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Investigation of interferences and development of pre-treatment methods for arsenic analysis by Anodic Stripping Voltammetry

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This thesis is submitted as partial fulfilment of Master of Science (Chemistry)

December 2014

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Abstract

Contamination of drinking water is a serious health issue in many developing countries and there is a recognised need for low cost portable systems that are capable of analysing drinking water down to low ppb levels. Anodic Stripping Voltammetry (ASV) instruments meet these requirements but suffer interferences from other species which may also be present in the sample, particularly organics, other metals and sulfides. The last of these has received surprisingly little attention in the literature, despite being a proven interferent.

This study investigates the impact of each of these interference types, as well as a number of traditional and novel techniques in resolving them in a three phase process. First, each interferent was evaluated individually to determine the concentration at which it would significantly and reliably cause significant errors in the determination of arsenic by ASV. Secondly, each individual interferent was subjected to a number of pretreatments to determine the most suitable pretreatment method to remove that interference. Thirdly, a combined pretreatment method, capable of pretreating a single sample contaminated with significant levels of all three interferent types was developed and tested.

Modifications to the basic analysis methodology provided by the instrument manufacturer had to be made, particularly in the elimination of residual interferents affecting clean test solutions analysed after a contaminated test solution. A number of pretreatment methods were successful for sulfide contamination, however only the ion exchange resin was reliably successful for copper interference and only UV digestion was totally successful for organic contamination at the levels investigated. Although other pretreatment methods did partially improve the response of test solutions contaminated with the organic interferent, their performance was not sufficient to consider them for the final combined pretreatment method. The final combined pretreatment method for all three interferences was successfully tested on artificial sample solutions.

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And last but not least, a big thank you to my wife, Kaoru, for her endless support and understanding.

Glossary of Terms

Analysis Cup	Small 30 ml plastic cup used with PDV6000plus voltammetric analyser in which the electrolyte, sample and standard are added so they can be analysed.
Analyte	The component of a sample which is to be determined.
ASV	Anodic Stripping Voltammetry. Voltammetric methods in which the Stripping Step changes the Working Electrode potential in a positive direction causing an oxidation reaction in the deposited analyte.
Counter Electrode	Electrode used in Voltammetry which delivers a compensating current, allowing the potential of the Working Electrode to be controlled.
Deposition step	Preconcentration in Anodic Stripping Voltammetry, in which a negative potential is applied to the Working Electrode to pre-concentrate the analyte onto the
Baseline	Imaginary line drawn over a voltammogram to give a starting point for peak height to be measured from. Ideally matches the voltammogram of the same solution with no analyte present.
CSV	Cathodic Stripping Voltammetry. Voltammetric methods in which the Stripping Step changes the Working Electrode potential in a negative direction causing a reduction reaction in the deposited analyte.
Electrolyte	A liquid that conducts electricity due to the presence of positive and negative ions. In voltammetry it usually also provides consistent pH.
ppm	Parts Per Million. Unit of concentration equivalent to mg/L
ppb	Parts Per Billion. Unit of concentration equivalent to µg/L
PDV6000	Portable Digital Voltammeter model 6000. Voltammetry instrument used in this study.
Reference Electrode	Electrode used in Voltammetry which provides a constant potential against which the potential of the Working Electrode is compared.
Spike	Small volume of known standard added to a sample solution.
Standard	A solution containing a known concentration of analyte.
Stripping Step	The measuring step of a voltammetric analysis in which the analyte deposited on the Working Electrode surface in

	the Deposition Step is oxidised (in ASV) or reduced (in CSV) producing a current which is the analytical signal.
Sweep Rate	Rate at which the potential applied to the Working Electrode is changed during the voltammetric Stripping Step.
USEPA	United States Environmental Protection Agency.
Voltammetry	An analytical method using the passage of current as a function of potential applied to the Working Electrode for the analytical signal.
Voltammogram	Graphical plot of the applied potential versus the measured current at the Working Electrode during the Stripping Step of a voltammetric analysis.
Working Electrode	The electrode at which the reactions being studied occur. In voltammetry, this is the reduction and oxidation of arsenic and other analytes.

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1 Introduction

1.1 Arsenic in the Environment

Arsenic (As) is a toxic substance widely distributed throughout the earth's crust and present in many natural waters due to both natural and industrial sources [1-3]. It has been reported as a contaminant in ground water in 20 countries including Australia, Chile, China, India, Mexico, Thailand, Vietnam and Bangladesh [1, 4], affecting the drinking water of over 100 million people [4]. Symptoms of acute As poisoning include vomiting, abdominal pain and diarrhoea [1]. Even at low levels (ppb), prolonged exposure to As by drinking As contaminated water leads to a variety of chronic illnesses such as vascular disease, hyperkeratosis of the hands and feet and cancers of the skin, lungs, bladder, and other organs [1]. Arsenic can occur in ground waters due to dissolution of naturally occurring As from rocks and sediments, a process that may be exacerbated by reduced water tables and changes to groundwater pH [5]. Arsenic can exist in oxidation states −3, 0, +3 and +5 [4]. In natural waters, the most common forms are the inorganic species As(III) (arsenite) and As(V) (arsenate), with smaller amounts of the methylated forms methylarsenite, methylarsenate, dimethylarsenite and dimethylarsenate [4]. Of these, the inorganic trivalent form is the most toxic, followed by inorganic pentavalent form [6]. Since the organic forms of arsenic are less toxic as well as less prevalent [1, 6], most analysis focuses on the inorganic arsenite and arsenate species [1,4]. In addition, the methylated forms of arsenic are generally not considered amenable to analysis by voltammetric techniques [7] and therefore will not be discussed here. It is also worth noting that the inorganic arsenic species behave as anions rather than cations, due to interactions with surrounding water molecules as shown in Figure 1.1. While most As contamination of drinking water is from natural sources, discharges from industrial sources can also be a source of contamination, particularly in developing countries [1]. Industries which have, or still do use arsenic include manufacturers of pigments, insecticides and herbicides, glass, alloys and electronics [6].

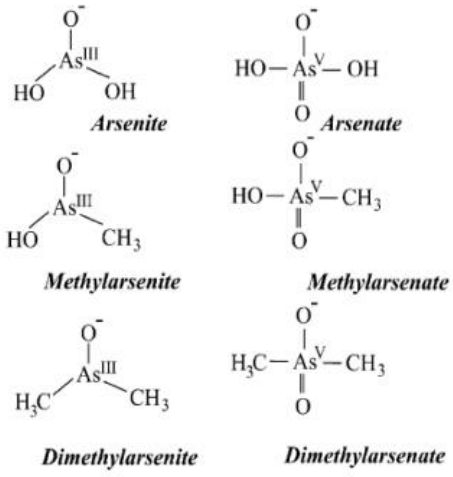

Figure 1.1 Arsenic species found in natural waters [4].

1.2 Arsenic Detection Techniques Overview

Accurate detection of arsenic in water samples is a major issue for human health in many places around the world, particularly in remote locations and developing countries. Laboratory analysis is often unfeasible (see Section 1.6 below), and authorities have often been heavily reliant on unreliable and unsafe arsine generation colourimetric test kits [1]. These kits work by adding chemicals to the sample to turn the arsenic into arsine gas which rises to an indicator paper or other sensor resulting in a colour change proportional to the As concentration [1, 4, 8]. These test kits generate dangerous levels of arsine gas, and their performance and reliability are generally poor [2-4, 8, 9].

A limit of 10 ppb As in drinking waters has been recommended by EU, US and WHO guidelines [1-3]. Other countries such as Bangladesh still have higher limits of 50 ppb [1], while a lower level of 7 ppb is recommended in Australia due largely to the higher incidence of skin cancer and the multiplying effect of As on that condition [10]. It has also been shown that the speciation of As affects its toxicity, with inorganic arsenite and arsenate being significantly more toxic than organic forms [1, 2]. For this reason, as well as the emphasis given to toxic metal speciation in the Australia and New Zealand Water Quality Guidelines [10], any technique which can give speciation data has obvious value to researchers and monitoring bodies.

The USEPA (United States Environmental Protection Agency) recognises a number of methods to detect As based on Atomic Absorption (AA) and Inductively Coupled Plasma (ICP) spectrophotometric techniques for measuring As in drinking water [11]. The basic AA and ICP techniques are not generally considered to have sufficiently low detection to analyse As at drinking water limit levels [8], so add-on systems such as Mass Spectrometer (MS), Graphite Furnace (GF) or Hydride Generation (HG) are often used, e.g. Inductively Coupled Plasma - Mass Spectrometer (ICP-MS), Graphite Furnace - Atomic Absorption Spectroscopy (GF-AAS) and Hydride Generation - Atomic Absorption Spectroscopy (HG-AAS). However, these methods are expensive, require highly skilled operators and cannot be used in the field [2, 3, 11, 12]. A sensitive, efficient and cheap method for As detection is therefore needed to assess drinking water, particularly in developing countries.

The following subsections outline the principles of each of these techniques, as well as the interferences and other problems associated with each technique.

1.2.1 Atomic Absorption Based Techniques

This range of laboratory based methods is based on the principle of atomic absorption spectroscopy, in which the atomised sample is placed between an

emitter and detector of light at the specific wavelengths known to correspond to the differences in the energy levels of the analyte atoms [13]. When a photon of this light interacts with the analyte atom, it causes one of its orbiting electrons to jump to a higher energy state and is thus absorbed by the analyte atom. This results in attenuation of the emitted light reaching the detector. The amount of light attenuation is therefore proportional to the amount of analyte element in the sample and can thus be used to calculate the analyte concentration [13].

These methods all function by first volatilising or atomising the sample and introducing it to a measurement chamber where it is exposed to the light of required wavelength, usually generated by a hollow cathode or electrodeless discharge lamp containing the analyte metal [13]. It is the different methods of sample volatilisation that separates these techniques, as explained in the following.

Flame Atomic Absorption Spectroscopy (Flame AAS) is the simplest and cheapest of the atomic absorption methods. With flame atomisation, the carrier gases draw the sample into a nebulizer by the Bernoulli Effect where it is converted into an aerosol along with the gaseous fuel and burnt to maximise atomisation [13]. The carrier gases may vary according to the temperatures required for different samples and analyte elements. While this technique can be used to measure arsenic, detection limits are generally considered to be in the 100 ppb range and thus too high to measure in the range of As drinking water regulations [13].

The Graphite Furnace or Electrothermal Atomic Absorption Spectroscopy (GF-AAS) method offers improved sensitivity over the older flame atomic absorption spectrometry techniques because of its faster atomisation of the whole sample. These systems typically consist of an open ended graphite tube placed along the generated light beam path, which is then heated in a series of steps to dry, ash and finally atomise the sample at temperatures up to 3000 degrees Celsius. These systems can typically detect 1 to 5 ppb of As in the sample[8] and so are orders of magnitude more sensitive than the flame methods due to more efficient volatilisation of the sample, but are also more expensive, time consuming and can be more sensitive to chemical interferences [8, 14].

The Hydride Generation Atomic Absorption Spectroscopy (HG-AAS) technique volatilises the sample by using zinc or sodium tetrahydroborate in an acid medium to produce hydrogen and convert As(III) to gaseous As(III) hydride or arsine (AsH_3) gas.

$$6H_{2(g)} + As_2O_{3(aq)} \rightarrow 2AsH_{3(g)} + 3H_2O_{(l)}$$ (Equation 1.1. Reduction Process)

Detection limits are in the region of 2 ppb [15]. Since As(V) must first be reduced to As(III) for this reaction to occur, the As(V) in the sample will react more slowly and hence show a lower sensitivity, so any As(V) present in the sample should first be reduced to As(III) for best results [8, 13, 15].

1.2.1 Inductively Coupled Plasma Based Techniques

Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES), also known as ICP – OES (for Optical Emission Spectroscopy), is the oldest and lowest cost of these laboratory based techniques, which also relies on changes in the energy states of electrons in the analyte element electron shells. An argon carrier gas is ionised by a spark and heated by magnetic field to temperatures up to 10,000K, generating plasma. The sample is then nebulised and aspirated into this plasma and heated, causing more complete atomisation than seen in the above AAS methods as well as excitation of electrons in the analyte atomic shells. As the analyte atoms progress to cooler regions of the flame, these electrons begin to return to lower energy states releasing photons of specific energy corresponding to the differences between the electron energy levels. These emitted photons are filtered by wavelength and measured at detectors. The intensity of light at a wavelength for a specific element will be proportional to the concentration of that element in the sample [13, 16]. This technique has the significant advantage of being able to measure multiple elements – typically over 20 – simultaneously. However, the detection limit for As is in the range of 35 ppb and hence insufficient for regulation levels in many countries, so it is often not considered an acceptable method for testing drinking water for As [8, 16].

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), through coupling the ionised sample atoms from the output of an ICP-OES system to a mass spectrometer, can significantly reduce the detection limit by an order of magnitude or more. This method brings detection limits to the range of 0.02 to 1 ppb [8], which is acceptable to analysts wishing to analyse below drinking water regulation concentration levels. The ionised sample ions from the ICP are passed through a magnetic field and their flight path deflection measured on the basis of their mass to charge ratio by a channel electron multiplier or Faraday detector [17].

1.2.2 Colourimetric Gutzeit Method Test Kits

Commonly used in field test kits for As [18], the Gutzeit method involves reduction of As to arsine (AsH_3) gas in a reaction chamber containing metallic zinc in an acid solution. This combination of zinc and acid produces hydrogen, which is the agent that actually reduces the As to arsine in the chamber [15] through a process similar to that used in HG-AAS techniques shown in Equation 1.1.

The generated arsine gas then rises through a scrubber, generally containing lead acetate on a glass wool or similar substrate, which removes interfering hydrogen sulfide from the gas [8, 11, 19].

The most widely used Gutzeit Method is the silver diethyldithiocarbamate (SDDC) method such as method 307B in Standard Methods for the Examination of Water and Wastewater (AHPA) [19]. The generated gas is passed into a solution of SDDC and the colour change caused by arsine is measured with simple photometric equipment. As with Hydride Generation AAS mentioned above, As(V) is best reduced to As(III) prior to arsine generation with KI and $SnCl_2$ for more accurate readings.

Other variations on these techniques use acidic sodium tetrahydroborate solutions similar to those mentioned above for HG-AAS to atomise the As in the sample or replace the SDDC indicator solution with a test paper coated in a reactive compound such as mercuric bromide which gives a colour change in the presence of arsine gas. These methods have the advantage of being usable in the field, but have been shown to have poor sensitivity and accuracy [4, 18]. Reported detection limits vary but are generally considered to be in the 10 to 50 ppb range [8, 11].

1.2.3 Atomic Fluorescence Spectroscopy

Atomic Fluorescence Spectroscopy (AFS) is a laboratory based technique that has been available for some years and is particularly well recognised as an accepted method for Hg and Se determination [10], although it is also recognised as a technique for determination of As [4, 8]. It is based on similar sample atomisation techniques as those used in HGAAS mentioned above, but the atomised sample is exposed to higher energy UV light to excite the electrons in the As atomic electron shells. When these electrons move back to a lower energy state, the photons emitted will again be of known wavelength for the element of interest and can be filtered and measured in a similar manner [11]. Detection limit is in the order of 10 ppb [8].

1.2.4 Voltammetric Techniques

Anodic Stripping Voltammetry (ASV) is an electrochemical technique in which the analyte metal in the sample solution is measured on a suitably prepared working electrode. The process can be broken down into two key steps. First, a negative potential is applied to the working electrode to reduce some of the analyte in the sample to its ground state on the electrode surface.

$M^{n+} + ne^- \rightarrow M^0$ (Equation 1.2. Reduction Process)

Secondly, this process is reversed by increasing the potential applied to the working electrode at a constant rate until the metal reduced onto the electrode surface is oxidised back into the solution.

$M^0 \rightarrow M^{n+} + ne^-$ (Equation 1.3. Oxidation Process)

At this point the applied potential and the concurrently measured current are plotted in a voltammogram where the oxidation current from the analyte metal is visible as a peak (see Figure 1.5). The metal is identified by the peak potential and the peak amplitude (measured in μA or μC), which is proportional to the analyte concentration in the solution.

ASV theory is covered in more detail in Section 1.3. It is currently the cheapest instrumental method for detecting As, the only one that is readily field portable [4] and is the only method to readily give speciation information without sample pretreatment [2, 4, 20]. It is also the only field-testing method recognised by the USEPA for arsenic determination [7, 11]. Reported detection limits vary, but are usually below 1 ppb [4].

1.2.5 Interferences in Arsenic Detection Methods

All analytical methods suffer from interferences to some degree, and these interferences affect the accuracy of As detection. For the Atomic Absorption spectrophotometric methods, salts are a major concern [8] as are ionisation effects. Spectral interferences occur from compounds either absorbing at similar wavelengths to the analyte or over a wide range of wavelengths and chemical interferences such as anions which may form compounds with the analyte that are not readily volatilised [13]. In addition, transition metals are thought to interfere with As analysis using HG-AAS by reacting with the $NaBH_4$ reductant [4].

ICP based techniques use significantly higher temperatures which result in more complete sample atomisation and hence reduce chemical interferences. However elemental interferences still persist due to overlapping spectral lines and other effects. For example, in ICP-MS, chloride can combine with the argon carrier gas forming ArCl which has the same mass as As [17].

The Gutzeit based techniques also suffer several interferences, notably from other metals which may interfere with the arsine generation step or cause a similar colourimetric response, such as Sb. Despite the lead acetate cleaning step, high levels of sulfide can still cause problems for these methods. Field tests of As test kits based on these techniques have often shown them to perform poorly [1,3].

In the case of ASV method there are also interferences, predominantly from other metals and organics. Therefore, any method for As detection, requires a clear understanding of any potential interferences and how to deal with them. The most significant interferences for voltammetric methods are covered in more detail in Section 1.5.

1.3 Voltammetric Analysis of Arsenic

1.3.1 Anodic Stripping Voltammetry Theory

The Anodic Stripping Voltammetry (ASV) method is likely to provide the cheapest, most accessible and reliable method to measure As in the field. A typical ASV system comprises an analytical cell with three electrodes (Figure 1.2). Firstly, there is a Working Electrode, where the metal of interest is preconcentrated and then analysed as described below. The material used for the surface of this electrode can vary depending on the analyte(s) being measured. The other two electrodes support the reactions occurring at the working electrode. The second electrode is a Reference Electrode which provides a reference potential against which the potentials applied to the working electrode are measured. Due to its relative robustness and simplicity, this is most commonly an Ag/ AgCl type, as was provided with the PDV6000 (Portable Digital Voltammeter, model 6000) instrument used in this study, although a number of other types of reference electrodes also exist [21]. All potentials quoted in this study are relative to Ag/AgCl/1M KCl reference electrode. Finally, there is usually a Counter Electrode, which provides a current path for the potentiostat (the electronics controlling the working electrode potentials) to control the potential at the working electrode without disturbing the equilibrium of the reference electrode. A platinum wire is most commonly used, as it was in this study, although glassy carbon is also sometimes used [21].

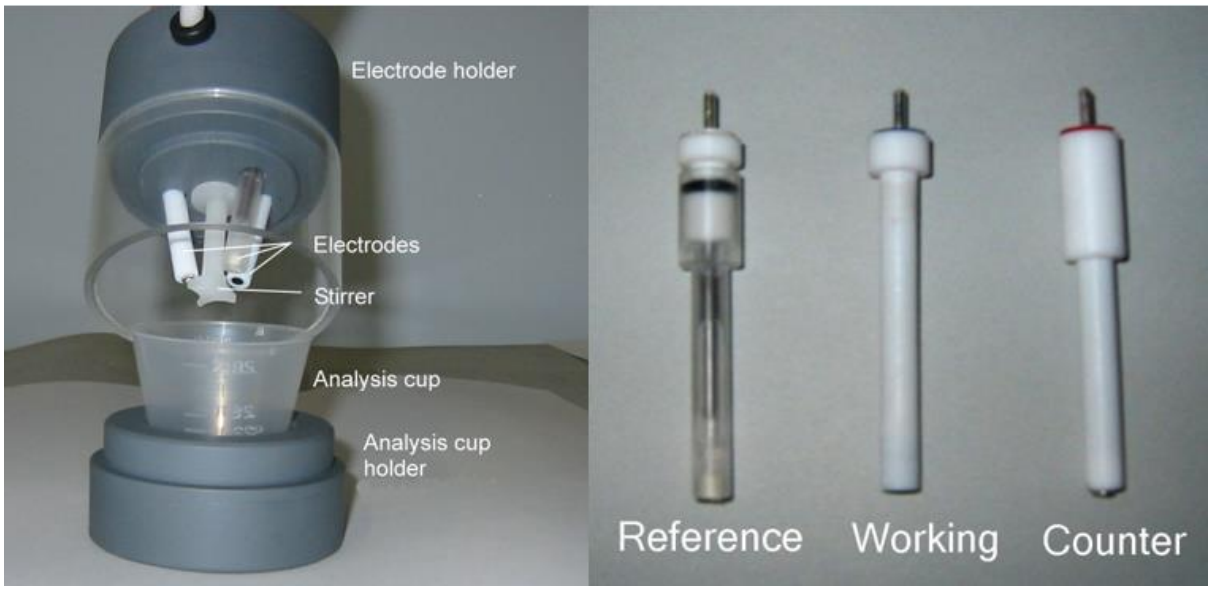

Figure 1.2 PDV 6000 Analysis Cell (left) and Individual Electrodes (right). Pictures taken from instrument manual.

The principle of Anodic Stripping Voltammetry is simple and essentially a two-step process. The first step is generally known as the "deposition" or "accumulation" step [21]. In this step, an appropriately negative potential is applied to the working electrode while the solution is stirred. This reduces the

target metal ions in the vicinity of the working electrode to the metallic state on the working electrode surface, much like the electroplating process for metals such as gold or nickel in industry (see Figure 1.3). This can be seen in Equation 1.2 as the reduction reaction where M is the analyte metal, n is the charge of the metal in the oxidized, ionic state, and e^- is an electron gained by the metal during the reduction reaction.

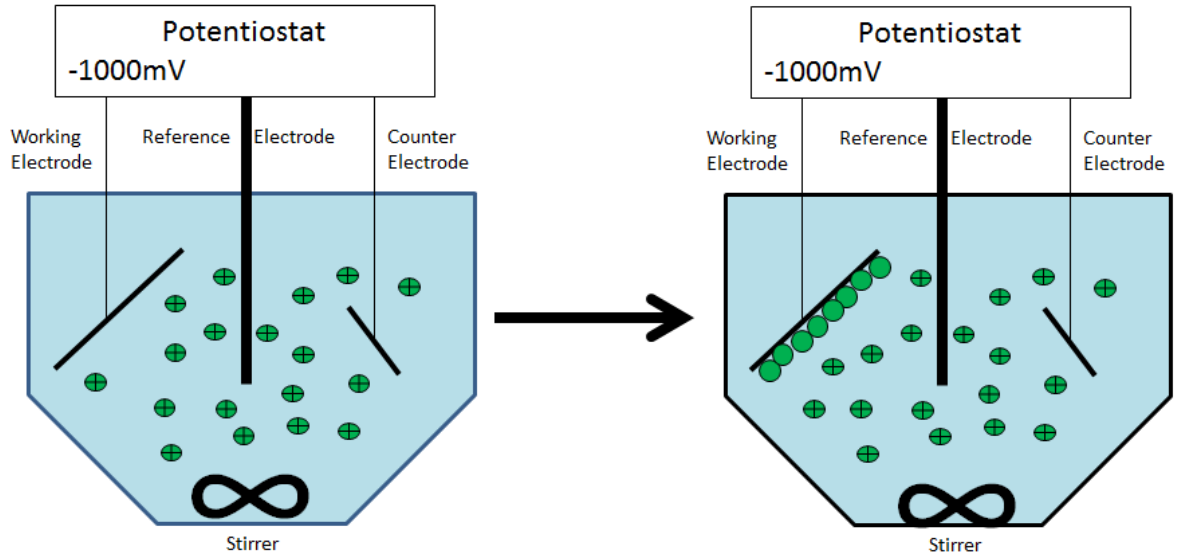

Figure 1.3 Schematic diagram showing the before (left) and after (right) the deposition step in the ASV method.

The longer the potential is applied for, the more metal is reduced and plated onto the surface of the electrode, concentrating the metal onto the electrode surface [21]. During this deposition step, the solution in the cell is stirred to increase the efficiency of transport of species to the electrode surface, since a deposition step occurring under stirring is significantly more efficient than one relying on diffusion and natural convection [21]. It should be noted, however, that friction and electrode rigidity near the working electrode surface form a thin layer where the forced convection of the bulk solution caused by the cell stirrer does not occur. This region is called the diffusion layer as diffusion is the mechanism of transport in this, the final region through which the reactants must pass to reach the electrode surface [13, 21]. The thickness of this layer varies with electrode and cell design, bulk solution convection and electrolyte constituents and concentration, but is generally tens of μm thick [13, 21]. This preconcentration effect on the electrode surface is what makes ASV one of the most sensitive analytical techniques available, giving detection limits in the sub-ppb range for many metals including arsenic [21]. The aim is not to collect all the metal from the analysis cell, but enough to give an analytical response in the desired concentration range.

