified with Au NPs. The performance of the electrodes before and after modification were evaluated by characterization in $\text{[Ru(NH}_3\text{)}_6\text{]}^{3+}$ and $\text{[Fe(CN)}_6\text{]}^{3-}$. When applied towards the detection of As(III) by ASV, only one modified electrode was able to detect As(III) in standards, all the other electrodes were unable to detect As(III) in both standards and real water samples.

Since the Au NPs modified carbon electrodes proved to be unsuccessful in As(III) detection for most of the electrodes prepared, the performance of the Au working electrode towards inorganic As detection is seen as superior at this stage. However, this study on Au NPs modified carbon electrodes and their application towards inorganic As detection is a developmental work. Further work on these modified
electrodes in the detection of inorganic As need be carried out to further evaluate its performance towards inorganic As detection or other analytes.

6.1 Future directions

The following are some recommendations for future work

a. Sampling
   - Increase the number of sampling sites so that the data collected will be a good reflection of the whole study area.
   - Include sediments in speciation analysis since inorganic As is also closely associated with sediments.
   - Sampling collection and analysis during wet and dry seasons. This will provide a good understanding on the levels of inorganic As in both seasons.

b. Given the toxicity of As(III) and the high levels of inorganic As in the two river systems studied, it is recommended that the levels of this metalloid be continuously monitored on a time basis. In addition, further assessment(s) should be carried out and if necessary, remediation procedures should be undertaken in consultation with relevant regulatory authority.

c. Electrode modification and As(III) detection
   - Various other experimental conditions and parameters should be utilized to improve the reproducibility of these Au NPs modified carbon electrodes towards As(III) detection in both standards and real water samples.
CHAPTER 7

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