When sufficient deposition time has elapsed, the stirrer is stopped and the potential maintained at a negative potential long enough to allow the cell solution to stop circulating. The potential applied to the working electrode is then increased at a constant rate while the current flowing through the working electrode is measured. Eventually the oxidation potential for the analyte metal deposited on the working electrode will be reached and an oxidation reaction will occur (see Figure 1.4), as seen in Equation 1.3, where M is the analyte metal, n is the charge of the metal in the oxidized, ionic state, and e^- is an electron released during the oxidation reaction [13,21].

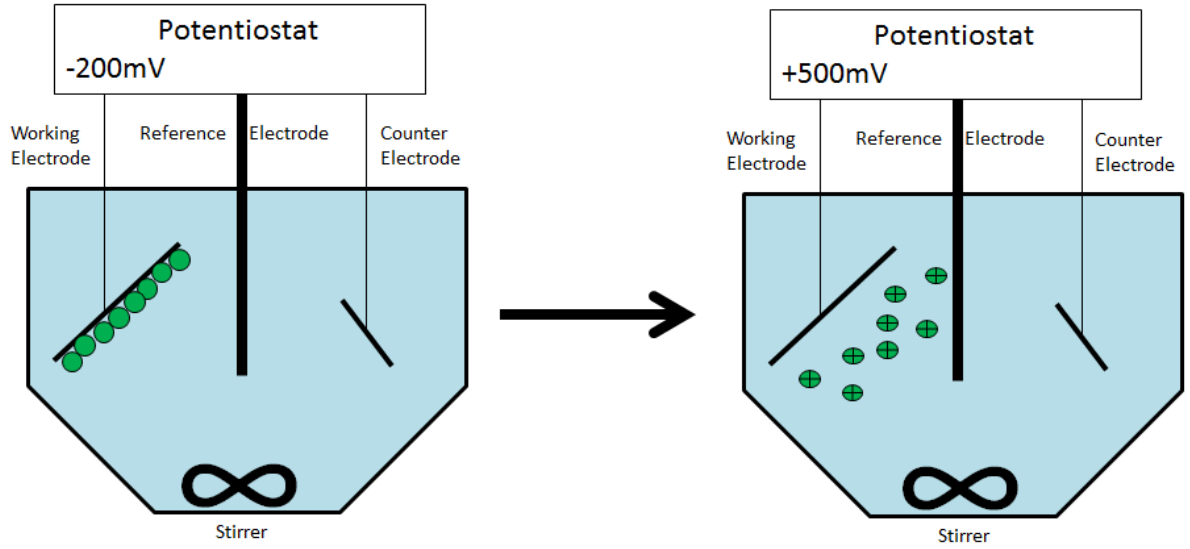

Figure 1.4 Schematic diagram showing the before (left) and after (right) the stripping step in the ASV method. Note different potentials applied at start and end of the stripping step.

This second step is known as the stripping step [13, 21]. The electrons released by this process form a current which is measured and plotted as a function of the applied potential to give a "voltammogram". Current from the oxidation of the metal will appear as a peak superimposed on a small background current (Figure 1.5). For a given electrode type and analysis cell solution matrix, the stripping peak for a metal can be predicted with some confidence. Thus, the potential at which the peak occurs is used to identify the metal, while the area or height of the peak is used to quantify the metal concentration by comparisons to internal or external standards.

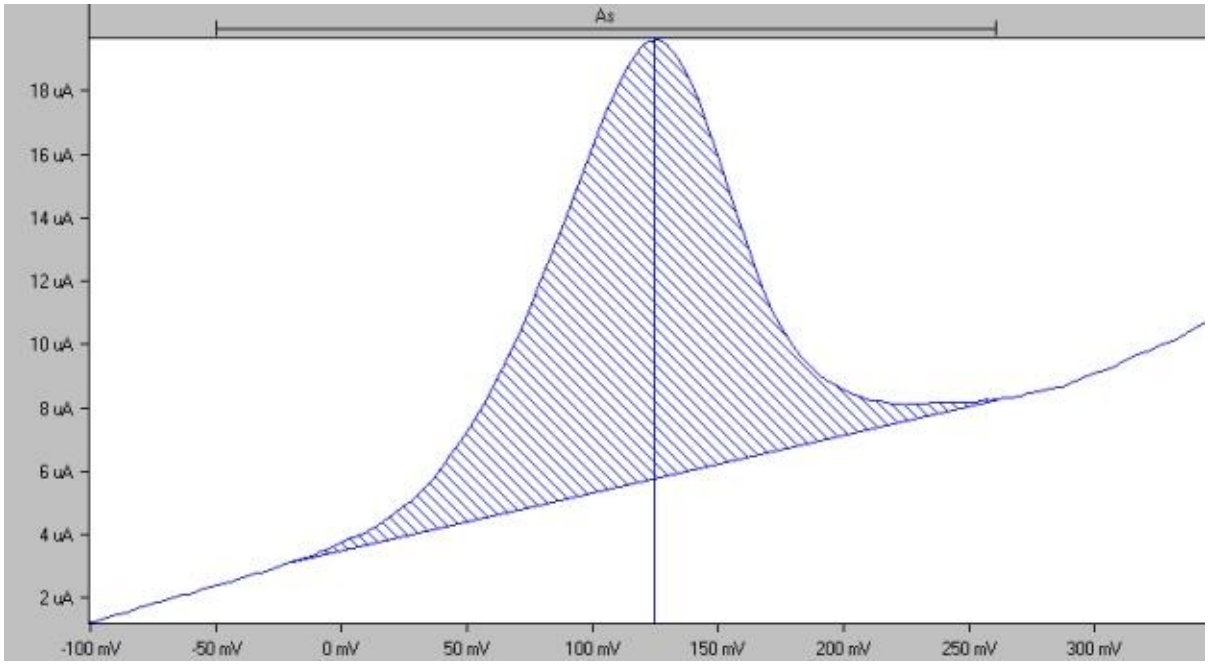

Figure 1.5 Voltammogram for arsenic at gold plated carbon electrode in the ASV method. Vertical axis is Current (μA) and horizontal axis is Potential (mV).

ASV has been successfully used to analyse a number of metals, including cadmium, lead, mercury and thallium, and has a number of advantages over other methods. Firstly, it is one of the most sensitive methods available, and has relatively low capital and running costs [12, 21]. Secondly, it requires no specialised infrastructure such as gas lines or fume extraction systems, thereby reducing operating costs and allowing the instrumentation to be highly portable for use in the field, and thirdly, it can also detect speciation of some analytes. In the case of As, As(III) or total free inorganic As (As(III) + As(V)) can be analysed by changing the potential applied during the deposition step. Organic As species require pretreatment to free the As ions before they can be analysed [4, 22].

1.4 Factors Affecting Voltammetric Response to Arsenic

While voltammetry is a highly sensitive technique with real advantages over other methods, a number of important variables must be kept in mind while developing and testing voltammetric methods. A combination of several of these factors – particularly temperature and, in the case of the solid gold working electrodes, the electrode surface condition and history are thought to contribute to variance of the response [18, 21, 23, 24]. Key conditions and variables, as summarized below, must be considered when performing voltammetric analysis of arsenic.

1.4.1 Electrolyte Components - Significant Background Ions

The two key elemental components of the most commonly used electrolyte for voltammetric As determination, HCl, are worth some consideration. In particular, the analysis of total inorganic As, as used in this study, is somewhat different to most ASV methods, due to As not being a true metal and the different chemistry of As(III) and As(V) measurements. While As(III) may be easily measured directly at a relatively positive deposition potential such as -200 mV on a gold electrode even at acid, neutral or caustic pH [18], As(V) gives no response under such conditions. In order to measure As(V), a much more negative deposition potential is required [18, 23, 26]. This not only provides a large overpotential during the deposition step, but generates the 'nascent' hydrogen, which is thought to be generated at the surface of the working electrode to help reduce the As(V) to As(0) [23], although other mechanisms are possible [25]. In any case, it is essential to have both an acidic electrolyte and a more negative deposition potential in order to form this nascent hydrogen on the electrode surface during the deposition step to permit As(V) analysis. As a side effect of this process, visible bubbles of H_2 gas are also generated on the electrode which partially cover the electrode, slowing the rate of transfer to the electrode surface and resulting in lower sensitivity for the total inorganic As method than would be seen for the As(III) method at the same As concentration [4, 18, 23]. It has also been proposed that a high H^+ concentration with a low deposition potential may result in the reduction of As(0) to arsine (AsH_3) and thus loss of As response [23]. For these reasons, the correct concentration of H^+ is important, as too much free H^+ can result in excessive gas generation at the working electrode surface, making it inaccessible, and insufficient H^+ can result in instability in repeat runs of a single solution due to H^+ loss in the first runs and insufficient 'nascent' hydrogen generation in subsequent runs to quantitatively reduce the As(V) transported to the electrode surface.

Chloride ions are also important because they facilitate the deposition process by acting as an ionic bridge between the dissolved As ions and the deposited As(0) [26]. A chloride ion$^-$ containing solution will give significantly better response than a Cl^- free solution. However, since modern voltammetric cells use a three electrode system, the counter electrode, usually platinum, is driven to a more positive potential by the potentiostat electronics, in order to achieve the negative potential required at the working electrode for deposition of As(V). At these potentials, Cl_2 is generated at the counter electrode, which if not removed, rapidly oxidises any As(III) present in the analysis cell to the pentavalent form, which cannot be determined with a deposition potential of -200 mV. In such cases, ascorbic acid or other reductant is added to the electrolyte solution to absorb the Cl_2 generated at the counter electrode [18].

Since As(III) is more easily deposited on the working electrode than As(V), and thus gives a higher response, ascorbic acid is not added to the analysis cell solution for total inorganic As analysis to ensures that all As(III) is quickly oxidised to As(V) by the Cl_2 generated at the counter electrode. This is to ensure

a consistent response for both inorganic As species and because the ascorbic acid is itself reduced at the total As deposition potential, leaving an insoluble residue on the electrode surface.

The PDV6000plus instrument manufacturer recommends either 0.25M HCl (in the analysis cell) or a more subtle mix of 0.5M HNO_3 and more dilute acetate buffer and chloride mixture. It is speculated that the acetate buffer helps preserve the H^+ concentration in the analysis cell during repeat analyses of the same solution and the lower Cl^- concentration allows for the improved oxidation peaks noted above, while avoiding excessive Cl_2 gas generation. Acetate buffer has been used in place of strong acid electrolytes in previous studies using the same instrument [27]. However, for this study, the 0.25M HCl electrolyte was used, as HCl is specified in the USEPA method [7], is much simpler to make, and is more widely used [4, 26]. Hence it is more likely to be applicable to other instruments.

1.4.2 Temperature

Voltammetric response is generally considered to increase between 1 and 2 % per degree Celsius, largely due to increased efficiency of the diffusion process in the deposition step [21, 24]. In both laboratory and field work, this is largely self-correcting as standard and sample solutions will have a chance to equilibrate to the same ambient temperature, however, it can be a cause of variance in response from one day to another. Sample temperature is considered sufficiently important that the USEPA method for As determination using ASV [7] specifically states that samples must be allowed to equilibrate to room temperature before analysis when they have been preserved by refrigeration.

1.4.3 Electrode Condition and History

Various studies have shown that electrode conditioning by application of an oxidizing potential is particularly important for solid gold electrodes [18, 23, 26] and that extended periods at negative potentials can 'passivate' the electrode surface by reversing this oxidizing effect. This is considered to be due to the formation of gold oxides on the electrode surface [18, 23, 26]. In the manufacturers recommended parameters for As determination, known as application notes, for the PDV6000plus instrument used here with a solid gold electrode, this was achieved before each analysis by cycling the potential between 0 and +800 mV for 30 seconds in the sample or standard / electrolyte mix. It is worth noting that this step is only used for the solid gold electrode method, and is not used for the otherwise similar gold film method, indicating a different morphology of the thin gold film to that of the solid gold electrodes. This solid gold conditioning step is at a much less positive conditioning potential than used by Salaun *et al.* [18, 23], who cycle their solid gold wire electrode up to +1500 mV in a separate $HClO_4$ or H_2SO_4 solution daily before commencing analysis. They do not seem to require a separate conditioning step before each

analysis, although this may be due to their use of micro-wire electrodes, as their early experiments with disk electrodes, more similar to those used with the PDV6000plus instrument used in this study, required the disk electrode to be polished after only 10 measurements [23]. The difference in conditioning potentials is likely explained by the electrolyte solutions used. Carrying out the oxidation step in the measuring electrolyte means the presence of significant levels of Cl^- ions which limit the anodic potential which may be applied before the gold electrode will start to dissolve. The lack of a preconditioning step between analyses may be due to the very small size of the electrodes used by Salaun *et al.* [18, 23] and the resulting smaller currents and greater sensitivity, which require shorter deposition times and hence less passivation of the electrode surface.

1.4.4 Key Voltammetric Analysis Parameters

The two parameters in a voltammetric analysis that have the most direct influence on response are the deposition time and the sweep rate [21, 24]. During the deposition step, the sample is stirred to increase the efficiency of the deposition step and the deposition potential is held on the working electrode for the deposition time. The longer the deposition time, the more metal can be preconcentrated onto the working electrode surface. The relationship between deposition time and metal concentration is roughly linear, however, the different nature of As compared to other analyte metals puts limitations on how far this can be utilized. One reason is that, unlike most metal analytes, the deposited ground state As on the electrode surface is non-conductive and so effectively fouls the electrode surface once a monolayer of As(0) is formed [18]. The PDV6000plus manufacturers recommend parameters for As determination, known as application notes, which recommend a maximum deposition time of 120 seconds [28, 29].

The effect of stirring speed is a little more complex, since its primary purpose is to decrease the diffusion layer at the surface of the electrode to increase the flux of metal ions to the electrode surface [24]. Within the diffusion layer, the concentration of the metal being deposited is lower than in the bulk solution, so a thicker diffusion layer due to lack of stirring results in a much lower response for parameters that are otherwise the same. Once again, in As analysis, this is a little more complicated than for other metals due to the gases generated at the working and counter electrodes as discussed in Section 1.4.1, since the stirrer must also be fast enough to remove these gas bubbles before they start to completely block the electrode surface [4, 18, 23], particularly in the instrument used in this study.

Higher sweep rates can similarly increase the measured response for a given As concentration. The deposited As will release the same total number of As ions and electrons irrespective of the sweep rate, but a faster sweep rate will result in this same charge being removed from the electrode surface at a faster rate, hence

showing as a higher current on the voltammogram. The limits to increased sweep rates are the capabilities of the potentiostat used (5V/sec. in the case of the PDV6000plus) and kinetic limitations on the speed of the As oxidation reaction. Also, increases in the background charging current, which can reduce signal to noise ratios, must be taken into account. In this study, it was found that As response improved until around 2.5V/sec. sweep rate, beyond which little improvement in signal to noise ratio was seen.

1.5 Voltammetric Interferences and Potential Treatments

An interference is when a species in the sample matrix produces a signal that is indistinguishable from the analyte or attenuates the analyte signal [13]. For ASV, the most commonly cited interferences are other metals, especially Cu and various organic compounds [3, 9, 12, 18, 30]. In the literature search for this study, it became apparent that sulphide studies are very limited as an interference for As by ASV, although it is widely recognised as an interferent in the determination of As by the Gutzeit method [8, 11, 19]. However, sulfide has been shown to reduce the voltammetric response for As [31]. Each of these interferences will be examined in more detail below.

1.5.1 Organic Interferences

Organic compounds, such as detergents or humic substances are most likely to interfere with voltammetric analysis by fouling the working electrode and preventing deposition of the analyte metal, although in some cases they can also form a complex with the target metal, thus making them unavailable for ASV analysis [21]. For these reasons, organic molecules can be serious interferences for ASV. Triton-X, a common laboratory detergent, is widely used to represent organic interferences in voltammetry research literature [18, 23, 26, 32]. It was initially intended to also test humic substances as these are likely to be the forms of organics encountered in natural waters. These would have to be fulvic acids, since humic acids precipitate in acid conditions. Reagents were ordered which, although specified as fulvic acids, turned out to be humic acids. This resulted in a precipitate being formed when acid was added, and thus, it was not possible to use these reagents in this project..

The usual pretreatment to prevent interferences by organic compounds for ASV is by treating the sample with ultraviolet light (UV), sometimes in conjunction with oxidising agents to break the organic compounds into smaller molecules that do not interfere with ASV [19, 33, 34]. UV digestion works partly by generating ozone within the sample [35]. The treatment of samples with ozone alone has been used for atomic absorption techniques [36] and water remediation [37] and could be a useful approach for ASV, however few references have been found for this [38].

A novel approach to organic interferences used more recently, is the use of ultrasound. This has been used both in the digestion step prior to analysis [34, 39] and by agitating the sample solution during the deposition step of ASV analysis [32, 40-42]. This approach has been shown to reduce the interference effects of organic compounds for various metals and has even been reported to allow highly organic samples such as petrol, blood and saliva to be analysed for Pb without the usual pre-treatment [32, 40-42].

1.5.2 Sulfide Interference

Sulfides, which are commonly found in anoxic natural waters [43], interfere with voltammetric analysis by both complexing and precipitating As from the solution and passivating the gold working electrode [3, 31, 44]. The latter process potentially has the most significant effect, as it may also affect subsequent analyses [31]. Sulfides are generally removed by oxidation. They are readily oxidised to sulfates in naturally oxygenated waters [43]. Sulfides are known to interfere with As determination by ASV [31], however, very few references specifically mention sulfide as an interferent. This may be due to most research being carried out in the lab after sulfide has been oxidised by dissolved oxygen [43] or, possibly converted to H_2S by acid [31] due to normal sample preservation techniques being followed [7]. Given the readily oxidisable nature of sulfides, it seems reasonable to expect oxidising pretreatment processes such as chemical oxidation and UV digestion and ozonation as possible processes to remove sulfide interference.

1.5.3 Metal Interferences

Metals which are electro-active under the conditions used to measure analytes can produce interferences in ASV [30, 44, 45]. This can result in peak overlap, where the interferent oxidation peak merges with that of the analyte of interest, making it difficult or impossible to measure the analyte peak accurately [30, 44, 45]. Metals can also interfere by competing for available deposition sites on the working electrode surface, thus reducing the response for the analyte [44]. This is especially true when the interfering metal is present in much higher concentrations than the analyte and/or is more easily deposited [44]. In some cases, interfering metals may form intermetallic compounds with the analyte metal on the electrode surface which may give an oxidation peak different to that of the analyte metal alone [44].

Copper and iron are the interfering metals most likely to be present in natural samples at concentrations high enough to have these effects on As analysis [7, 18, 30, 45]. Fe is not actually detected by ASV on a gold electrode, but is thought to reduce and oxidise in the region between 0 and -1V on a gold electrode [28, 29]. In the application notes given for As determination with the PDV6000plus instrument used in this study, it is stated that this interference is overcome by

alternating the deposition potential between -900 mV and -200 mV to prevent build-up of Fe on the electrode surface [28, 29].

Where Cu is present in a sample, the Cu peak may not only overlap that of As, but may also cause a noticeable drop in the height of the As peak (Figure 1.6), either by competition for active sites on the working electrode surface, or by formation of an intermetallic compound with As [30]. Approaches to preventing Cu interference have included ion exchange pretreatment of the sample to selectively remove the Cu [46, 47], and novel types of electrode material which show greater resistance to Cu interference [26, 30]. Some Cathodic Stripping Voltammetry methods make use of the Cu-As intermetallic formations by measuring the reduction peak of the complex [22, 26, 45], but these methods require use of a mercury drop electrode, which is unsuitable for field applications.

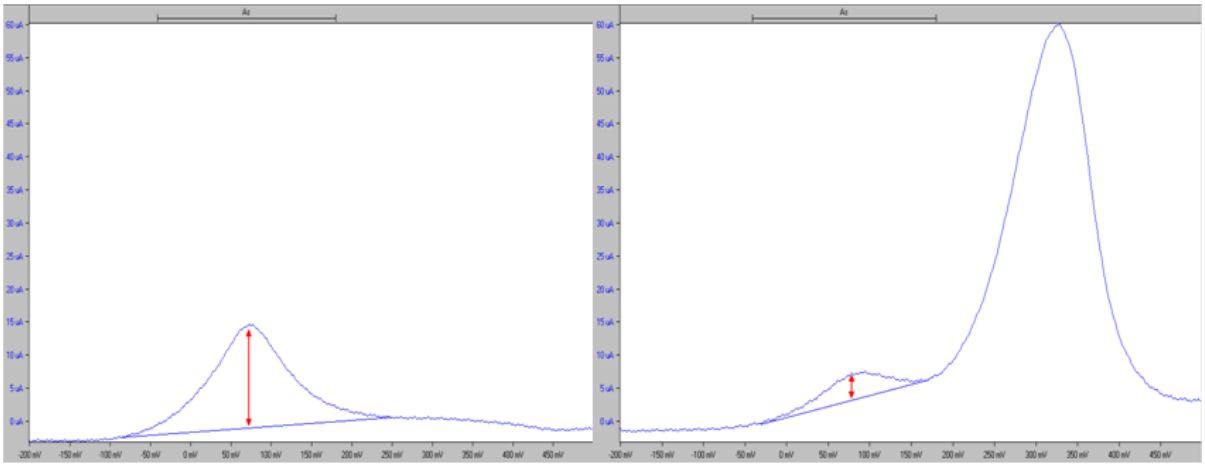

Figure 1.6 Voltammograms for 20 ppb As with 0 ppb (left) and 60 ppb (right) Cu in solution, on a solid gold electrode. Vertical axis is Current (µA) and horizontal axis is Potential (mV).

It should be noted that the USEPA [7] method for As by ASV also mentions bismuth and antimony as producing oxidation peaks in the As region. Bi is not considered a common contaminant in natural waters [48, 49], while Sb is not considered to be a significant interferent with the method for total inorganic As, since the generation of Cl_2 at the counter electrode during the deposition step would rapidly oxidise any Sb present to the electrochemically inactive Sb(V). This cannot be measured by ASV at the potentials used for total inorganic As [23].

1.6 Project Aims

Analysis of As and other toxic metals on site gives a number of advantages over laboratory analysis and interest in more reliable field testing methods for As is growing [1, 4, 8]. Firstly, results are known immediately, so that fast action can

be taken and further interactive sampling can be carried out to rapidly evaluate the extent of the contamination [2]. Furthermore, traditional laboratory testing methods may not be realistic or affordable options in rural areas of poorer countries, such as Bangladesh and Vietnam, which have significant and widespread problems with As in drinking water [1, 4, 8]. While ASV has been shown to be a sensitive and accurate technique [7, 12, 26], problems with interferences remain [12, 26, 30]. The most common interferences for As analysis by ASV being Cu, sulfide and organics, which can often be present in natural waters, although the analyst will often not know beforehand which, if any of these interferents may be present in a given sample before analysis.

The broad aim for this study was to improve the ability to accurately determine As by ASV in samples containing interferences, by evaluating all three key interferent types in a single study. To achieve this, there are three objectives. The first objective was to confirm and quantify the interfering effects of key interferences on the determination of As by ASV and to provide baseline values to evaluate the pretreatment methods that are to be tested. It should be noted that this study is not intended to be an in depth study of the effects and processes of these interferents, as that is a broad enough subject to warrant a separate project in itself.

The second objective of this project was to investigate and compare the individual effectiveness of a number of traditional and novel approaches to overcome individual interferences separately.

The final objective was to determine the best combination of treatments to remove all three types of interference from a single sample. This was intended to lead to a single, albeit multi-step procedure, for pretreatment of samples, the interfering components of which are likely to be unknown. Given the widely acknowledged need for low cost field testing of As [1- 3, 8, 11, 12], and the unique position of ASV as a recognised instrumental technique capable of field analysis [3, 7, 10, 11], preference will be given to treatment methods that are easy to use, low cost and easily portable.

2 Methodology

2.1 Initial Set-Up of Anodic Stripping Voltammetry

ASV determination of As initially followed the PDV6000plus manufacturers recommended parameters (application notes) for determination of total inorganic As [28]. The analysis parameters from this application note are shown in Figure 2.1. The electrolyte was changed to make the results from this study applicable to other instrument models and more closely match the USEPA method 7063 [7], in which a gold plated carbon electrode with 0.25M HCl as the electrolyte was used. For this reason, alternate methods using other electrode materials were not considered, even when literature suggested these alternate materials may be more resistant to interferences. Analytical grade reagents and 18 megaohm deionised water were used throughout the study. Fresh, disposable analysis cups were used for each test. External standard comparison calibration was used as this method is specified in USEPA method 7063 [7].

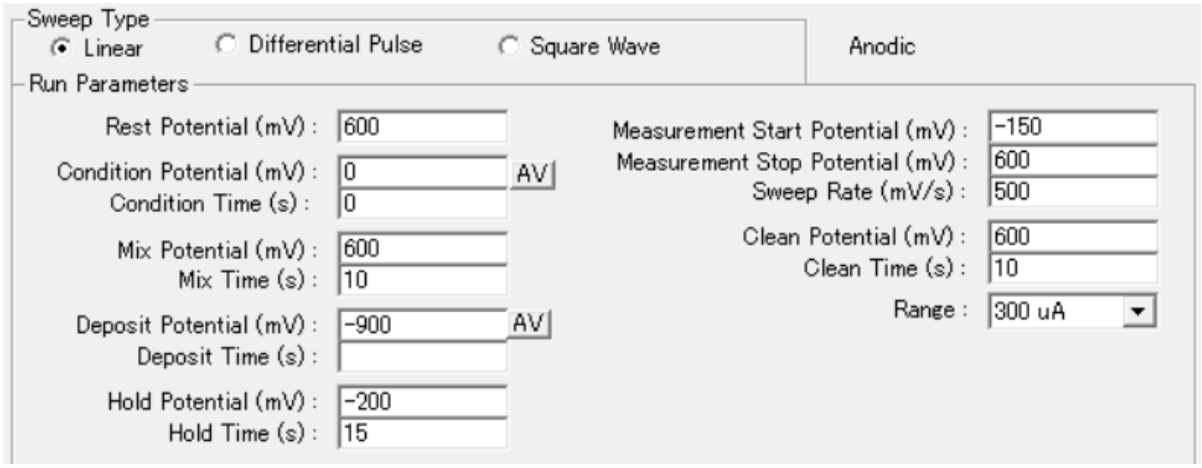

Figure 2.1 Instrument parameters for determination of total inorganic As at a thin gold film electrode.

Sample stock solutions consisting of 7 ppb As and 0.25M HCl electrolyte were prepared daily to minimise errors from pipetting and dilution between test solutions. Following electrode pretreatment, as described in the application note, and an initial blank 0.25M HCl solution, a clean 20mL aliquot of stock solution was analysed 5 times. This was repeated with a fresh aliquot of stock solution at least 3 times, or until the response was stable within a Coefficient of Variation (CV) of 5%. It was essential to have a stable response in the clean stock solution before progressing further, as this was to be the yardstick against which the effects of the interferences and pretreatment methods being tested would be measured.

The study was carried out in the following phases:

1. Firstly, for Objective 1, the individual interferents were tested to determine at which levels they produce a significant effect on the size of the As peak at a given concentration of 7 ppb (Phase 1).
2. Then, for Objective 2, each individual pretreatment method was tested with each relevant individual interferent in turn (Phase 2).
3. From the results of Phases 1 and 2, different treatment method combinations were to be chosen to be tried on test solutions containing all three interferents for Objective 3 (Phase 3).

2.1.1 Phase 1

This phase consisted of validation of the basic analysis method, especially focusing on stability testing, and the determination of the concentration of each individual interferent (copper, Triton-X and sulfide) to cause a significant drop in As response. It should be noted that this was not intended as a detailed study into the causes and effects of each interferent type. The aim was purely to determine levels of each interferent that could reliably show a noticeable effect, so that the pretreatment methods described in Section 1.5 and summarised in Table 2.1.1 could be evaluated.

Since the aim of this phase was to determine the level of interferent to be used in the following treatment tests, the interferent concentration had to be enough to cause a reasonably large drop in As response, easily distinguishable from expected analytical errors. For this reason, variations of up to $\pm$25% between the clean standard response and that of the standard containing interferent were to be considered acceptable in this phase. This was based on the USEPA practice of accepting $\pm$25% variation from true values in instrument validation studies and standard addition calibration checks [7].

Each interferent was assessed by adding an aliquot of the relevant interferent to the solution, and analysing 5 times (Figure 2.2). If the difference in response compared to a clean solution was not seen, this was repeated with a larger aliquot of interferent added until the variation of >25% from the original stock solution response was seen. At this point, the concentration of interferent added was to be recorded. The size of these added increments was to be determined experimentally since the magnitude of each interferent`s effect was not yet known.

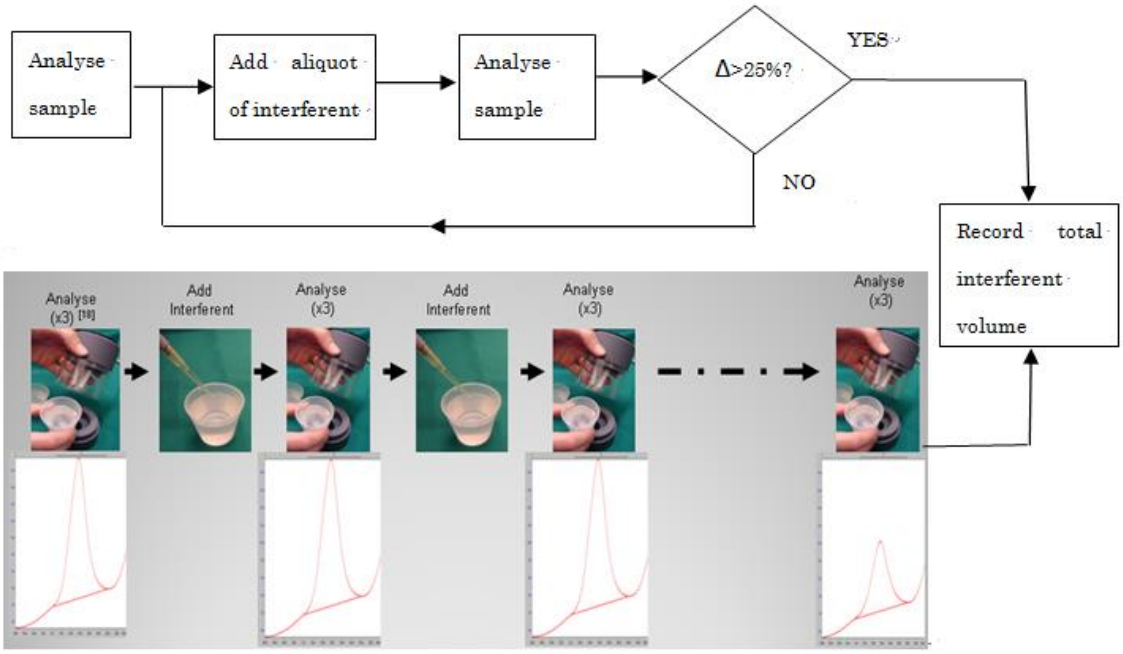

Figure 2.2 Schematic of general procedure for Phase 1.

Testing in Phase one highlighted some issues with the basic voltammetric analysis methodology that required modification before the project could be continued. These issues, and the steps taken to resolve them, are described in the following subsections.

2.1.1.1 Gold Film Method Development

Initial ASV determination of As was based on the parameters given in the application notes provided by the manufacturer with the instrument, but it was decided to use a simpler hydrochloric acid electrolyte rather than the more complex mix of HNO_3, NaCl and acetate buffer from the manufacturer. This was to better match USEPA method 7063 [7], in which a gold plated carbon electrode and hydrochloric acid electrolyte is used. The thin gold film was deposited from a solution of 40 ppm Au in 2% HCl at -500 mV for 300 seconds. Brief testing at the start of the project resulted in some modifications to the voltammetric parameters as described below, due to the required measurement concentration of 7 ppb As being close to the instrument's stated detection limit of 2 ppb and a possible loss of sensitivity due to the change in electrolyte. These tests resulted in minor changes to the parameters to increase sensitivity, namely increasing the deposition time to 150 sec from the recommended 120 sec and the sweep rate to 1 V/s from the recommended 0.5 V/s, as shown in Figure 2.3.

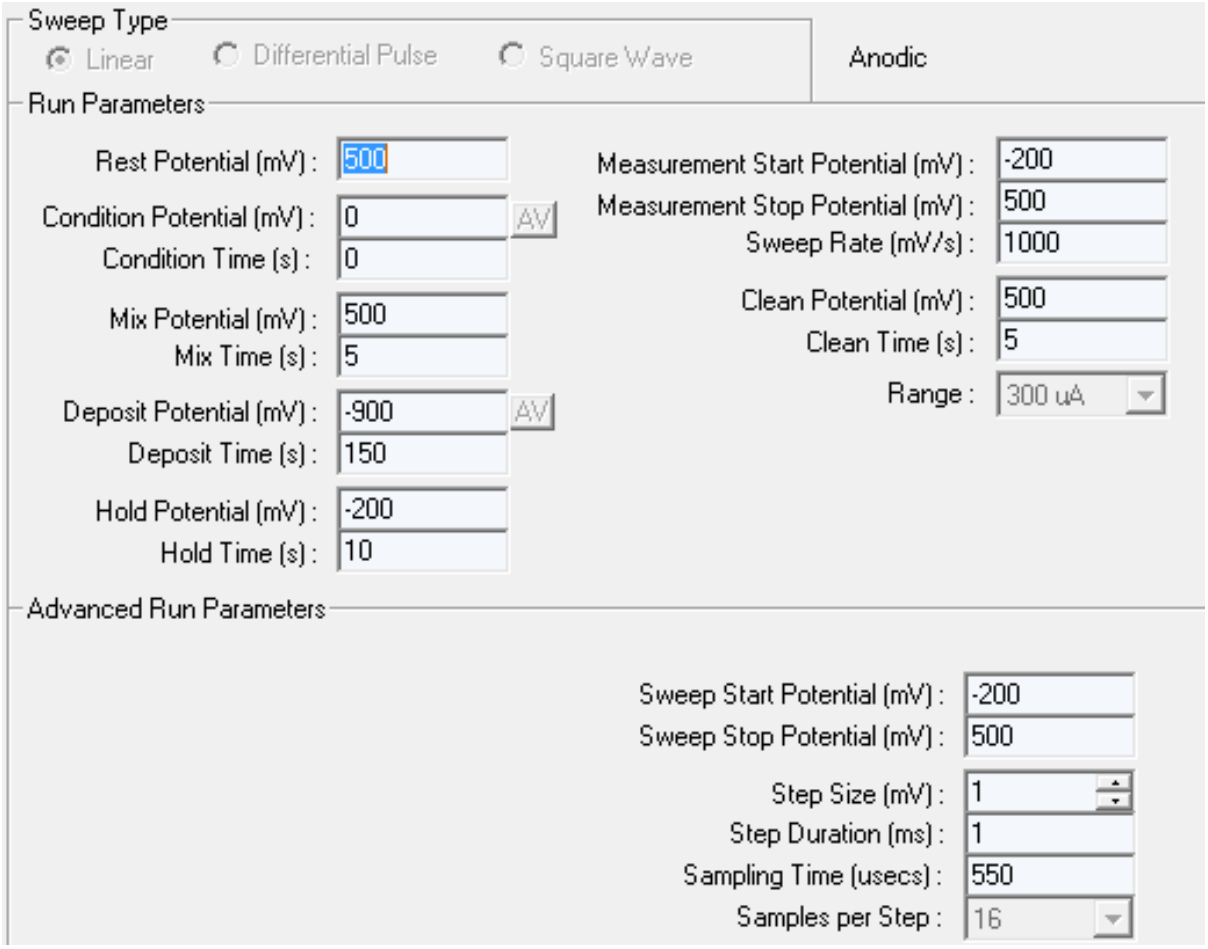

Figure 2.3 Adjusted As analysis parameters on gold film.

It was also found that the 5th repeat of each aliquot showed a dip in response compared to the previous 4 runs. This drop in the peak height could be explained by the consumption of the electrolyte (0.25M HCl) at both the working and counter electrodes during the relatively long (150 second) deposition step. The selection of HCl as electrolyte and importance of the concentration is discussed above in Section 1.4.1.

Working Electrode $2H^+ + 2e^- \rightarrow H_{2(g)}$ (Equation 2.1)

Counter Electrode $2\ Cl^- \rightarrow Cl_{2(g)} + 2e^-$ (Equation 2.2)

For this reason, subsequent aliquots were only analysed 3 times for stability rather than 5 and a new aliquot was used for repeat testing when further stability tests or interferent additions were required.

2.1.1.2 Rinsing Steps to Minimise Interferent Carryover Effects

Initial testing of the Triton-X interferent showed that addition of Triton-X to a test solution affected the response not only of that solution, but also the subsequent clean As stock solution, unless a cleaning step was carried out between tests. A procedure of rinsing the analysis cell first with 1M NaOH, then deionised water, then 0.2M HCl containing 0.0001M $KMnO_4$ was most effective in removing this carryover effect. 1M NaOH rinse was chosen because it is a suggested method for removing residual organic interference from the PDV6000plus manufacturer. However, using NaOH alone showed other adverse effects on the response, presumably due to residual NaOH reacting with the HCl electrolyte and possibly passivating the working electrode. Therefore, a second rinse step containing HCl to neutralise any residual NaOH and $KMnO_4$ to re-oxidise the electrode surface was added – the reasoning for selection of $KMnO_4$ as oxidising reagent is covered in Section 2.1.2. This HCl / $KMnO_4$ rinse was also tested by itself and found to be insufficient. If there was a drawback to this two-step rinsing method, it was that after each rinsing, the response of the interferent free solutions tested had a tendency to increase as shown in Table 3.3. It is not clear if this was due to removing some previously existing interferent in the analysis cell or some other sensitising effect on the Working Electrode such as electrode oxidation. Thereafter, this rinse step was carried out before all analyses, including interferent free solutions.

When this stronger rinsing regime was tested over multiple test solutions, a drop in response of close to 10% was seen after the analysis of about 5 sample solutions (see Section 3.1.1 for more details). While this is considerably less than the 25% drop cut off point for a significant interference selected for this study, it is still a significant error. It did not coincide with a change of stock solution and occurred after several quite stable analyses, making it hard to predict or compensate for with shorter calibration intervals. After further testing, it appeared that the NaOH-DI-HCl/$KMnO_4$ rinse was damaging the Au film after several runs, causing the response drop seen in Table 3.2, so it was decided to move onto testing with the more resilient solid gold electrode as an interim step. Thereafter, all testing carried out in Phases 1 and 2 utilized the solid gold electrode and the NaOH-DI-HCl/$KMnO_4$ rinse. Phase 3 reverted to the thin gold film electrode, as by that time, the treatment methods for removing the interferent had been shown to be effective, and carryover effects could therefore be reasonably discounted.

2.1.1.3 Solid Gold Electrode

The instrument manufacturer recommends slightly different operating parameters when measuring As with solid gold electrodes compared to a gold film. The main difference being an oxidation step at the alternating potentials of 0 & 800 mV, in an unstirred solution, at the start of each analysis. The daily electrode conditioning procedure also changed in accordance with the As at solid gold electrode application note. The new daily electrode conditioning procedure

was a firm electrode polish, followed by conditioning with a higher concentration As solution in the same 0.25M electrolyte. Even with this extra built-in oxidation step, and high concentration As solution conditioning, the sensitivity was noticeably lower than the gold film electrode, so sweep rate was increased further to 2.5V/s to compensate for that, as described in Section 1.4.4. Parameters used for analysis of As with solid gold electrode are shown in Figure 2.4.

First tests of stability with these parameters and the NaOH-$KMnO_4$/HCl rinsing system showed a slow increase in response over the first few solutions. The slow increase in response was suspected to be a result of slow oxidation of the electrode surface by the $KMnO_4$ rinsing step, thus increasing sensitivity in accordance with the theory of solid gold electrode oxidation described in Section 1.4.3. It was also considered possible that an ongoing cleaning effect of the gold electrode by the NaOH step was a factor, or that electrode roughness was increasing. To test this, the following day, the conditioning procedure was changed from electrode polishing – high concentration As solution – blank – standard, to adding a 5 minute rinse in the NaOH solution and then another 5 minutes in the HCl/$KMnO_4$ solution after the polishing step and before the high concentration As solution. Results following this daily routine are shown in Table 3.4.

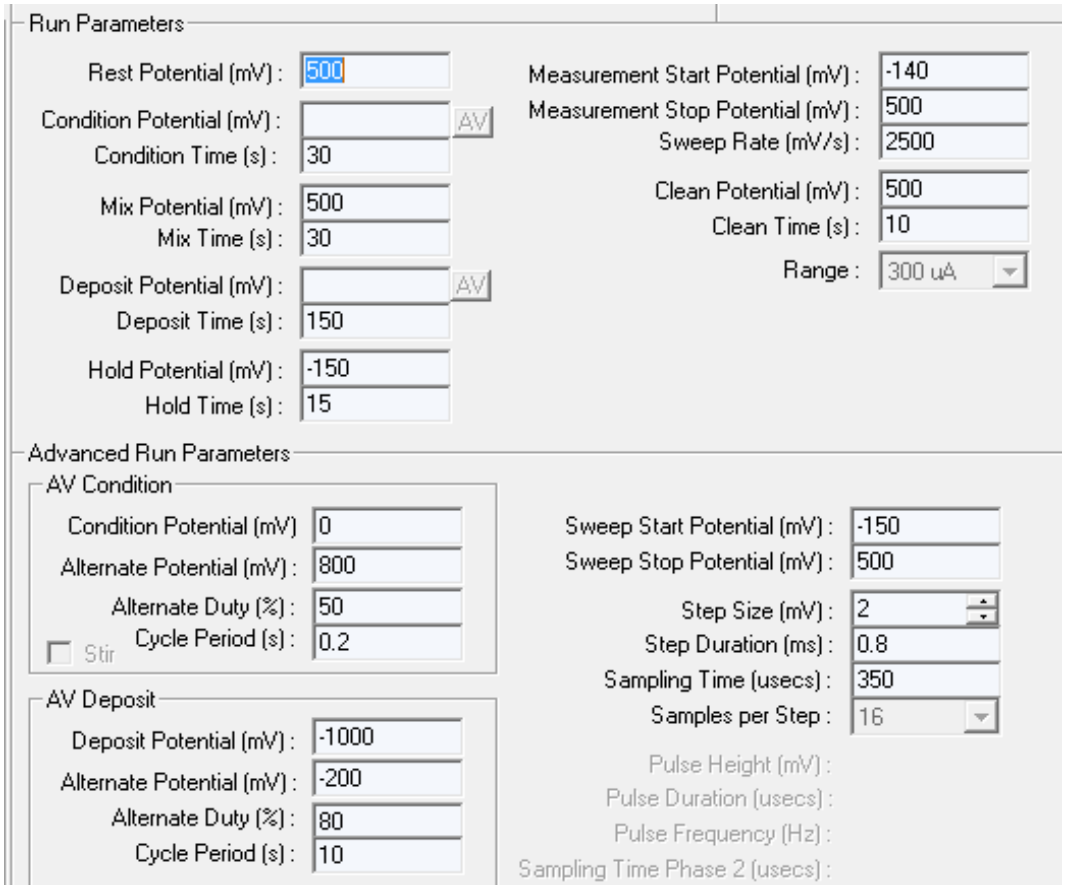

Figure 2.4 Parameters for As analysis with solid gold electrode.

It was suspected that the rinsing with $KMnO_4$ was slowly oxidizing the gold electrode surface further, thus increasing sensitivity, and the 5 minute rinse allowed the electrode surface to reach a stable oxidised state faster. It is not clear if the 5 minute NaOH rinse is necessary, though it could have some cleaning effect and is recommended as a contamination removing procedure in the instrument application notes when contaminated samples have been measured or the cell or electrode history is uncertain.

In a separate development, after some periods of inactivity, the solid gold electrode was found to show a peak in blank solutions. Peak size was almost unchanged when deposit time was changed from 150 seconds to 1 second, indicating there was something on the surface of the working electrode rather than a metallic contaminant in the bulk solution. This surface contaminant was suspected to be an interaction of the gold with chloride at positive or floating potentials since it was seen both after inadvertently applying highly positive potentials (+1V) to the electrode in HCl solutions, and after leaving the electrodes overnight in an HCl solution with the PDV6000plus instrument powered down, but was not seen after testing the high voltage conditioning potentials mentioned by Salaun, *et al.* [18, 23] in chloride free acid solutions. Normal polishing with the kit provided with the PDV6000plus instrument, helped to reduce the peak a little, but was very slow and tedious. A more robust polish, with polishing paper from the maintenance kit for a gold electrode used in a WTW (Wissenschaftlich Technische Werkstätten) dissolved oxygen meter, was found in the OSU laboratory and tried. Polishing the PDV6000plus gold working electrode with this paper left a visible Au residue on the paper and completely removed the background peak as shown in Figure 2.5. Response for standard As test solutions thereafter was stable, although the baseline was higher, presumably due to the coarser grain of the WTW paper roughening the gold electrode surface and thus effectively increasing its surface area.

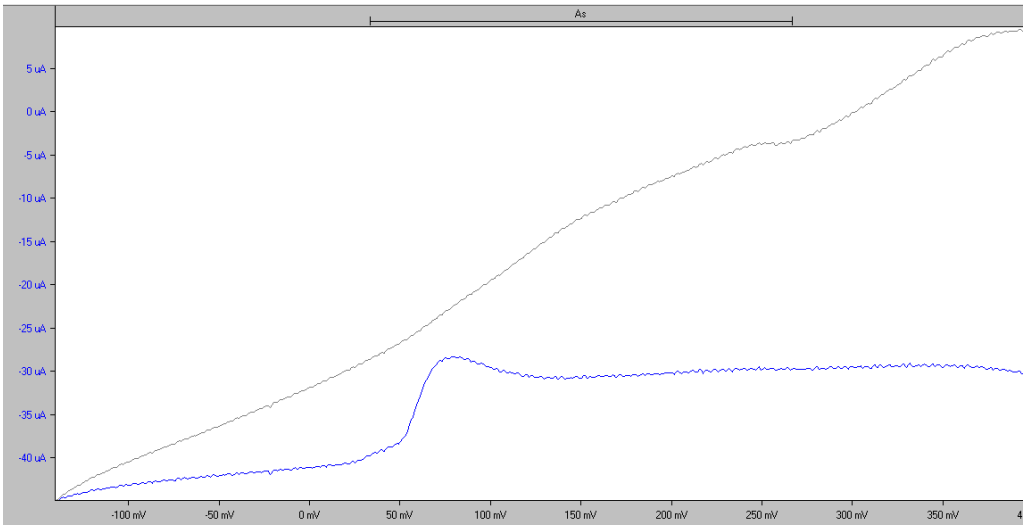

Figure 2.5 Voltammograms of blank solution showing background peak before (blue) and after (grey) use of WTW polishing paper. Vertical axis is Current (µA) and horizontal axis is Potential (mV).

2.1.2 Phase 2

In Phase 2, each individual pre-treatment method was tested with each relevant individual interferent. Appropriate pretreatment methods were tested for each interferent (Table 2.1), based on known effects of those pretreatments on these or other interferents, as outlined below. Some pretreatments were expected to remove the effects of more than one interferent, but no pretreatment was expected to work on all three interferents. Note that no single pretreatment was expected to target all interferences, hence the expected requirement for a combination of treatments, which is examined in Phase 3.

Table 2.1 Interferents and potential pretreatments ("Y" indicates where a treatment was expected to effectively treat an interferent).

Interferent	**Pretreatment Method**					
	UV	O_3	Chemical Oxidation	Ultra-Sonic Deposit	Resin Column	Selective Electro-plating
Copper					Y	Y
Sulfide	Y	Y	Y	Y		
Organics	Y	Y	Y	Y		

Ultraviolet irradiation is a standard ASV pretreatment method for organic interferences [19, 33]. It is effective in breaking down organic compounds both by direct interaction of ionising radiation with the organic molecule and by generation of oxidising radicals such as H•, •OH, H_2O^+ & H_2O_2, in the sample, due to interactions of UV light with water molecules [37]. While no references for the effect of UV irradiation on sulfide were found, the ready oxidation of sulfide by dissolved oxygen in natural waters [43] made UV a likely candidate to remove sulfide interference also. An MTI UVI-4000 UV irradiation system was available in the Osaka Sangyo University (OSU) lab for this work.

Ozone treatment is a common method for removing organic pollutants in drinking water and other water treatment systems [37]. Not only is ozone itself highly oxidising (E^0 for O_3 in H_2O = 2.07V), but its decomposition in water also forms other highly oxidising radicals such as ·OH [37]. While no specific references were found for use of ozone in in removing sulfides, the fact that sulfide is known to oxidise to sulfate even in naturally oxidised water [43], it seem reasonable to expect ozone to have some effectiveness in oxidising sulfide.

While ozone generators are commercially available and used for industrial and domestic applications, most were prohibitively expensive and a cheaper domestic system was expected to be sufficient for the purpose of this project. Details of the ozone generator used and its incorporation into a portable system are given in Section 2.2.1 Initial testing using the ozone oxidation procedure on clean 7 ppb stock As solution showed a large and distinguishable peak near the As peak (Figure 2.6). Further investigation revealed this was coming from the air pump, not the ozone generator, and the problem was resolved by adding an air filter between the air pump and ozone generator. The nature of this interference was not determined, but is thought to be an unidentified metal wearing from mechanical parts within the air pump.

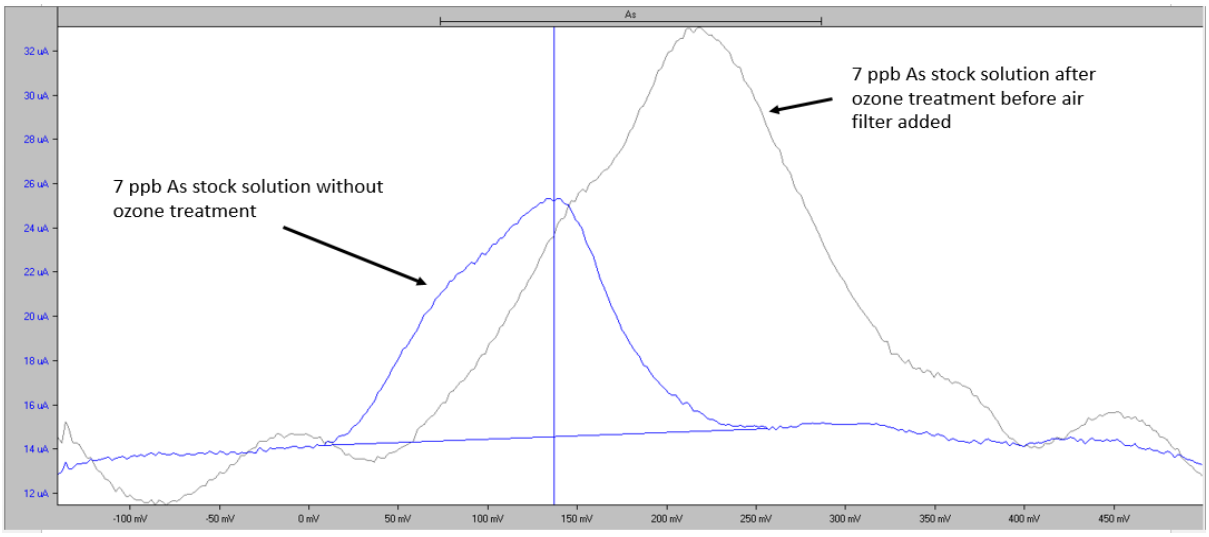

Figure 2.6 Voltammograms showing effect of unfiltered air used in ozone system. Vertical axis is Current (μA) and horizontal axis is Potential (mV).

The method for ultrasonic pre-treatment was based on that used by Compton *et al.* [21, 32, 40-42] where in several studies it was shown to be effective in overcoming organic interferences in various samples. This technique is thought to be effective due to formation of microbubbles on the surface of the working electrode which quickly collapse in on themselves causing strong shear flows across the electrode surface which are thought to have a cleaning effect which prevents electrode fouling [21]. Consequently, an ultrasonic horn was purchased and the analytical cell modified so that the horn replaced the stirrer motor in the analysis cell. Since the usual 5V voltage delivered to the stirrer motor was insufficient to drive the horn, a relay mechanism providing the correct voltage was made.

Resins and the procedures for their use in cation exchange for the separation of metal species are readily available [46, 47]. These remove metals from a solution passed through them by adsorbing the metal ions onto the resin and releasing another cation back into solution, generally H^+. Since inorganic As is present in natural waters as an anion (Figure 1.1) due to interaction with surrounding

water molecules, it does not get adsorbed by the resin. Standard manufacturer procedures were followed to gain maximum efficiency. The procedure and a picture of the disposable syringe system used for these tests are given in Section 2.2.3.

Due to the wider claimed working pH range of 2 to 6 [47], the Mitsubishi Diaion resin was chosen for testing. Due to the relative complexity of As analysis, it was decided to do preliminary testing using a much simpler method for Cu on a gold electrode to determine the effectiveness of the resin in removing Cu before progressing on to testing its effect on As in the sample. A number of resin pretreatment methods were tested before successful results were seen. Using the resin directly as supplied and after acid or caustic and acid washing were unsuccessful. Best results were seen when resin was prepared by leaving in deionised water overnight before use. Once prepared by this overnight soaking, 2mL of resin was put in a 25mL plastic syringe with a 0.45µm filter on the end. 20mL of sample was passed through the syringe. Blank runs were carried out both to ensure that clean sample passed through the resin column was not contaminated with any interfering metals and that the As could pass through without statistically significant loss.

Electrolytic processes to remove Cu from contaminated water have been demonstrated in remedial applications [50, 51] and less commonly as a pretreatment for ASV [37]. This works via the same process used in the ASV deposition step illustrated in Figure 1.3. A negative potential is applied to a large electrode, which reduces the dissolved Cu ions to the metallic state onto the electrode surface as follows.

$$Cu^{2+} + 2e^{-} \rightarrow Cu^{0} \qquad \text{(Equation 2.3)}$$

Since each metal has a characteristic potential below which this process occurs at a given electrode [21, 44, 52], it was expected that careful control of the applied potential will allow selective removal of Cu, but not As. No evidence was found in the literature of this technique being used for interferent removal purposes, although a similar technique has been used to pre-concentrate low levels of Hg in air and water samples for various techniques. However, its demonstrated ability to deposit Cu, as seen in Figure 1.6, made it a useful candidate to explore as a pretreatment process for ASV.

The electrolytic or selective electroplating method of removing Cu required a purpose built electrochemical cell. Since this process is essentially the same as the ASV deposition step, but with a potential that only reduces the dissolved Cu and not As, this new cell was designed to be driven by the PDV6000plus

instrument used for analysis but a much larger working electrode. Details of this assembly are given in Section 2.2.4.

Four oxidants, namely dichromate, chlorine gas, Cl_2, H_2O_2 and $KMnO_4$, were initially considered for interferent oxidation testing. Dichromate was quickly rejected as it is known to be toxic. Chlorine gas was also rejected because it is generated in the cell at the counter electrode, as described in section 1.4.1 and it was preferred to use oxidants that would not otherwise be present in the analysis cell. This left two oxidizing agents which were readily available in the laboratory - H_2O_2 and $KMnO_4$. $KMnO_4$ was initially preferred due to its greater stability and strong purple colouration which was hoped could be used as an indicator of it's continued oxidising efficacy in reducing conditions. Attention therefore initially focussed on $KMnO_4$. One possible issue was whether the manganese component would be electro-active and interfere with the As analysis. To investigate this, a Mn standard was initially run to determine the reduction and oxidation potentials. Due to the hydrogen reduction wave potential on a gold electrode being more positive than the Mn peak potential in an acid electrolyte [53] measuring Mn in the As electrolyte would not be possible. A higher pH acetate buffer electrolyte was therefore tested as this is the electrolyte used for Mn analysis at Hg film electrodes in the PDV6000plus instrument application notes. It was found that, while electro-active and giving a peak that is suitable for voltammetric analysis, the Mn required a more negative deposition potential than that used for As analysis, with the oxidation peak in the region of -1100 to -900 mV as shown in Figure 2.7, which was close to that reported by Gibbon-Walsh *et al.* [54] for Mn in seawater. Since the method used for As in this study was to deposit the As at alternating potentials (-900 & -200 mV) to minimise interference by other metals such as Fe, Zn & Pb, no significant build-up of Mn on the electrode was expected.

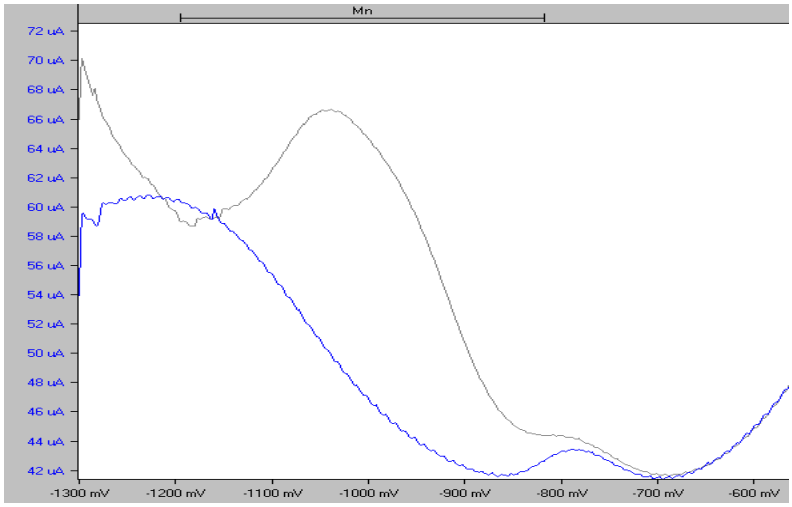

Figure 2.7 Voltammograms of 0 ppb (blue) & 50 ppb (grey) Mn in acetate buffer on solid gold electrode. Note Mn peak potential between -1200 mV and -800 mV. Vertical axis is Current (μA) and horizontal axis is Potential (mV).

To further ensure no negative effect was caused by addition of $KMnO_4$ to the As test solutions, the same amount as was used in the rinse solutions was added to

a clean test solution. This resulted in an increase in As peak size, even after the 5 minute NaOH & $KMnO_4$ preliminary daily conditioning described in Section 2.1.1.3.

Initially, a test solution with 4 ppm sulfide and 200µL 0.01M $KMnO_4$ solution was tested, since this was the amount used in the rinse solution. However, this amount of $KMnO_4$ failed to restore the As peak, although it did bring the background closer to that of a sulfide free solution. Since the addition of 200µL 0.01M $KMnO_4$ to the sulfide test solution also failed to change the solution to the same deep purple colour of the rinse solution or clean test solution, it was decided to add more $KMnO_4$ until a similar colour was achieved and remained for 5 minutes after the addition of the last aliquot of $KMnO_4$. This colour change occurred after adding a total of 500µL 0.01M $KMnO_4$.

A brief investigation was also carried out for H_2O_2 which showed that with 10µL of 30% H_2O_2 in the analysis cup, the As response was greatly reduced as shown in Figure 2.8. While it is possible that careful addition of the correct amount of H_2O_2 could also prevent the sensitivity issues noted above and resolve some interferences, the known instability of H_2O_2 and lack of any visible indicator when the correct amount of H_2O_2 is added makes this impractical in field situations, so further investigation into H_2O_2 oxidation was not pursued.

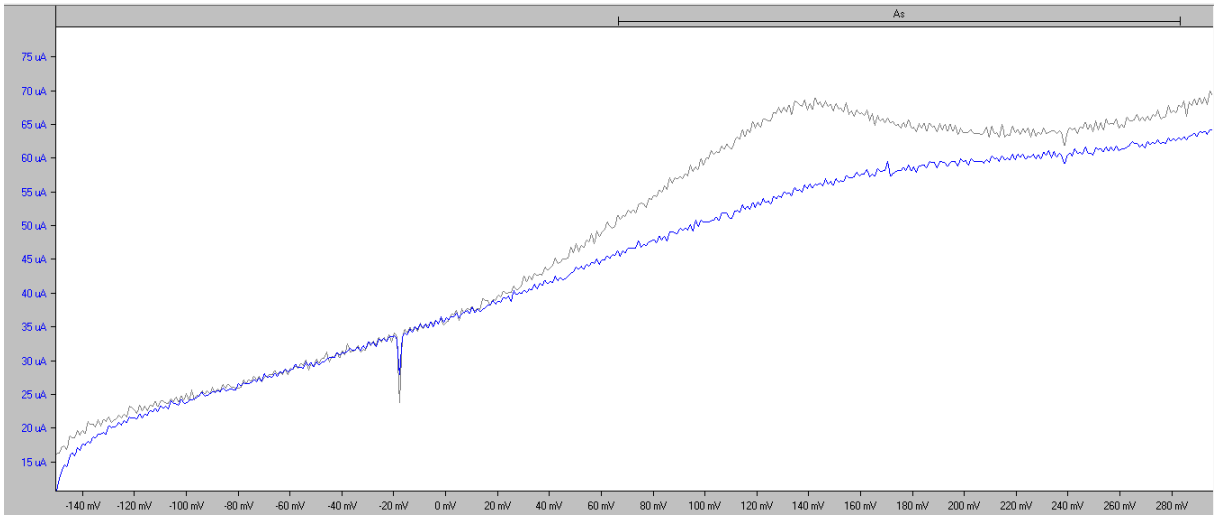

Figure 2.8 Voltammograms showing 7ppb As before (grey) and after (blue) addition of 10µL 30% H_2O_2. Vertical axis is Current (µA) and horizontal axis is Potential (mV).

2.1.2.1 Phase 2 - Procedures

Each pretreatment method was first tested on a 7 ppb As standard without any interferent added to ensure no adverse effects from the pretreatment methods themselves. The response of each individual interferent to each individual

treatment was then analysed at the interferent concentrations determined to cause an unacceptable difference in response in Phase 1. For each day's work, a stock 7 ppb As in 0.25M HCl solution was made, aliquots of which were spiked with interfering levels of the relevant interferent determined in Phase 1 and treated as required.

After each of the various treatments, including those on the 7 ppb As standard solution without interferent, a percentage recovery comparison of As in the treated and untreated solutions was used to determine the most promising treatment methods, the percent recovery (R) being calculated from the following equation, where H_T is the measured peak height of the test solution and H_S is the measured peak height of the clean stock solution sample.

$$R = (H_T / H_S) \times 100 \qquad \text{(Equation 2.4)}$$

Since each interferent was being added at a level which caused at least a 25% difference in response in Phase 1, any treatment method which failed to give a % recovery (R) between 75% and 125% in this test was rejected for the remainder of the project. This is illustrated in Figures 2.9 and 2.10 below.

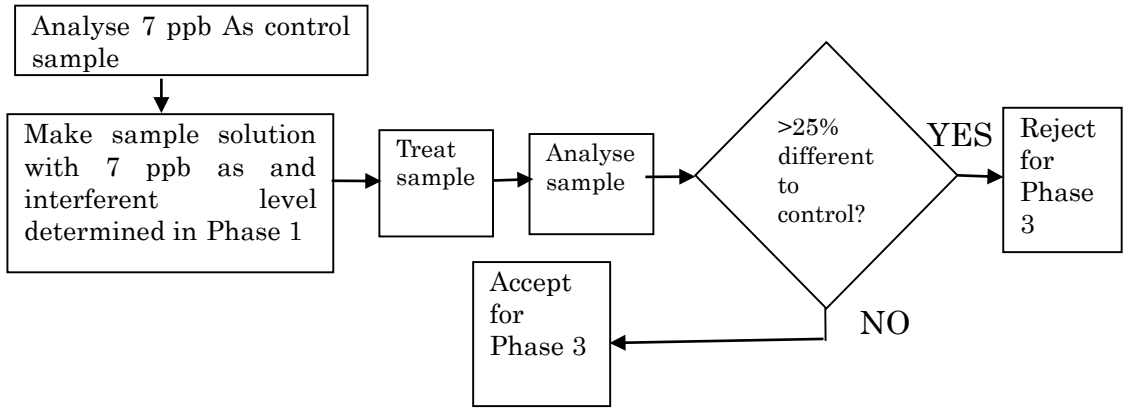

Figure 2.9 Flow diagram for process of Phase 2.

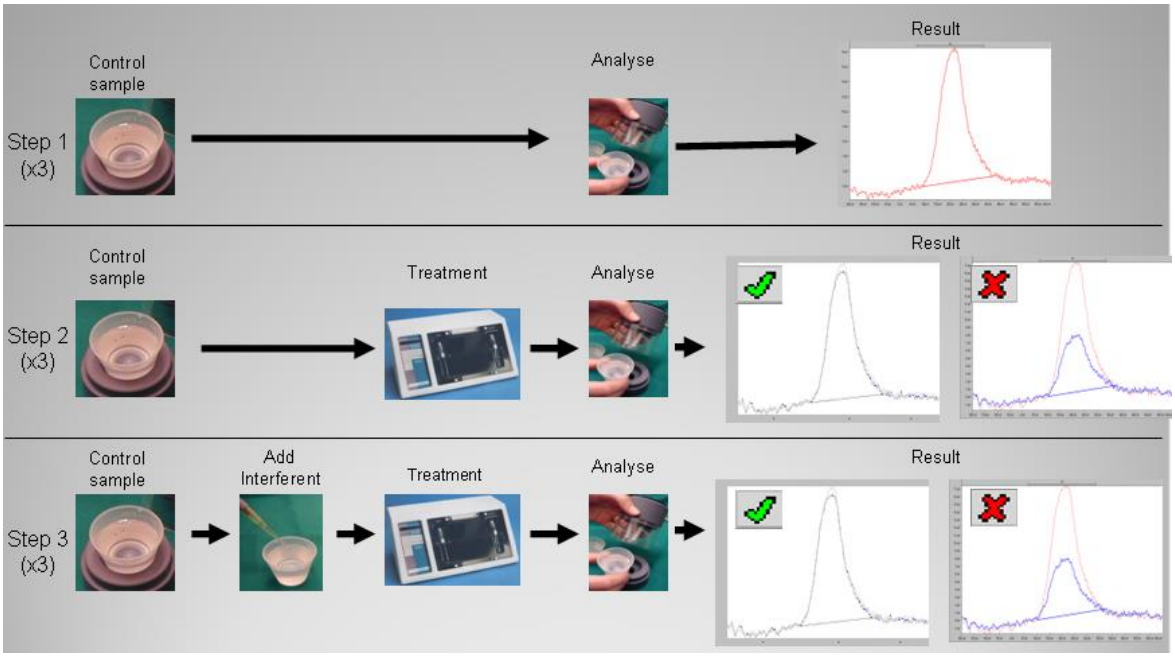

Figure 2.10 Schematic of process for Phase 2.

2.1.3 Phase 3

Once the best pretreatment method for each interferent type had been selected, the different combinations of treatment methods were tried in solutions containing all three interferents (as shown in Figure 2.11 below).

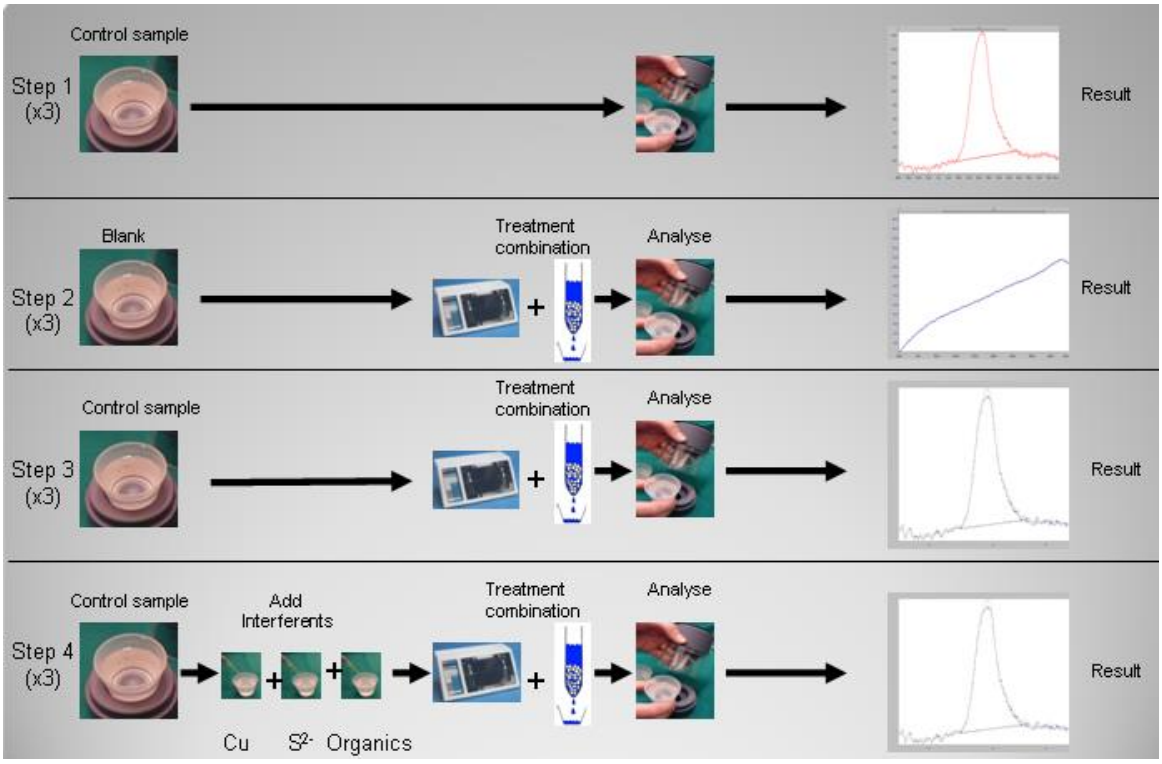

Figure 2.11 Schematic of process for Phase 3.

Since the change to solid gold electrodes described in Section 2.1.1 was made in response to residual interference from organic and sulfide interferences, and that those interferences were shown to have been removed by the pretreatment methods selected after the testing in Phase 2, it was decided to return to a gold film electrode for Phase 3. This was to maintain consistency with the USEPA method and the superior sensitivity and ease of electrode preparation seen with the gold film electrode compared to the solid gold electrode in Phase 1. Since $KMnO_4$ oxidation had by this stage been selected as one of the pretreatment methods, requiring all analysed solutions to contain 0.0001 M $KMnO_4$, the first test of Phase 3 to be carried out was a test to ensure that the gold film instability described in Section 3.1.1 and shown in Table 3.2 was a result of the NaOH rinsing as expected, and not caused by the $KMnO_4$ component of the NaOH-HCl/$KMnO_4$ rinsing regime. Results for this test are shown in Table 3.13 and confirmed the suitability of a mixed HCl-$KMnO_4$ electrolyte solution with the gold film electrode, which was used for the remainder of the study.

2.2 Reagents and Equipment

A range of reagents (Table 2.2) and specialised equipment (Table 2.3) was used in the analysis and pretreatment of test solutions in this project. All tests were carried out using the PDV6000plus instrument. The electrolyte was changed to make the results from this study applicable to other instrument models and more closely match the USEPA method 7063 [7], in which a gold plated carbon electrode with 0.25M HCl as the electrolyte was used. The UVI4000, a new design of UV digester (Figures 2.12 & 2.13) by the same manufacturer as the PDV6000plus instrument differs from the previous UVI3000 mainly in having a more powerful 18W lamp and its smaller size due to it being controlled by an external PC. This makes the UVI-4000 more portable, although the mains power required for operation still limits it for the field testing application envisaged in this study. The usual premixed sample (7 ppb As in 0.25M HCl) was digested with a setting of 20 minutes at a set sample volume of 25 ml. This system works by pumping the sample into the reaction chamber, which is a UV transparent quartz glass coil wrapped around an 18W Hg vapor UV lamp. Once the exposed portion of the quartz coil is full of the sample, the software stops the pump for the pre-set time, in this case 20 minutes. Since the volume of the UV exposed quartz glass coil is only 15 mL, 2 digestion steps were required to digest the 20ml sample volume used for this test. Ideally another hour should be allowed to run a blank between each sample, making this quite a slow process.

Table 2.2 Reagents Used.

Item #	Reagent	Supplier / Grade	Purpose
1	Arsenic standard 1000 ppm	Specified standard materials of Measurement Act (Wako Pure Chemical Industries)	Calibration standard
2	Gold standard 1000 ppm	Specified standard materials of Measurement Act (Wako Pure Chemical Industries)	Thin gold film electrode preparation
3	Copper standard 1000 ppm	Specified standard materials of Measurement Act (Wako Pure Chemical Industries)	Accurately measure effect of Cu interference and efficiency of Cu removal treatments
4	Hydrochloric acid, 10M	Metal analysis grade (Wako Pure Chemical Industries)	Analysis electrolyte (0.25M) and sample preservation
5	Acetic Acid, Glacial	Super special grade (Wako Pure Chemical Industries)	Component of acetate buffer
6	Sodium Acetate	Sigma-Aldrich, Sigma Ultra	Component of acetate buffer
7	Nitric acid, 16M to 0.1M	Electronic industry grade (Kanto Kagaku)	Analysis cell cleaning and sample preparation.
8	Perchloric acid	Reagent grade, Japanese Industrial Standards (Wako Pure Chemical Industries)	Solid gold electrode preparation
9	Potassium Chloride solid	Reagent grade, Japanese Industrial Standards (Wako Pure Chemical Industries)	Reference electrode electrolyte when made 1M in DI water
10	Hydrogen peroxide 30%	Reagent grade, Japanese Industrial Standards (Wako Pure Chemical Industries)	Proposed sample pretreatment for organic interference
11	Sodium sulfide	Reagent grade, Japanese Industrial Standards (Wako Pure Chemical Industries)	Measure effect of sulfide interference and efficiency of sulfide removal treatments
12	Sodium Hydroxide – solid	Reagent grade, Japanese Industrial Standards (Wako Pure Chemical Industries)	Removal of residual organic contamination from analysis cell and other containers
13	Triton-X	Chemical grade (Wako Pure Chemical Industries)	Simulate organic interference and test effectiveness of organic removal systems
14	Resin Ion Exchange	Mitsubishi Diaion CR-20	Selective removal of Cu without As removal.
15	Potassium Perman-ganate	Reagent grade, Japanese Industrial Standards (Wako Pure Chemical Industries)	Pretreatment of sulfide and mild organic contamination.

Table 2.3 Equipment Used.

Item #	Item	Supplier	Proposed Purpose
1	PDV6000plus voltammetric analyser	Modern Water Ltd (UK)	Determination of As and Cu in test solutions by ASV
2	Glassy carbon Working Electrode 3 mm diameter	Modern Water Ltd (UK)	Determination of As with PDV6000plus using thin gold film method
3	Solid gold Working Electrode 3 mm diameter	Modern Water Ltd (UK)	Determination of As with PDV6000plus using solid gold Working Electrode method
4	Ag/AgCl/1M KCl Reference Electrode	Modern Water Ltd (UK)	Determination of As with PDV6000plus
5	Platinum Counter Electrode	Modern Water Ltd (UK)	Determination of As with PDV6000plus
6	UVI3000 & UVI4000 UV digesters	Modern Water Ltd (UK)	Destruction of organic interferences by UV irradiation
7	Ozone generator L/75	Adex (Japan)	Destruction of organic interferences by ozone oxidation
8	Ultrasonic horn, VC-80	Labsonic (China)	Destruction of organic interferences by ultrasound

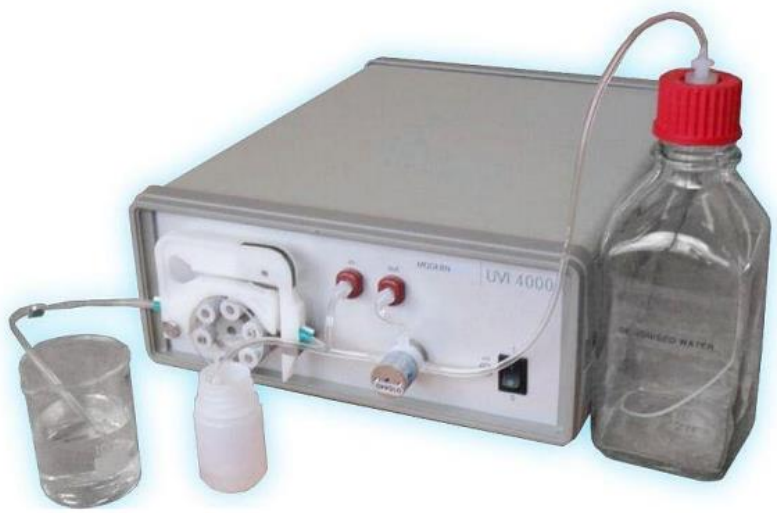

Figure 2.12 UVI4000 UV digestion system. Containers shown from left to right are for raw sample, digested sample and rinse water - image from instrument manual.

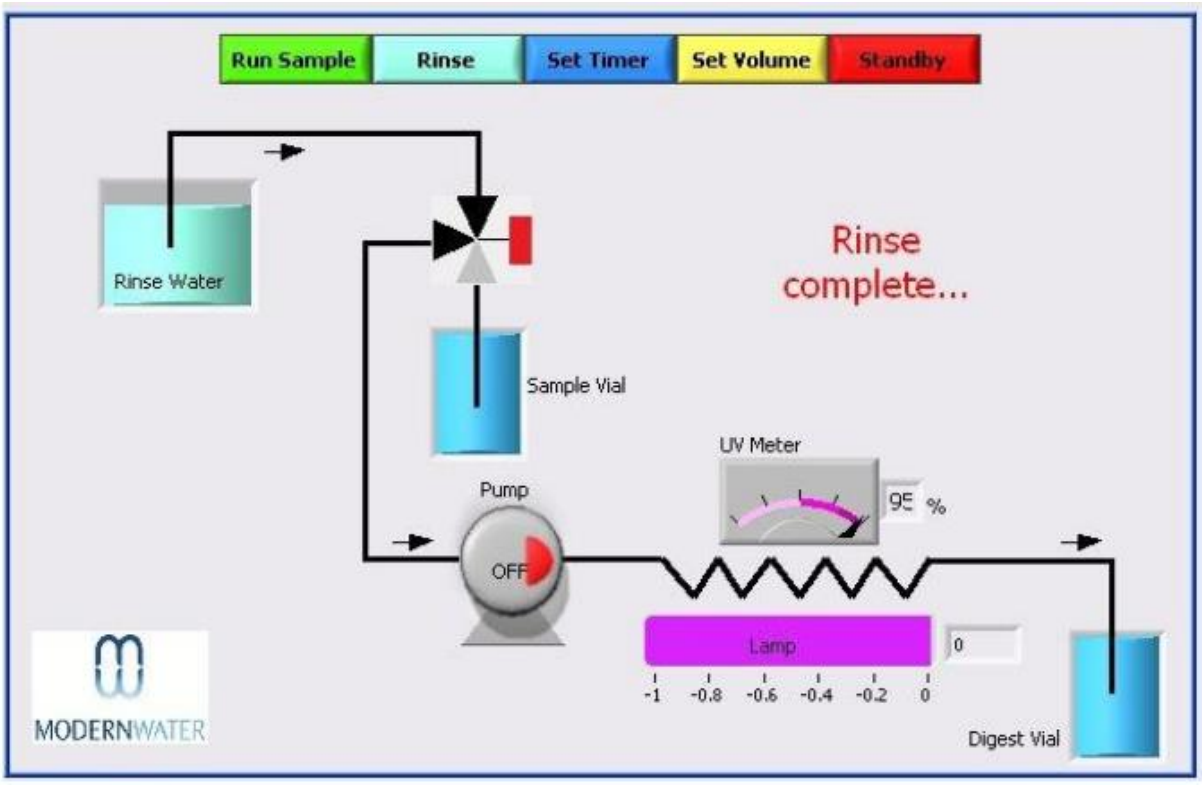

Figure 2.13 Screen capture from UVI4000 software showing operation schematic.

Some of the pretreatment methods evaluated in this study required custom made equipment or modifications to existing equipment. A short description of each of these is given below.

2.2.1 Ozone Pretreatment System

In principle, ozone oxidation should pretreat the sample by oxidizing interferences like organic compounds and sulfide [37, 38]. A commercial ozone generator, designed for use with domestic aquariums was purchased along with a small air pump. An air-line ran from the air pump to the ozone generator, via a small desiccator supplied with the ozone generator intake. This pushed the ozonated air out of the ozone generator and into a 30 or 50mL HDPE bottle containing the sample to be treated. Exhaust air coming from the bottle was directed to a 1L bottle of tap water to absorb residual ozone and all tube holes into these bottles were sealed with super glue. This layout is shown in Figure 2.14.

Since both the air pump and ozone generator required 110V AC power and a portable system was envisaged, all components were fitted into a small carrier case and a 12V motorcycle battery and car cigarette lighter to 110V AC converter were also fitted to the carrier case to allow field use, although in practice, direct AC power was almost always used for experimental work.

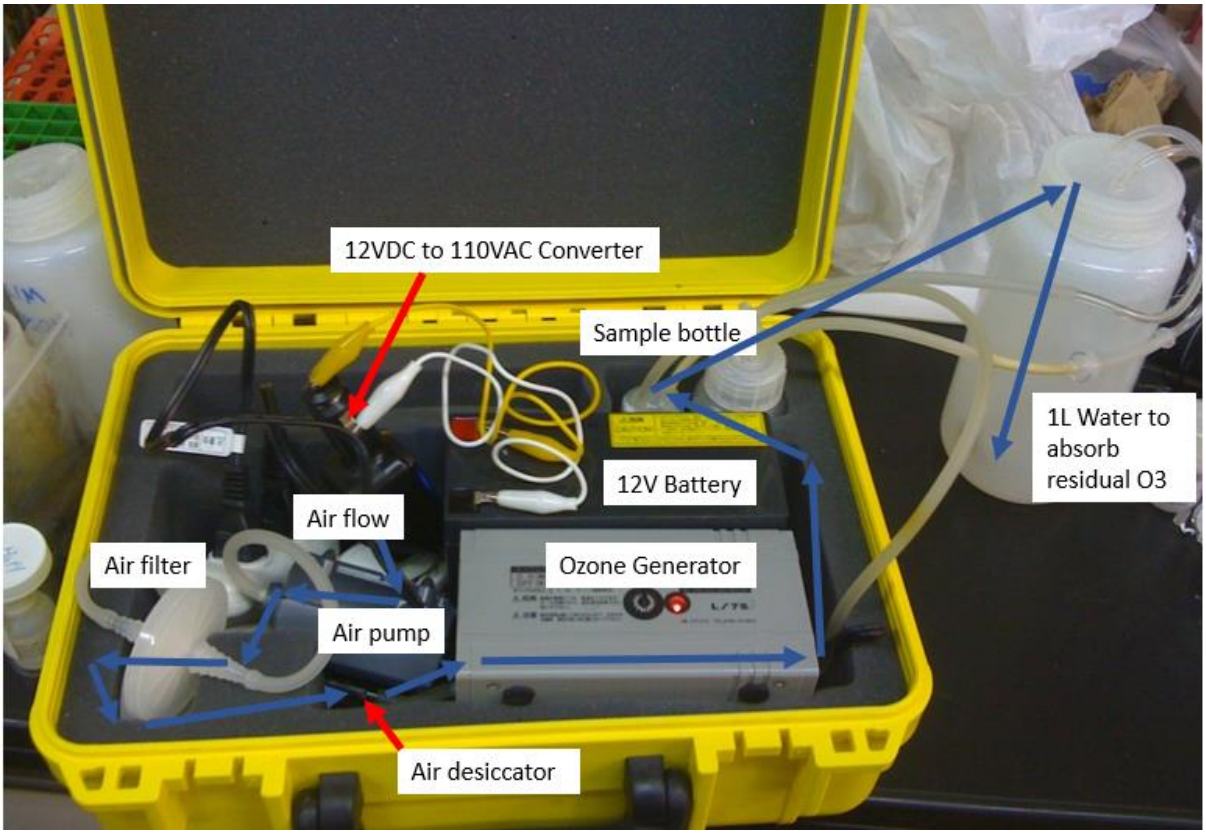

Figure 2.14 Ozone pretreatment system.

2.2.2 Ultrasonic Horn Integration with Analysis Cell

This ultrasonic horn (Labsonic, VC-80) used in this study had a fixed output of 80 Watts at 23 KHz. It was originally intended to use the horn in place of the in situ analysis cell stirrer, in a similar fashion to the experiments carried out by Compton *et al.* [21, 32, 40-42]. To do this, the horn was connected to the PDV6000plus instrument by removing the stirrer from an old analysis cell and inserting the horn, held in place by a retort stand. A crude relay box was made which allowed the PDV6000plus instrument's normal stirrer output to activate the horn (see Figure 2.15) in place of the normal analysis cell stirrer since the 5V output from the PDV6000plus potentiostat was not enough to activate the ultrasonic horn. This was to remove human error that would otherwise have occurred if the horn was activated manually by the operator during the analysis cycle.

Figure 2.15 PDV6000plus with ultrasonic horn agitated analysis cell (left) and activation relay (lower right).

2.2.3 Copper Removal using Resin System

Early tests with the selected resin beads were intended to simply swirl the beads in a small beaker or analysis cup. However, it was found that the beads were small enough to be drawn into the 10mL pipette used to transfer treated sample, and hence would also be transferred into the analysis cup where the acid HCl electrolyte would release any interfering metals adsorbed on the transported beads. It was therefore decided to use a filtration system to separate the beads from the treated sample after treatment. This was done using readily available disposable 20mL syringes with 0.45µm screw on filters, often used to separate labile from non-labile metals [7, 10]. In this configuration (see Figure 2.16), the filter was first attached to the syringe and then the plunger removed and 5mL of resin (soaked overnight in DI water to prepare in accordance with manufacturer's instructions) was put into the syringe. 20mL of sample was then poured into the syringe and the plunger re-inserted into the top of the syringe, just enough to seal the syringe top. The syringe was then shaken for 5 minutes

before the treated sample was extracted into a clean container by pushing the plunger down slowly.

Figure 2.16 Cu removal resin package with syringe / filtration assembly.

2.2.4 Copper Removal using Electrochemical System

In this system, the Cu ions in the sample were to be electrolytically deposited onto a piece of thin gold foil approximately 5cm^2 using the same principal as the ASV deposition step described in Section 1.3.1. Since control of the applied potential at the gold foil in such a system is critical, it was decided to use the PDV6000plus instrument to control this potential. A simple electrochemical cell was made utilising the reference and counter electrodes from the PDV6000plus analysis cell, with the gold foil acting as a working electrode. These were placed in a 100mL plastic container, along with a magnetic spin bar on top of a standard laboratory magnetic stirrer (see Figure 2.17). Since this was an external treatment method and timing of the stirrer function was not considered to be critical, the magnetic stirrer was operated manually and the required potential set separately with the PDV6000plus PC software rather than controlling the stirring via a relay, as was used for the ultrasonic horn shown in Section 2.2.2.

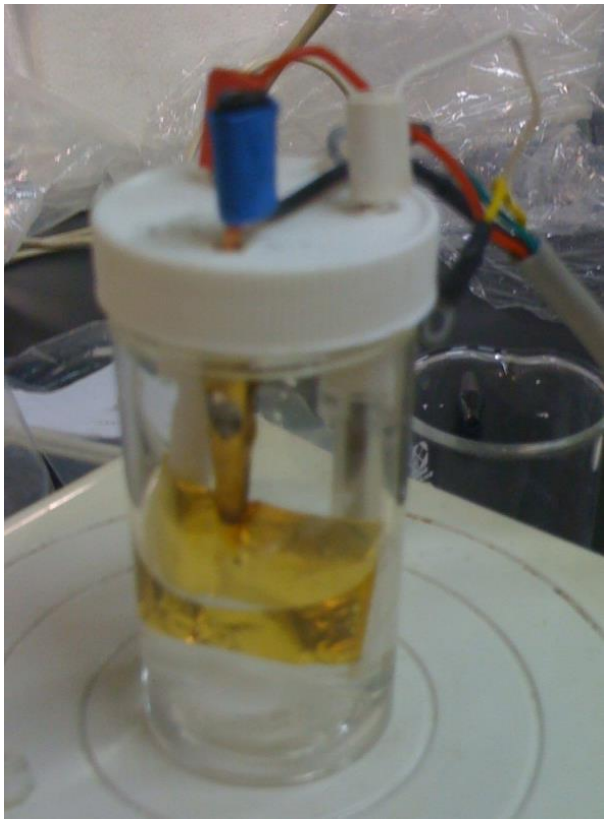

Figure 2.17 Electrolytic Cu removal cell.

3 Results

3.1 Phase 1 – Investigation of Individual Interference Effects

Initial testing was carried out on thin gold film electrode, however, it was found in the testing of sulfide and Triton-X interferents that residues from interferent test solutions had a very significant effect on subsequent clean sample solutions. This necessitated a change in the methodology to remove this residual interference and a subsequent change to the more robust, though less sensitive solid gold electrode as described previously, in Section 2.1.1.3.

3.1.1 Initial Gold Film Analysis Method and Stability Tests

Before interference testing was carried out, an investigation of method stability was undertaken to determine baseline values for accuracy and precision of the procedures. It was found that at the 7 ppb level, the response was initially stable (within the 5% coefficient of variation stated in the application notes [28, 29]), but started to drop outside of this range on the 5th re-analysis of a single solution (Figure 3.1). It was also noted that the first analysis of an aliquot often gave a slightly lower response than the subsequent two repeats (Figure 3.1). The cause of this is not clear and since the difference was <5%, it was not investigated further, but is presumably due to the recent introduction of the sample aliquot into the cell in some way –possibly a slight excess of H^+ or Cl^- ions causing excessive gassing, or a conditioning effect of the electrode after it's exposure to air during the change of sample solution. Since these solutions were 20mL aliquots of a premixed stock solution of 7 ppb As in 0.25M HCl, sample homogeneity wasn't considered a factor.

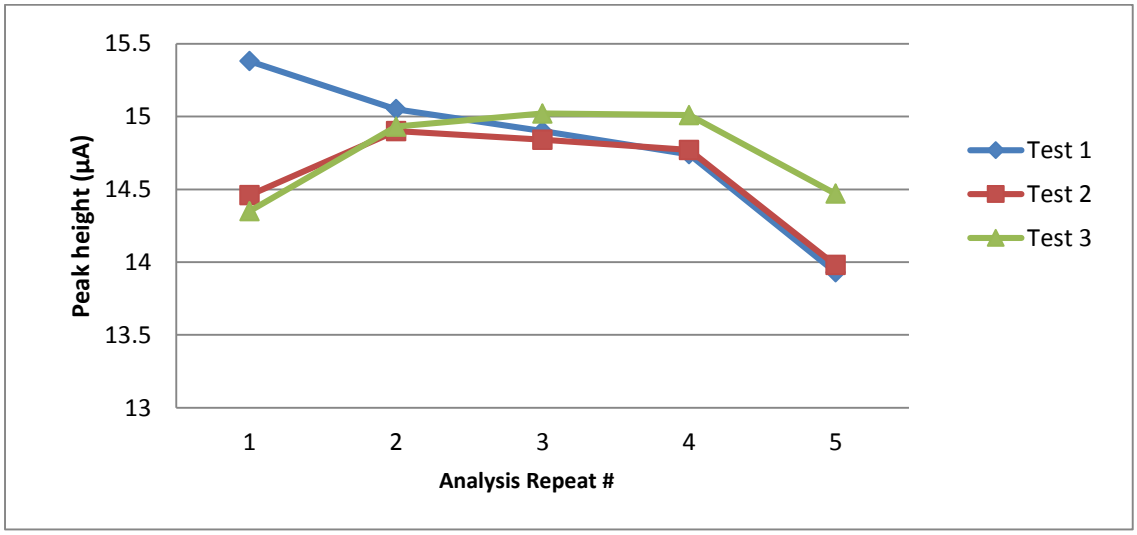

Figure 3.1 Peak heights for repeat analyses of 7 ppb As test solutions at thin gold film without interferents.

3.1.2 Copper Interference

An incremental increase in Cu concentration showed a slight and unexpected increase in As response at 10 ppb Cu level, this was likely due to random variation. Thereafter, both overlap and suppression of As peak effects became clear. In the first test, the 25% level was reached at 40 ppb of Cu, but a potential source of error was identified. Although it could be argued that a 20 ppb addition of Cu caused the 25% As peak reduction criteria if the baseline is drawn between the start of the As peak and the start of the Cu peak, as seen on the left side of Figure 3.2, a baseline drawn to the end of the Cu peak showed a much smaller change in the As peak height, as seen in the right side of Figure 3.2. It must be remembered that the purpose of this phase was to determine the level at which each interferent consistently and clearly caused a >25% change in As response. It was, therefore, decided to use the less ambiguous concentration which showed a clear peak drop of >25% no matter how the baseline is drawn.

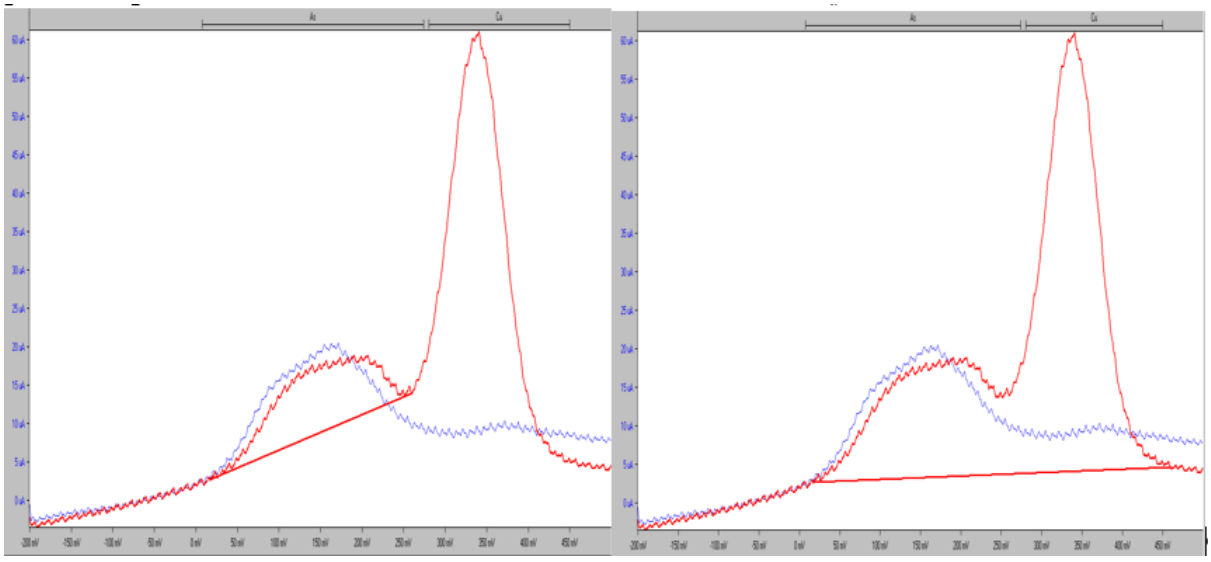

Figure 3.2 Voltammograms showing two possible baseline locations for As with Cu interference (red voltammogram). As voltammogram without Cu interference shown in blue for reference. Vertical axis is Current (μA) and horizontal axis is Potential (mV).

The tests for the effect of Cu interference were repeated two more times, with deionised water rinsing between solutions, to confirm the original test data. Repeat tests carried out on different days showed quite different results, with the stipulated 25% drop in peak height occurring after anything from 20 to 60 ppb Cu, but a 25% drop in peak height consistently occurred at 60 ppb (Table 3.1). Therefore, 60 ppb was selected as the default Cu value for the interference removal tests since this met the initial criteria of reliably causing more than a 25% difference in As response compared to a clean stock solution.

Table 3.1 The effect of different concentrations of Cu added to 7 ppb As stock solutions on different days. Note the different concentrations of Cu required to produce the 25% change in response on different days (highlighted yellow).

Date	Cu Added	Run 1	Run 2	Run 3		Mean	% Change from Clean Solution
30/Mar	No Cu	14.35	14.93	15.02		14.77	
30/Mar	10 ppb Cu	15.95	16.44	17.03		16.47	12%
30/Mar	20 ppb Cu	14.09	14.9	15.45		14.81	0%
30/Mar	40 ppb Cu	11.8	11.97	12.18		11.98	-19%
30/Mar	60 ppb Cu	8.1	8.25	8.461		8.27	-44%
15/Apr	No Cu	15.06	14.88			14.97	
15/Apr	10 ppb Cu	14.9	16.5	17.02		16.14	8%
15/Apr	20 ppb Cu	15.44	15.58	15.95		15.66	5%
15/Apr	40 ppb Cu	10.27	10.1	10.12		10.16	-32%
15/Apr	60 ppb Cu	7.41	7.871	7.399		7.56	-49%
19/Apr	No Cu	12.38	12.09	11.4		11.96	
19/Apr	10 ppb Cu	10.68	10.94	10.54		10.72	-10%
19/Apr	20 ppb Cu	8.796	8.98	8.88		8.89	-26%
19/Apr	40 ppb Cu	5.143	5.088	4.218		4.82	-60%
19/Apr	60 ppb Cu	2.035	1.748	1.454		1.75	-85%

3.1.3 Organic Interferences

Investigation of this interference proved a little more complex since addition of Triton-X to a test solution affected the response not only of that solution, but also clean subsequent solutions (see Figure 3.3). This section is therefore divided into residual effects of clean solutions measured subsequent to Triton-X containing solutions and direct effects of Triton-X determined in Triton-X containing solutions once these residual effects were resolved.

3.1.3.1 Residual Effects of Triton-X

As can be seen in Figure 3.3, the effect of residual Triton-X on subsequently analysed clean As solutions causes a significant reduction in response. Rinsing with HCl/$KMnO_4$ solution improved the response slightly, but a rinse with 1M NaOH, then deionised water, then 0.25M HCl / 0.0001M $KMnO_4$ restored the response to its original level. Please note that, for clarity, Figure 3.3 only shows the subsequent clean solutions to highlight the residual effect of Triton-X on the electrode, as explained previous in Section 2.1.1.2.

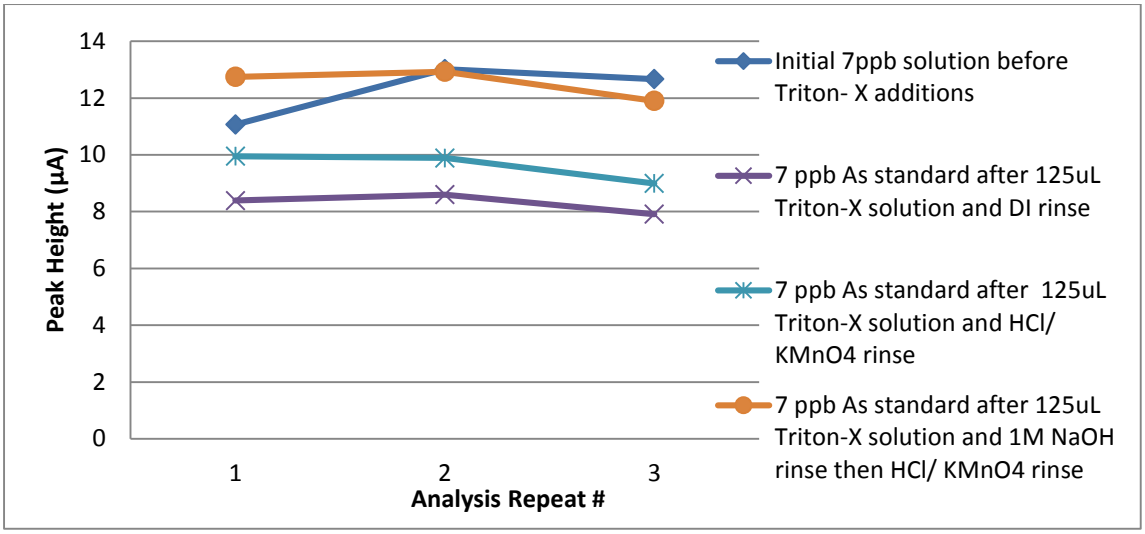

Figure 3.3 Effect of different rinse regimes on Triton-X free As solutions, each after running a Triton-X solution, at thin gold film electrode.

While this rinsing regime was initially successful, it later became apparent that, in the longer term, it was also having a detrimental effect on the response (Table 3.2). Eight solutions were analysed to be sure that the electrode response would at least be stable for two standard solutions to check initial stability after electrode preparation plus three repeats of paired solutions in later testing. A clear and increasing drop in response was observed at the 6th As solution to be analysed (highlighted yellow in Table 3.2). It is thought that this was due to physical damage to the gold film, although this was not visible when inspecting the electrode. It was, therefore, decided to change to a more physically robust solid gold electrode for the remainder of Phase 2.

Table 3.2 Analysis of 8 aliquots (cell solution) of 7 ppb As on gold film electrode, showing long term effects of 1M NaOH, -DI - 0.25M HCl with 1x 10-4 M KMnO4, -DI rinse between each analysed solution.

Cell Solution #	Run 1 (µA)	Run 2 (µA)	Run 3 (µA)	Run 4 (µA)		Mean (µA)	SD (µA)	RSD %	Change (%) from Soln. 1
1	19.0	19.5	20.0	19.5		19.5	0.408	2.1%	0%
2	18.7	19.2	19.3	19.1		19.1	0.263	1.4%	-2%
3	18.7	19.8	20.1	21.0		19.9	0.949	4.8%	2%
4	19.0	19.5	20.6	20.6		19.9	0.825	4.1%	2%
5	20.0	20.3	19.6	19.3		19.8	0.440	2.2%	2%
6	18.0	18.1	17.5	17.1		17.7	0.465	2.6%	-9%
7	16.8	17.5	17.2	16.3		17.0	0.520	3.1%	-13%
8	17.0	17.1	16.7	16.6		16.9	0.238	1.4%	-14%

3.1.3.2 Gold Electrode Stability Tests

The solid gold electrode proved to be more reliable than the thin gold film electrode when using the NaOH - DI - $KMnO_4$ /HCl rinse between each cell solution, with no sudden drops in response, as can be seen in Table 3.3. However, it was noticed that after rinsing, the response of interferent-free solutions after interferent tests were actually higher than the initial interferent free baseline values. Also, running several clean solutions immediately after each other showed a slow increase in response (Table 3.3). It is not clear if this was due to removing some previously existing interferent in the analysis cell or some other sensitising effect on the Working Electrode such as oxidation discussed in Section 4 or increasing electrode roughness and hence surface area.

Table 3.3 Stability Test of 8 separate solutions of 7 ppb As at solid gold electrode with 1M NaOH, -DI - 0.25M HCl with 1x 10-4 M KMnO4, -DI rinse between each cell solution.

Cell Solution #	Run 1 (µA)	Run 2 (µA)	Run 3 (µA)	Run 4 (µA)	Mean (µA)	Mean Change	SD (µA)	SD%
1	9.20	9.30	9.97	10.05	9.63	-	0.443	4.60%
2	10.38	10.21	10.28	10.30	10.29	6.89%	0.070	0.68%
3	11.24	10.94	11.47	10.96	11.15	8.36%	0.252	2.26%
4	13.08	12.39	12.83	13.00	12.83	15.00%	0.308	2.40%
5	14.38	14.73	13.47	13.68	14.07	9.67%	0.590	4.19%
6	14.98	15.73	13.46	13.53	14.43	2.56%	1.117	7.74%
7	14.66	13.08	13.19	16.73	14.42	-0.07%	1.703	11.8%
8	15.78	15.89	15.47	15.19	15.58	8.10%	0.316	2.03%

The slow increase in response was resolved by starting each working day with the usual polishing step, followed by a 5 minute rinse in first the NaOH solution and then another 5 minutes in the HCl/$KMnO_4$ solution. Using this daily procedure, responses were far less variable across the different solutions and runs (Table 3.4) and no further electrode conditioning was required for the remainder of the day.

Table 3.4 Stability test of 8 separate solutions of 7 ppb As at solid gold electrode with 1M NaOH, -DI - 0.25M HCl with 1x 10-4 M KMnO4, -DI rinse between each cell solution after 5 minute rinse in NaOH and then 5 minutes in HCl/$KMnO_4$ at the start of each day.

Solution #	Run 1 (µA)	Run 2 (µA)	Run 3 (µA)	Run 4 (µA)	Mean (µA)	Mean Change	Std Dev (µA)	SD%
1	14.4	15.7	15.6	15.9	15.4		0.571	3.7%
2	14.3	15.1	14.5	14.3	14.6	-5.4%	0.326	2.2%
3	15.4	15.5	15	14.8	15.2	4.2%	0.266	1.8%
4	15.5	15.6	15.6	14.8	15.4	1.3%	0.351	2.3%
5	14.7	15.4	15.2	14.7	15.0	-2.4%	0.331	2.2%
6	15.6	15.7	15.8	15.1	15.5	3.5%	0.287	1.9%
7	15.8	16.0	15.9	15.6	15.8	1.9%	0.150	0.9%
8	15.7	15.9	15.7	15.6	15.7	-0.6%	0.112	0.7%

3.1.3.3 Direct Effects of Triton-X

Once the rinsing steps required to remove residual Triton-X interference on subsequent clean solutions were tested, experiments at intermediate interference concentrations (around 0.0025% v/v Triton-X), gave an initial peak response which was within the 25% limit, but deteriorated with each repeat run, indicating a slow cumulative effect (Figure 3.4). Further increase of interferent also showed a decrease of response with repeat runs, especially after the first analysis, but produced a >25% drop in response even on the first analysis. Although higher interferent levels (around 0.005% v/v Triton-X), gave a final response much less than the 25% drop cut off point envisaged in the initial project proposal, this concentration was used as the test solution concentration in further phases since the interference effect is more clearly defined.

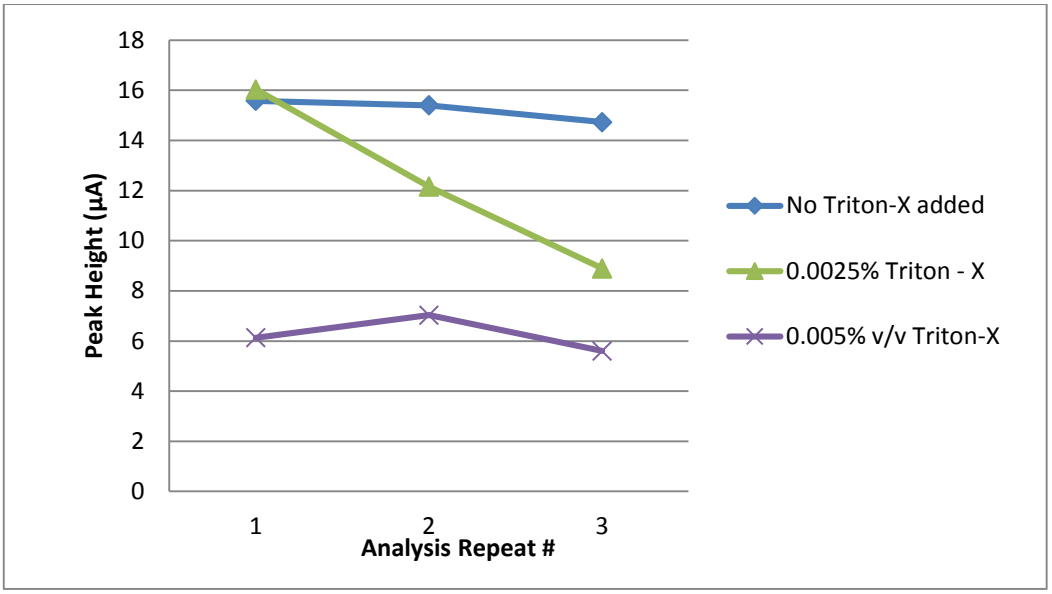

Figure 3.4 Effect of different Triton-X concentrations on 7 ppb As peak height. Analysis cell rinsed with 1M NaOH, then deionised water, then 0.25M HCl with 1x 10^{-4} M $KMnO_4$, then deionised water again between each aliquot.

Results varied on different days and it was also noted that a background peak appeared in the As region that increased with Triton-X concentration. This Triton-X peak varied from day to day, but was usually visually distinguished from As (Figures 3.5 and 3.6), since it was much broader, but it still had the potential to be mistaken as an arsenic peak unless compared directly to a true arsenic peak.

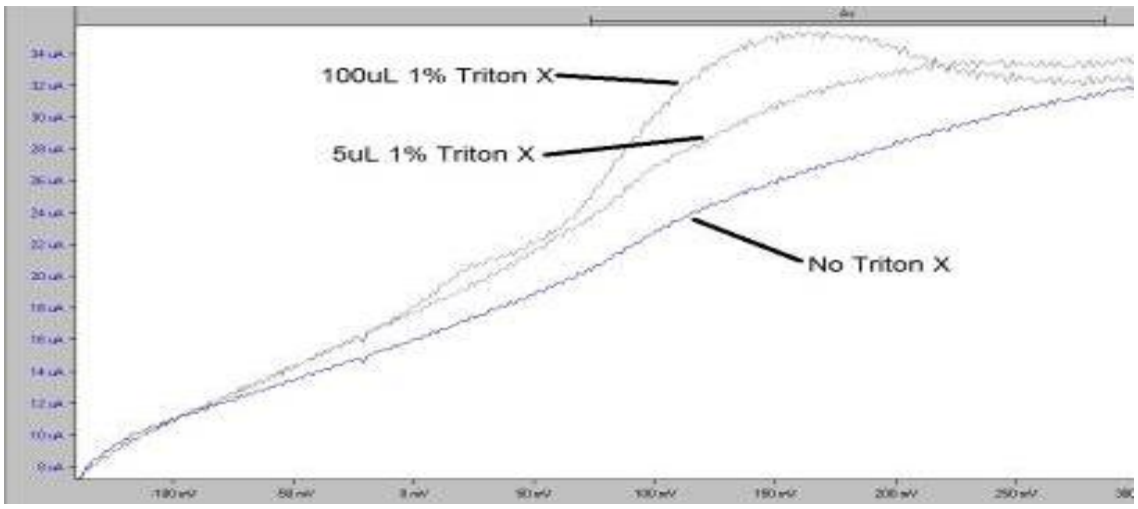

Figure 3.5 Voltammograms of As free 0.25 M HCl solutions with 0µL, 5µL and 100µL 1% Triton-X, showing peak in the As region caused by Triton-X alone. Vertical axis is Current (µA) and horizontal axis is Potential (mV).

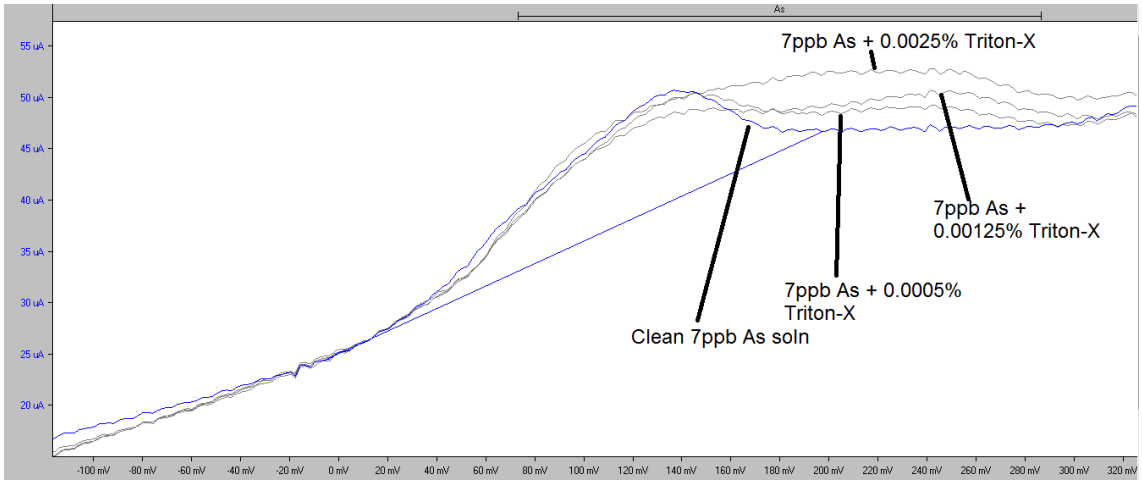

Figure 3.6 Voltammograms of 7 ppb As solutions with additions of Triton-X showing interference with the As peak caused by Triton-X. Vertical axis is Current (µA) and horizontal axis is Potential (mV).

3.1.4 Sulfide Interference

Initial sulfide interference results indicated that between 650 ppb and 2.6 ppm of sulfide was required to cause significant interference (Table 3.5). However, residual effects on subsequent clean samples, similar to those noted for Triton-X, were observed. Thus, repeat testing with NaOH – DI – $KMnO_4$/HCl rinsing, which had successfully removed residual Triton-X interference, was carried out. This rinsing regime greatly reduced residual interference from the sulfide containing sample (Table 3.5). Recovery was initially only about 75%, although it was increasing with repeat runs.

Table 3.5 Effect of sulfide additions on solutions of 7 ppb As without 1M NaOH, -DI - 0.25M HCl with 1x 10-4 M KMnO4, -DI rinse between solutions.

Solution	[S] ppb	Run 1 (µA)	Run 2 (µA)	Run 3 (µA)		Mean (µA)	% drop from clean solution
1	0	10.1	10.7	10.8		10.53	
2	162.5	9.7	10.0	10.3		10.00	-5%
3	325	11.3	11.8	11.2		11.43	9%
4	650	11.1	11.1	11.3		11.17	6%
5	2600	5.74	2.64	3.72		4.03	-62%
6	0	1.37	1.45			1.41	-87%
7	0 (after NaOH - DI - $KMnO_4$/ HCl rinse)	6.87	7.14	9.76		7.92	-25%

Once the rinsing regime was optimized, further, the sulfide interference tests could be repeated. Results are summarized in Figure 3.7.

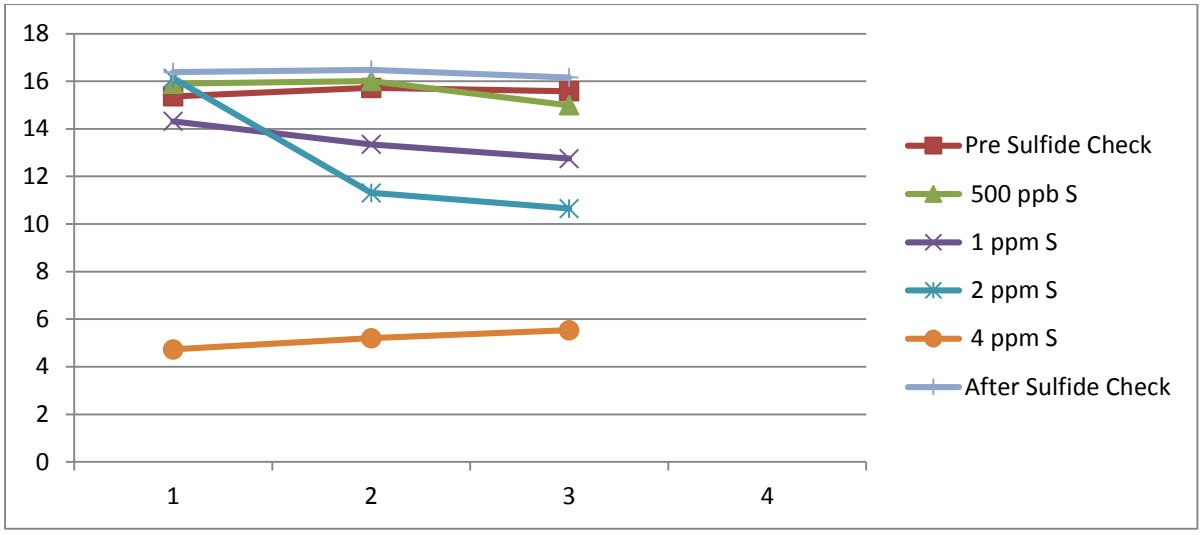

Figure 3.7 Sulfide interference tests with 1M NaOH, -DI - 0.25M HCl with 1x 10-4 M KMnO4, -DI rinse between solutions

3.2 Phase 2 - Investigation of Individual Pretreatment Methods

3.2.1 Cation Exchange Resin to Remove Copper Interference

Using a method for determining Cu with a gold electrode, Cu removal was approximately 90% effective using the resin method, with the response dropping from 88 µA for the untreated solution to 8 µA for the treated solution (Figure 3.8). This test was repeated twice with similar results. It was also repeated with the sample being passed through resin after mixing with acetate buffer (pH 4.5) with no loss of efficiency.

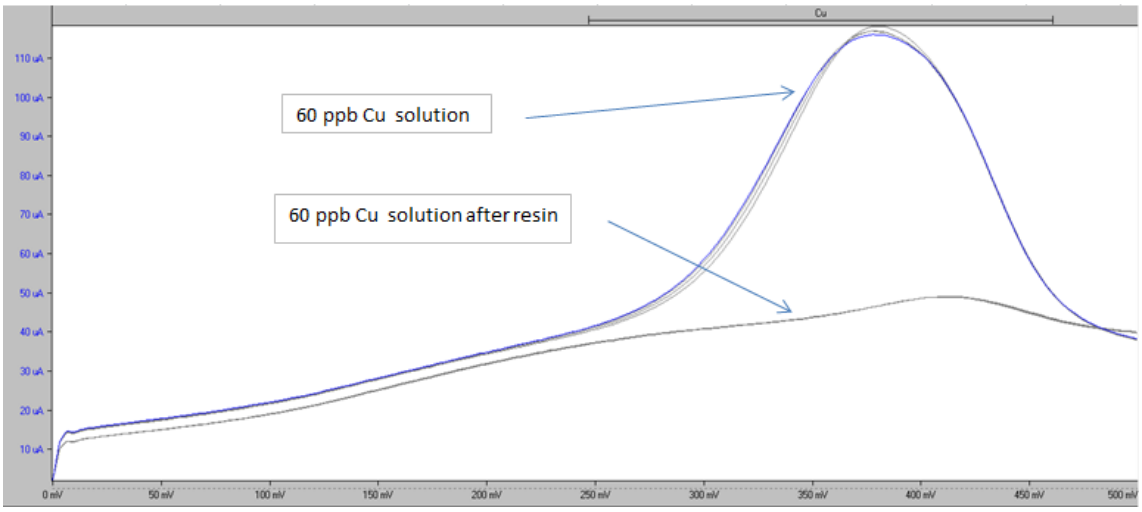

Figure 3.8 Voltammograms of 60 ppb Cu solution analysed with and without resin treatment, showing almost complete removal of Cu peak after resin treatment. Vertical axis is Current (µA) and horizontal axis is Potential (mV).

To test the effectiveness of this method at higher concentrations, a single test was carried out using a 1 ppm Cu solution with a shorter deposit time to reduce

sensitivity and prevent the Cu response going over range. This also showed a significant reduction in Cu response from 47 µA to 2.7 µA (Figure 3.9).

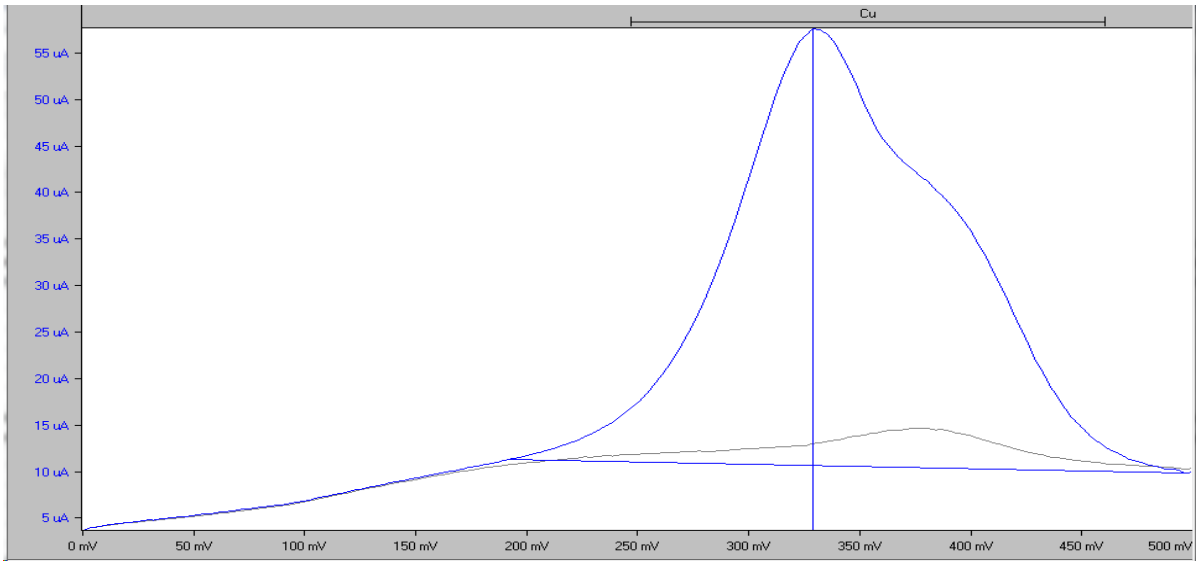

Figure 3.9 Voltammograms of 1 ppm Cu solution analysed with (grey) and without (blue) resin treatment, showing almost complete removal of Cu peak after resin treatment. Vertical axis is Current (µA) and horizontal axisis Potential (mV).

Testing on a mixed solution of 7 ppb As with 60 ppb Cu in deionized water indicated that the As response was similar to that shown in Cu-free solutions (Figure 3.10).

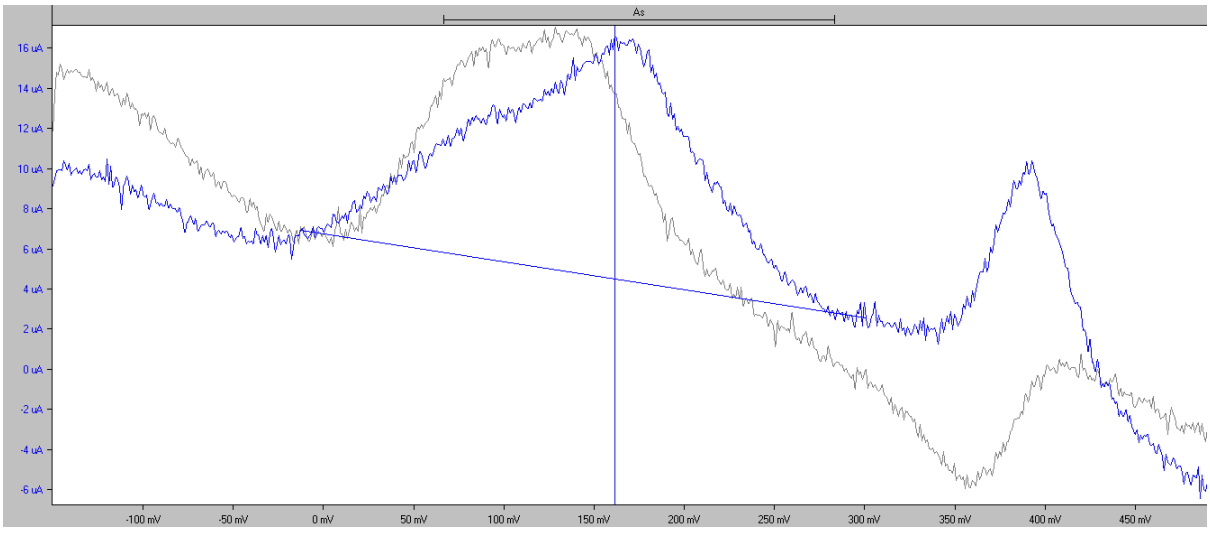

Figure 3.10 Voltammograms showing Cu free solution of 7 ppb As (grey) and test solution of 7 ppb As with 60 ppb Cu in deionised water after treatment with Cu removal resin. Vertical axis is Current (µA) and horizontal axis is Potential (mV).

Due to the manufacturers stated optimal pH range of 2 to 6 and the likelihood of having to test samples preserved to pH2 or lower in real world applications, it

was decided to test the manufacturers claim that this resin would function at an easily buffered pH. When acetate buffer was added to the test solution to bring the pH to 4.5, there was a similar limited effect (~5%) of Cu on the As peak (Table 3.6).

Table 3.6 7 ppb As with 60 ppb Cu solution in 0.01M acetate buffer after resin treatment compared to 7 ppb As solution with acetate buffer.

Solution	Run 1 (μA)	Run 2 (μA)	Run 3 (μA)	Mean (μA)	% Change
7 ppb As only	20.2	19.9	19.8	19.85	
7 ppb As with 60 ppb Cu after resin treatment	18.6	19.1	18.5	18.8	-5%
7 ppb As only	20.7	20.5	20.3	20.2	
7 ppb As with 60 ppb Cu after resin treatment	18.9	19	19.2	19.1	-5%
7 ppb As only	19.4	20.2	19.3	19.2	
7 ppb As with 60 ppb Cu after resin treatment	18.0	18.2	18.0	18.1	-6%

3.2.2 Electrochemical Pretreatment for Copper Interference

A successful response for 7 ppb As + 0.25M HCl + 60 ppb Cu test solution both before and after electrochemical pretreatment is shown in Figure 3.11. It should be noted that most attempts at pretreatment were not successful, with most attempts showing no removal of Cu, even under the same conditions as the successful tests. This was thought to be due to difficulty in correctly removing the gold foil electrode from the sample solution.

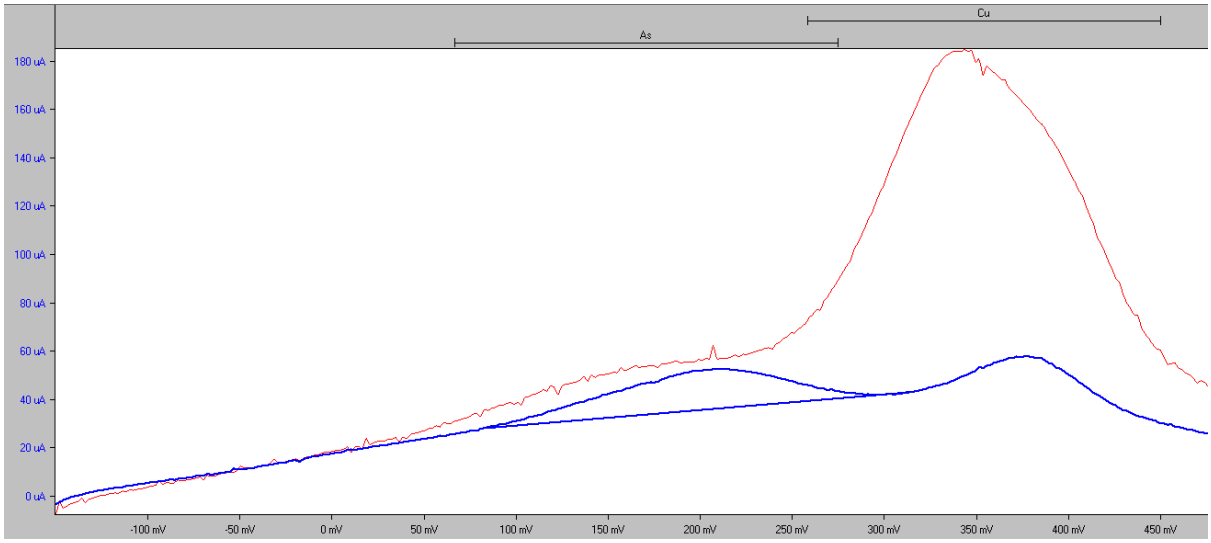

Figure 3.11 Voltammograms of stock 7 ppb As in 0.25M HCl + 60 ppb Cu shown before (red) and after (blue) successful electrochemical pretreatment at -400 mV for 60 minutes. Note metal potential windows at top of the picture. Vertical axis is Current (μA) and horizontal axis is Potential (mV).

3.2.3 Ultraviolet Digestion to Remove Sulfide Interference

Immediately after UV digestion the sample was observed to have been heated to 38 degrees C during the digestion process and required approximately 40 minutes to cool to the room temperature of 24 degrees C to avoid errors associated with sample temperature described in Section 1.4.2. This cooling time brought the total pretreatment time for UV digestion to almost 2 hours. Faster cooling options were briefly tested but proved unsatisfactory – a water bath due to the tendency of the plastic bottles and analysis cups to float, risking sample spillage or contamination, and refrigeration due to the readiness to over cool the sample, causing the user to wait even longer for it to warm back up to room temperature.

UV digestion was very successful for sulfide contamination, with every UV treated solution having a response within 10% of a clean 7 ppb As stock solution measured immediately beforehand (Table 3.7 & Figure 3.12). Table 3.7 shows the results for all three tests comparing UV treated sulfide contaminated solutions compared to clean As standards analysed immediately beforehand.

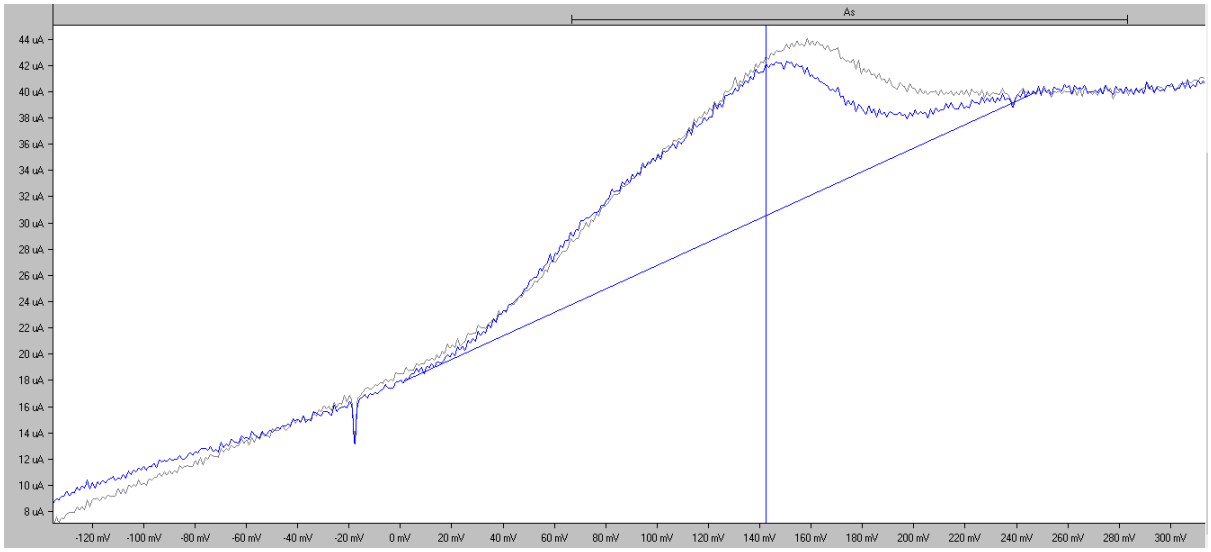

Figure 3.12 Voltammograms showing clean 7 ppb stock As solution (grey) and stock solution contaminated with 4 ppm sulfide after UV pretreatment (blue). Vertical axis is Current (µA) and horizontal axis is Potential (mV).

Table 3.7 Effect of UV digestion on sulfide contaminated solutions of 7 ppb As, compared sulfide free solutions of 7 ppb As analysed immediately beforehand.

Solution	**Run 1 (µA)**	**Run 2 (µA)**	**Run 3 (µA)**	**Mean (µA)**	**% Change**
Clean 7 ppb As soln	16.4	16.0	15.6	16.00	
7 ppb As soln + 100uL 600mg/L $Na_2S.9H_2O$ UV 10 min	15.1	14.8	13.7	14.53	-9%
Clean 7 ppb As soln	16.4	15.0	14.5	15.30	
100uL 600mg/L $Na_2S.9H_2O$ UV 10 min	15.4	14.1	15.3	14.93	-2%
Clean 7 ppb As soln	16.8	15.5	13.4	15.23	
100uL 600mg/L $Na_2S.9H_2O$ UV 10 min	14.2	14.3	13.8	14.10	-7%

Previous work indicated that sulfide interference could be reduced by leaving the sample in HCl solution for extended times, so it was important to confirm that this possible alternate process wasn`t contributing the results of the UV treatment of sulfide. To ensure this, a separate stock 7 ppb As solution was acidified and left for 90 minutes before analysis. No As peak was seen in this test.

3.2.4 UV Digestion to Remove Triton-X Interference

UV digestion proved to successfully remove Triton-X interference. Results are summarised in Table 3.8 and the typical peaks shown in Figure 3.13 make it clear that this peak is not merely an artefact of the background peak caused by Triton-X described in Section 3.1.3.3, although there is an indication around +200 mV that a very small Triton-X residue may remain. Table 3.8 shows results for 3 tests comparing UV treated Triton-X contaminated solutions compared to clean As standards analysed immediately beforehand.

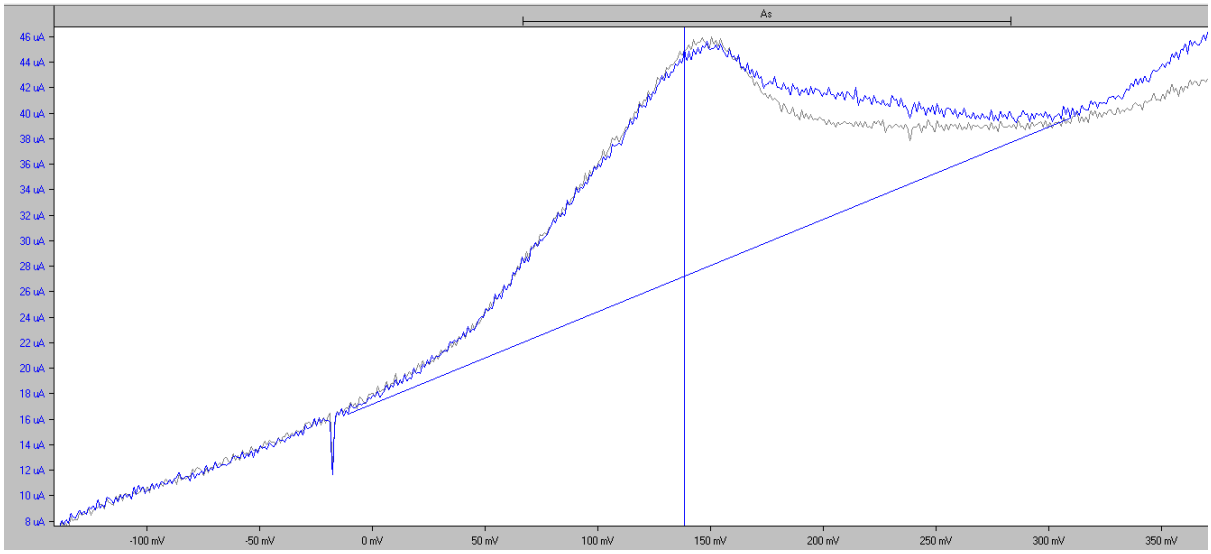

Figure 3.13 Voltammograms showing clean 7 ppb As stock solution (grey) and 7 ppb As stock solution with 0.005% Triton-X after UV treatment. Vertical axis is Current (µA) and horizontal axis is Potential (mV).

Table 3.8 Effect of UV digestion on Triton-X contaminated test solutions.

Solution	Run 1 (µA)	Run 2 (µA)	Run 3 (µA)	Mean (µA)	% Change
Clean 7 ppb As stock	17.3	17.6	16.8	17.2	
Stock with 0.005% TX after 20 min UV	18.0	18.2	17.8	18.0	4%
Clean 7 ppb As stock	11.8	11.4	11.2	11.5	
Stock with 0.005% TX after 20 min UV	11.5	10.9	10.7	11.0	-4%
Clean 7 ppb As stock	12.3	11.6	11.4	11.8	
Stock with 0.005% TX after 20 min UV	10.7	10.5	10.3	10.5	-11%

3.2.5 Chemical Oxidation to Remove Sulfide Interference

For the test solution of 7 ppb As and 4 ppm sulfide, the addition of 200µL 0.01M $KMnO_4$ failed to change the solution to the same deep purple colour of the clean test solution, so more $KMnO_4$ was added until a similar colour was achieved and remained for 5 minutes. This stable colour change occurred after adding a total of 500µL 0.01M $KMnO_4$. This solution was then tested and the response compared to both the sulfide containing and sulfide free solutions. As can be seen in Figure 3.14, no As peaks were seen in solutions containing 7 ppb As with 4 ppm sulfide or 7 ppb As with 4 ppm sulfide and 200µL $KMnO_4$. However a good As peak, approximately 20% larger than the clean test solution, was seen, when a total of 500µL $KMnO_4$ as added, indicating that the stable colour change is a good indicator of the effectiveness of the $KMnO_4$ .It was also observed that the 500µL test solution containing 500µL of $KMnO_4$ actually showed a higher As response than the sulfide free solution containing 200µL of $KMnO_4$, presumably due to extra electrode oxidation as described in Section 1.4.3.

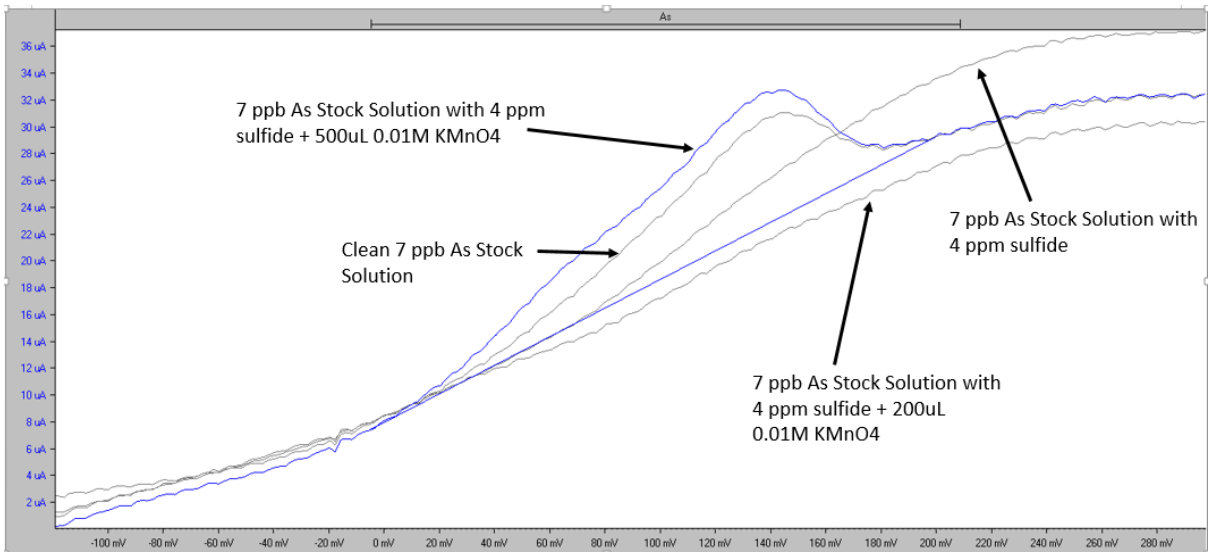

Figure 3.14 Voltammograms showing effects of sulfide and $KMnO_4$ on 7 ppb As solution. Note the lack of an As peak for sulfide contaminated solutions containing less than 500 µL of $KMnO_4$. Vertical axis is Current (µA) and horizontal axis is Potential (mV).

This treatment of sulfide contaminated As solutions with $KMnO_4$ was then repeated three times with response compared to clean 7 ppb As solutions with 200 µL $KMnO_4$. Results are summarised in Table 3.9

Table 3.9 Repeat runs of sulfide contaminated solutions treated with $KMnO_4$.

Solution	Run 1 (μA)	Run 2 (μA)	Run 3 (μA)	Mean (μA)	% Change
7 ppb As + $KMnO_4$	15.1	14.8	15.2	15.0	
7 ppb As + 4 ppm S + $KMnO_4$	15.8	15.6	15.7	15.7	+5%
7 ppb As + $KMnO_4$	15.9	16.4	15.8	16.0	
7 ppb As + 4 ppm S + $KMnO_4$	16.6	15.9	16.0	16.2	+1%
7 ppb As + $KMnO_4$	16.2	17.1	16.3	16.5	
7 ppb As + 4 ppm S + $KMnO_4$	16.0	15.4	15.2	15.5	-6%

As a final check, an aliquot of clean test solution was also measured with 500μL 0.01M $KMnO_4$. This showed an As peak within 10% of the 4 ppm sulfide contaminated sample that had been treated with 500μL $KMnO_4$ solution. It will be recommended in the final procedure, given in Section 5.2, that 0.01M $KMnO_4$ be added to the test solution in 100μL aliquots until the test solution achieves a similar colour to a premade 20mL rinse solution containing 200μL 0.01M $KMnO_4$.

3.2.6 Chemical Oxidation to Remove Triton-X Interference

The addition of $KMnO_4$ to the As test solution containing Triton-X until it remained a similar colour as that of the $KMnO_4$ rinse solution, resulted in an undetectable As peak (Figure 3.15), indicating this is not a suitable pretreatment for this interferent at this concentration. It was observed that the background peak seen with Triton-X in Figure 3.5 was not visible. This is briefly investigated in Appendix 2.

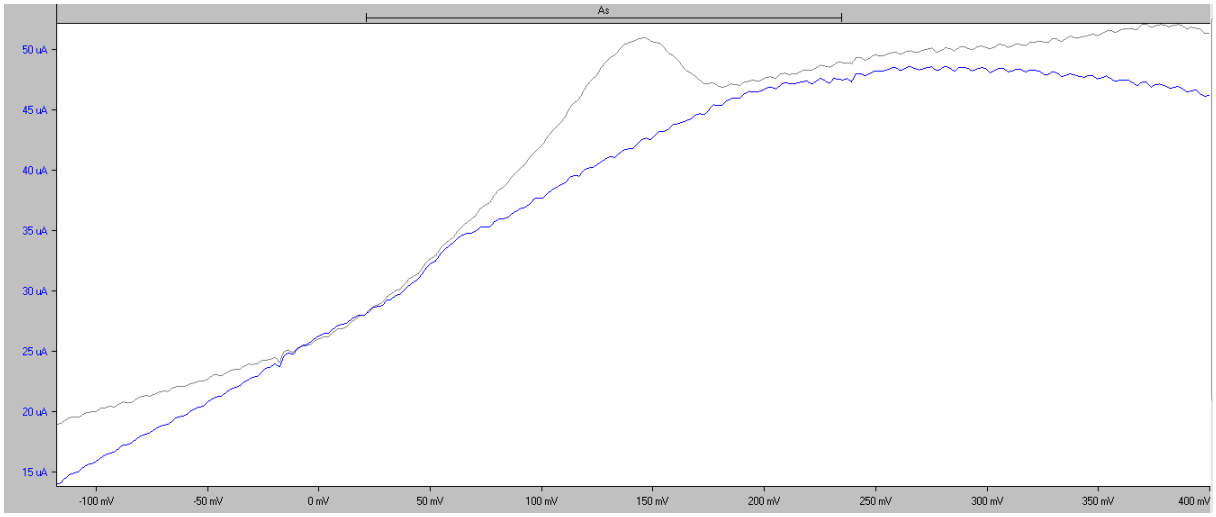

Figure 3.15 Voltammograms showing clean As test solution (grey) and As test solution with 0.005% Triton-X and $2.5x10^{-4}$ M $KMnO_4$ (blue). Vertical axis is Current (μA) and horizontal axis is Potential (mV).

3.2.7 Ozone Oxidation to Remove Sulfide Interference

Ozone treatment proved to remove the effect of sulfide on the detection of As. The magnitude of the As peaks in solution containing sulfide differed by <10% of that of the clean As solution for all three tests (Figure 3.16 & Table 3.10). To ensure the improvement in response seen in the sulfide contaminated solutions was actually due to the ozone and not simply air bubbling through the sample, the sulfide test solution was retested after bubbling filtered, but not ozonated, air through it for 30 minutes. Again, the peak strength was within 10% of that for the clean As solution as can be seen in in the final data row of Table 3.10, indicating that the toxic ozone isn`t actually required for removal of sulfide interference and simple oxygenation of the sample is sufficient.

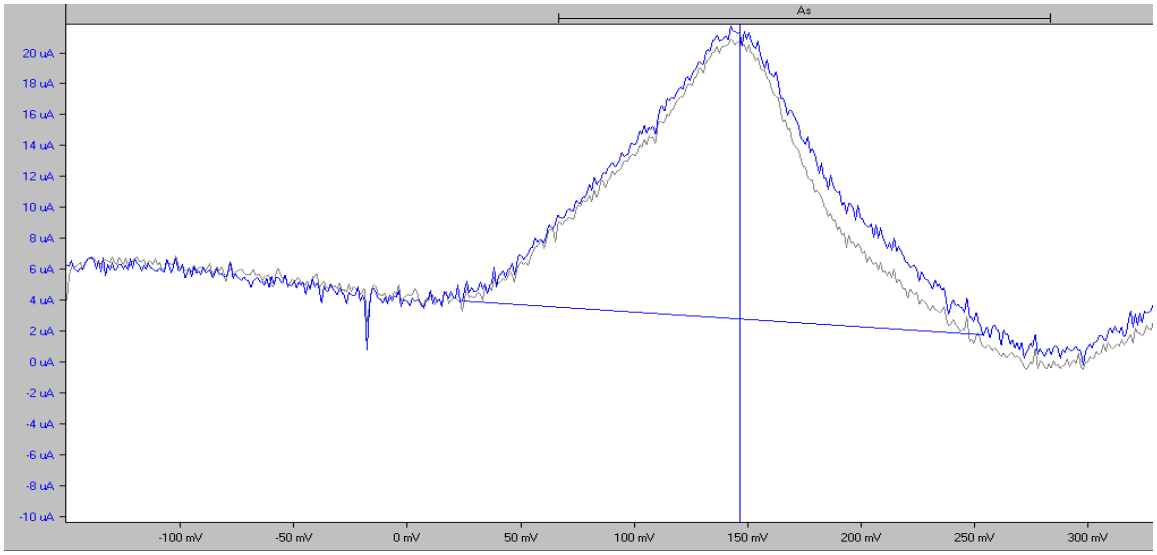

Figure 3.16 Voltammograms of Clean 7 ppb As test solution (grey) and As test solution with 4 ppm sulfide after ozone treatment (blue). Vertical axis is Current (μA) and horizontal axis is Potential (mV).

Table 3.10 Effect of O_3 and air bubbling treatment on test solution of 7 ppm As with 4 ppm sulfide in DI water.

Solution	Run 1 (μA)	Run 2 (μA)	Run 3 (μA)	Mean (μA)	% Change
Clean 7 ppb As soln 1	19.6	19.8	18.6	19.3	
S contaminated 7 ppb As soln after 30 min O_3 soln 1	19.1	18.6	18.0	18.6	-4%
Clean 7 ppb As soln 2	19.2	19.9	18.9	19.4	
S contaminated 7 ppb As soln after 30 min O_3 soln 2	18.8	18.1	17.9	18.3	-6%
Clean 7 ppb As soln 3	19.1	18.3	17.9	18.4	
S contaminated 7 ppb As soln after 30 min O_3 soln 3	18.7	18.3	16.9	17.9	-7%
Clean 7 ppb As soln 4	20.0	18.4	18.0	18.8	
S contaminated 7 ppb As after 30 min air bubbling only	17.2	17.0	17.9	17.4	-8%

3.2.8 Ozone Oxidation Treatment for Triton-X

Ozone treatment for Triton-X produced a defined As peak that was considerably reduced compared to a clean As sample (Figure 3.17 & Table 3.11).

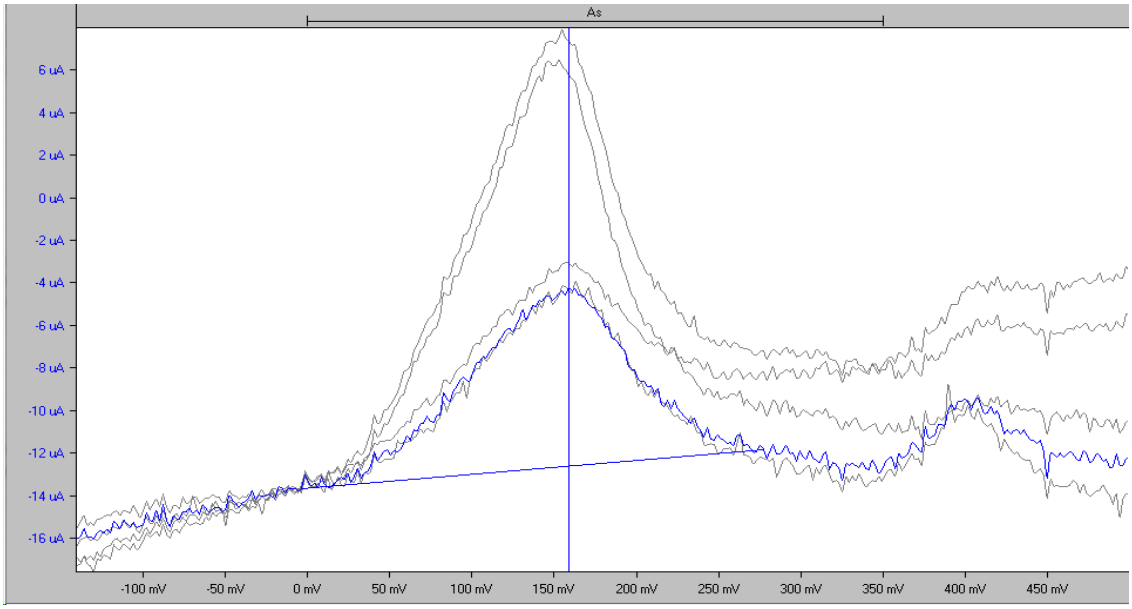

Figure 3.17 Voltammograms of Clean 7 ppb As solution (grey) and 7 ppb As solution containing 0.005% Triton-X after 2 hours of O_3 treatment (blue). Vertical axis is Current (µA) and horizontal axis is Potential (mV).

Table 3.11 Effect of O_3 treatment on test solutions containing 0.005% Triton-X.

Solution	Run 1 (µA)	Run 2 (µA)	Run 3 (µA)	Mean (µA)	% Change
Clean 7 ppb As soln 1	15.3	16.9	16.7	16.3	
0.005% Triton-X + 7 ppb As soln 1 after 120 min O_3	6.84	6.92	-	6.88	-58%
Clean 7 ppb As soln 2	17.6	18.2	-	17.9	
0.005% Triton-X + 7 ppb As soln 2 after 120 min O_3	7.53	8.42	8.51	8.15	-55%

3.2.9 Ultrasonication Treatment for Copper

Due to the potential for problems arising from possible excessive gas build-up on the working electrode surface if the cell stirring technique was changed for the total inorganic As method, it was decided to carry out an initial investigation into the general utility of ultrasonic stirring for use in the deposition step of ASV with the simpler Cu analysis method. While the system operated well as a stirrer, giving good peaks in clean standards (Figure 3.18), sensitivity varied and peaks resembling those of As and Cu sometimes appeared in the blanks. In addition, the peak in the Cu region increased steadily, indicating some Cu contamination leaching into the cell. It is possible that this was at least partly a function of an increase in the temperature of the cell solution since, after several runs, the sample solution being analysed was heated to almost 60 degrees C by

the horn which would be expected to have a significant positive effect on As response (see Discussion Section).

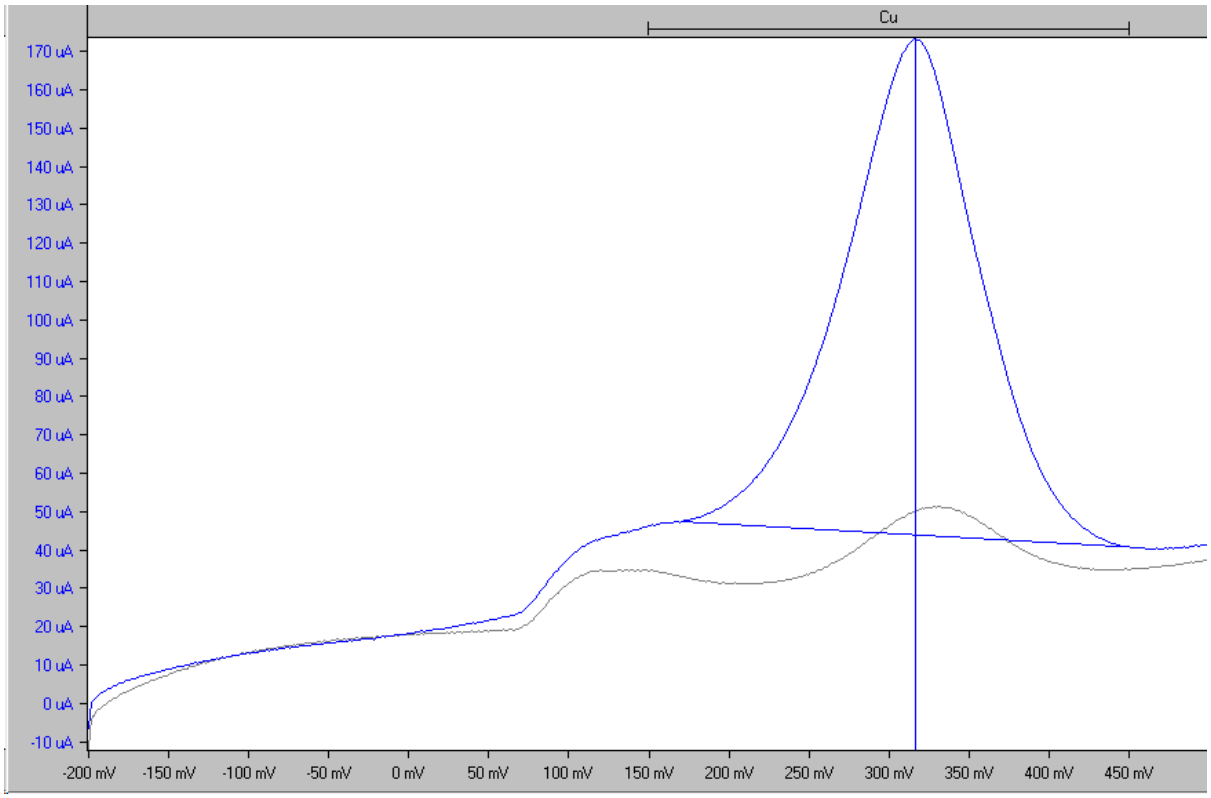

Figure 3.18 Voltammograms of blank solution (grey) and 50 ppb Cu spike (blue) using ultrasonic stirring in analysis cell. Notice blank peaks in both the Cu & As regions. Vertical axis is Current (μA) and horizontal axis is Potential (mV).

Placing the analysis cup in a water bath to overcome the temperature increase in further tests proved unsuccessful, possibly because the ultrasonic horn tip was closer to the working electrode than either of them were to the cooled edges of the analysis cup, reducing the effectiveness of the bath cooling the solution at the working electrode surface. Furthermore, placing the ultrasonic horn as a pretreatment method outside the analysis cell, and allowing the sample to cool to room temperature before analysis, proved unsuccessful. Given the time, cost and effort that would have been required to develop this treatment procedure, it was decided to discontinue testing this procedure for sulfide interference.

3.2.10 Ultrasonication Treatment for Triton-X

Using the approach of using the horn to treat the sample outside the analysis cell (see above) for treatment of Triton-X also proved ineffective. Figure 3.19 shows the characteristic Triton-X background peak (red) seen in Figures 3.5 and 3.6 at a positive potential relative to the clean As peak (blue).

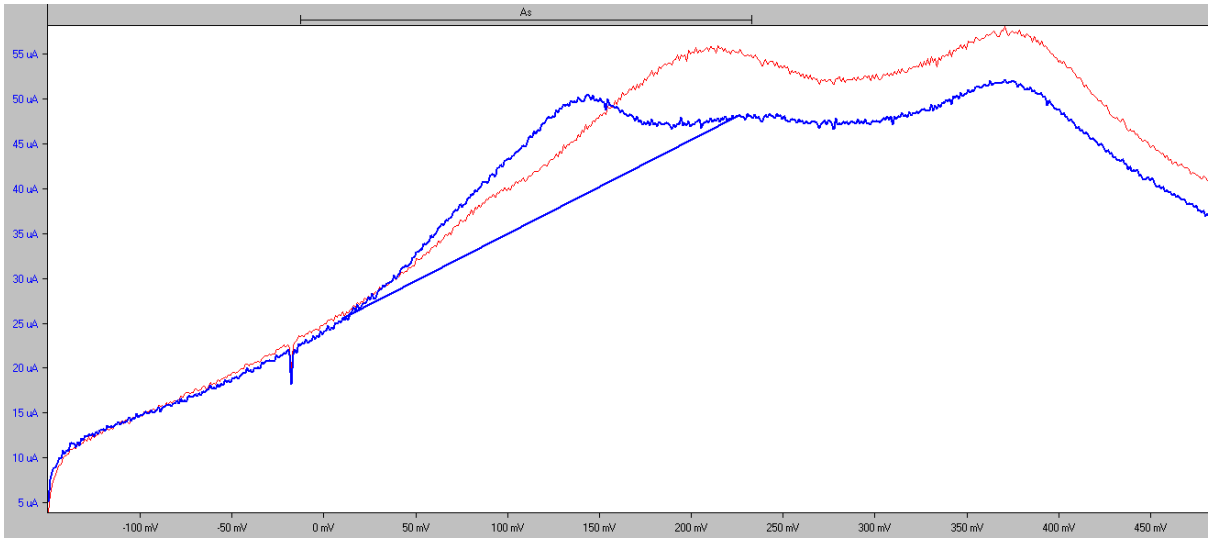

Figure 3.19 Voltammograms showing effect of Ultrasonication on Triton-X interferent. Clean untreated solution (blue) and 30 minute ultrasound treated 7 ppb As + 0.005% Triton-X test solution (red). Vertical axis is Current (μA) and horizontal axis is Potential (mV).

3.2.11 Ultrasonication Treatment for Sulfide

As for Triton-X, the only option available was to try using the ultrasonic horn as a pretreatment method outside the analysis cell before allowing the sample to cool to room temperature before analysis. No peak for the 7 ppb As was observed after treatment (Figure 3.20).

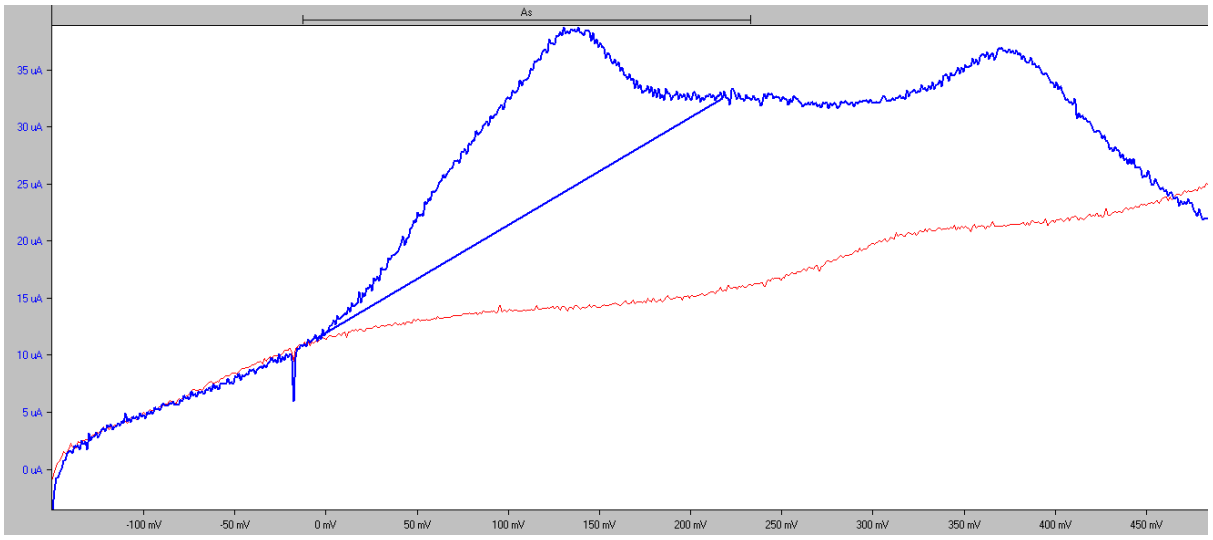

Figure 3.20 Voltammograms showing solutions containing clean, untreated 7 ppb As test solution (blue) and 7 ppb As + 4 ppm sulfide after 30 minute ultrasonication and cooling (red). Vertical axis is Current (μA) and horizontal axis is Potential (mV).

3.3 Phase 3 - Investigation of Mixed Pretreatment Methods

The success of each pretreatment method with each tested interferent is summarised in Table 3.12. From the pretreatment combinations considered to have passed Phase 2, one treatment method for each interferent type was chosen for further investigation on the grounds of its effectiveness and ease of use. Treatments and justification are outlined below.

Table 3.12 Summary of Phase 2 results.

Interferent	Pretreatment Method					
	UV	O_3	Chemical Oxidation $KMnO_4$	Ultra-Sonication	Ion Exchange Resin	Selective Electro-plating
Copper					Pass	Fail
Sulfide	Pass	Pass	Pass	Fail		
Organics	Pass	Fail	Fail	Fail		

Cu: Ion exchange resin was considered the most promising pretreatment method for Cu. While the electrochemical separation method also gave a couple of good results and had some potential advantages over ion exchange resin, it was very unreliable and difficult to operate. The resin method was therefore chosen on grounds of low cost as well as speed, reliability and relative ease of use.

Sulfide: $KMnO_4$ chemical oxidation was considered the best method for pretreatment of Cu. The colour change feature of the $KMnO_4$ oxidation method made it easy to adjust the dose to match the level of interferent in the sample and also had the added benefits of serving as an indicator for organic contamination and giving some improvement to the basic method by increasing sensitivity.

Triton-X: UV digestion was considered the best procedure to treat Triton-X interference. Although the ozone system was considerably cheaper and had the advantage of being more readily portable and battery powered, the UV digestion method was the only one shown to completely remove the Triton-X interference in an acceptable timeframe.

The chosen treatments for each class of interferent (Cu, sulfide and Triton-X) were then tested in combination, to ensure no cross contamination/interference would arise which may cause an undesirable response.

3.3.1 Testing of Gold Film Electrode with $KMnO_4$ Reagent

The problems arising with residual contamination from sulfide and Triton-X treated test solutions in Phase 1 required a harsh cleaning regime using both 1M NaOH and 0.25M HCl with 0.0001M $KMnO_4$ between test solutions measured in the analysis cell. This rinsing regime was found to damage the thin gold film used at that point, so it was decided to change to a more robust solid gold electrode for the tests requiring this rinsing regime in Phases 1 and 2. For Phase 3 it was assumed, as demonstrated in Phase 2, that the treatment methods used would remove sulfide and Triton-X interference, thus removing the need for this rinsing regime. However, since addition of $KMnO_4$ to the analysis cell was a selected pretreatment method for sulfide interference, testing was required to ensure that $KMnO_4$ in itself did not damage a gold film.

To this end, a stock test solution of 7 ppb As in 0.25M HCl was made. 20mL aliquots of this stock solution were tested with a freshly plated gold film after addition of 0.0001M $KMnO_4$ to each aliquot immediately before analysis. Only a single blank solution of 0.25M HCl was analysed between the thin gold film plating and the 7 ppb As test solutions in accordance with USEPA method 7063 [7]. Results are shown in shown in Table 3.13.

Table 3.13 Stability testing of gold film electrode with aliquots of 7 ppb As in 0.25M HCl+0.0001M $KMnO_4$.

Solution	Run 1 (µA)	Run 2 (µA)	Run 3 (µA)	Run 4 (µA)	Mean (µA)	% Change from previous solution
1	14.2	14.9	15.7	15.4	15.33	
2	14.5	14.7	14.5	15.2	14.80	-3%
3	13.8	12.7	13.1	13.9	13.23	-11%
4	15.6	16.3	16.2	16	16.17	22%
5	17.9	17.9	18.1	18.5	18.30	13%
6	19.7	19.1	19.7	19.4	19.40	6%
7	18.9	19.1	18.7	19.2	19.00	-2%
8	19.5	19.6	20.1	19	19.57	3%
9	20.1	20.5	20.8	20.4	20.57	5%
10	20.8	20.1	20.1	19.7	19.97	-3%

Except for a single 11% drop in response seen in solution 3, stability was quite acceptable between solutions, although a slight trend of increasing peak height can be seen for the first 5 solutions. This may indicate that a 5 minute rinse in HCl / $KMnO_4$ solution immediately after a new thin gold film may be useful, but this was not explored further.

3.3.2 UV, $KMnO_4$ and Copper Removal Resin Mixed Testing

UV digest was carried out first, due to concerns about the strength of the Triton-X reagent causing problems with both the $KMnO_4$ and resin treatment steps. After the UV treated sample was allowed to cool to room temperature, acetate buffer was added until the sample solution was 0.02M in acetate buffer. It was then treated with the Diaion CR-20 resin for 5 minutes. Due to the long pretreatment time, a fresh clean standard containing 0.25M HCl, 7 ppb As and the same amount of acetate buffer as the sample, was analysed during this period to allow for any change in electrode condition that may have occurred since the previous sample was analysed. For consistency, and as a final check for residual organic contamination, $KMnO_4$ was added to the sample and a 5 minute wait, to ensure a stable pink colour remained, was carried out. HCl was then added to the sample solution to make it 0.25 M in HCl before analysis.

Results were in an acceptable range, although some difference in baseline and peak position were visible and Cu removal was less complete than seen in the individual pretreatment tests (Section 3.2.1), as can be seen by the residual Cu peak between +300 and +450 mV (Figure 3.21). Despite leaving a detectable residual concentration of Cu in the sample, Cu removal was sufficient to prevent it from being a significant interferent in the solutions tested. All three tests indicated the strength of the As peak was within 10% of that for the clean As solutions (Table 3.14). However, the strength of As peaks varied among the three paired tests (Table 3.14).

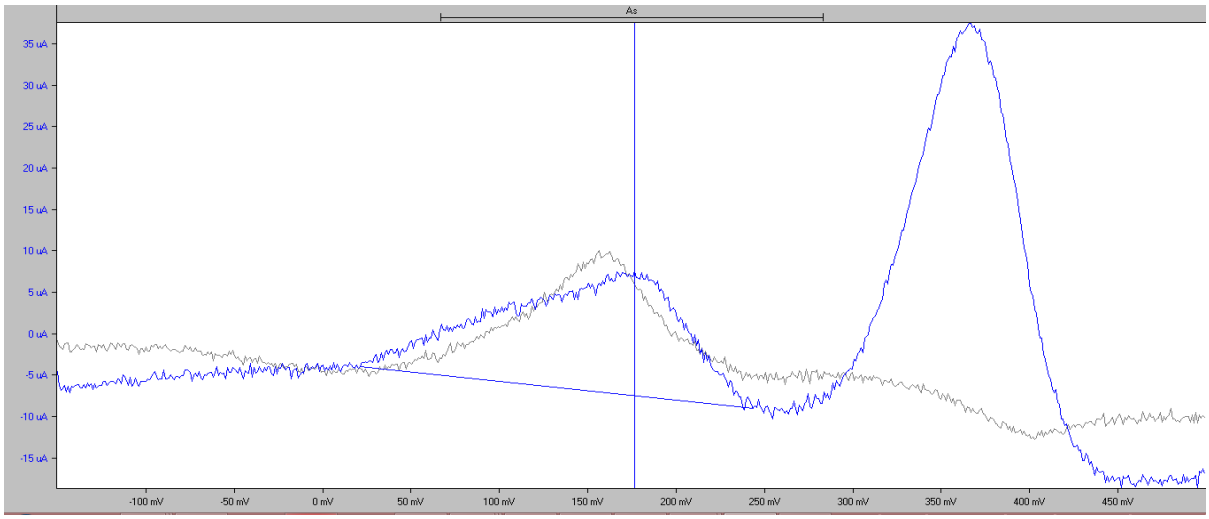

Figure 3.21 Voltammograms of clean 7 ppb As solution with $KMnO_4$ (grey) and 7 ppb As with 0.005% Triton-X, 4 ppm S & 60 ppb Cu after UV digest, acetate buffer addition, resin treatment then $KMnO_4$ & HCl addition. Vertical axis is Current (μA) and horizontal axis is Potential (mV).

Table 3.14 Replicate analyses of test solution containing 0.005% Triton-X, 4 ppm S & 60 ppb Cu after UV digest, acetate buffer addition, resin treatment then $KMnO_4$ & HCl addition.

Solution	Run 1 (µA)	Run 2 (µA)	Run 3 (µA)	Mean (µA)	% Change from previous clean standard solution
Clean standard 1	14.9	15.1	15.2	15.15	
Mixed interferent & treatment 1	14.8	14.2	14.4	14.3	-6%
Clean standard 2	12.7	12.7	12.8	12.75	
Mixed interferent & treatment 2	12.3	11.9	11	11.45	-10%
Clean standard 3	13.1	12.5	11.8	11.8	
Mixed interferent & treatment 3	11.2	10.9	11.5	11.2	-5%

4 Discussion

4.1 Interference Testing

4.1.1 Arsenic Voltammetric Determination Methodology

The interference testing phase in this study was not intended as a detailed study of the exact levels of each interferent that would cause a 25% change in response, or the conditions which may influence the change in response to each interferent at a given level. The purpose was simply to find an interferent level which consistently gave at least a 25% change in response, so that the pre-treatment methods that were being developed and tested could be easily validated. As discussed in Section 2.1.1, this 25% criterion was derived from the USEPA practice of accepting up to a 25% variation from true values in instrument standard addition calibration checks [12, 16].

A reduction in the absolute As peak height was observed when Cu was in the solution. The exact level of Cu that was required to be added to gain a 25% reduction varied somewhat on different days of testing, but there was always at least 25% reduction at the 60 ppb level. It isn't clear why this happened, but presumably the condition of the thin gold film electrode each day and possibly environmental conditions such as temperature were factors. It's worth noting that Table 3.1 also shows indications of a possible correlation with lower initial As Peak height and increased sensitivity to Cu interference. This could be due to a poorer quality Au film being the cause of the lower As results. If this is the case, the smaller number of available active working electrode sites could mean greater competition for these sites from the more easily deposited Cu ions.

Cu interferes with As determination either by peak overlap, competing for active sites on the gold electrode surface or by forming the intermetallic compound As_2Cu_3 with As [30]. It was often difficult to accurately measure the size of an As peak with Cu present, even when the absolute peak height was not significantly affected. However, Cu interference has the advantage of being easily visible as a peak at a positive potential compared to the As peak, so treatment, although easy, is not necessary unless a significant Cu peak is seen.

Sulfide is a significant interferent in As determination in the solution being analysed, since it both complexes and precipitates As from the solution and passivates the gold working electrode [3, 44]. At lower concentrations of sulfide, the As response was initially comparable to a sulfide free solution but dropped quickly on repeat analyses of a single solution, so a concentration of 4 ppm sulfide was selected since it gave 25% reduction in peak size from the first analysis. It was also found to strongly affect subsequently analysed solutions,

even sulfide free ones, due to residual effects much like the organic interferences did. This residual interference was resolved by rinsing the analysis cell with 3 separate rinse solutions; 1M NaOH, deionised water and 0.2M HCl with 0.0001M $KMnO_4$, between each solution analysed in the cell. As well as removing any residual interferents, it is surmised that this rinsing process also resolved residual negative passivating effects, discussed in Section 1.4.3, on the working electrode. In the earlier tests without NaOH-HCl/KMnO4 rinsing, sulfide caused the significant 25% drop in As peak size in the concentration range of 0.5 to 2.5 ppm. The level of sulfide required to cause a 25% drop increased to 4 ppm with the later data using the NaOH-HCl/KMnO4 rinse between solutions, possibly due to residual KMnO4 in the analysis cell from the rinsing step. To be sure of visible sulfide interference, 4 ppm sulfide was used in further testing of the pretreatment methods.

This rinsing process was successful in removing residual interferent effects between solutions, but also damaged the gold film after several samples, which required switching to a more physically robust solid gold electrode. The solid gold electrode was then found to show an accumulating positive response to As after each 3 step rinse, which only stabilized after repeat analysis of several solutions. This was presumably due to a combination of increasing cleaning and oxidation of the electrode surface with each individual rinse process, with the oxidising effect being similar to that of pretreating gold electrodes with very positive potentials described by Salaun *et al.* [18, 23]. To counteract this variation in response at the start of each working day, a further pretreatment rinse step had to be added to the daily start-up procedure.

From the data generated in this study, Triton-X appears to be a poor choice of interferent to represent organics in water, since it not only reduced the size of the As peak, but also caused a background peak overlapping that of As at high concentrations. However, it is a defendable choice due to its widespread use in the literature as a reagent which is used to simulate organics in voltametric measurements [18, 23, 32, 54]. Triton-X is a very strong organic reagent and the concentration of 0.005% v/v (approximately 50 ppm) which was shown to cause a >25% shift in the As peak, was considerably higher than the maximum of 1 to 10 ppm dissolved organic matter that would be expected in natural waters [18, 43]. The Triton-X required in this study to cause a significant drop in As response is consistent with the results of Salaun *et al.* [18]. In Salaun's paper, no significant effect was seen for 4 ppm of Triton-X in the determination of total inorganic As, which was determined at pH 1 with a deposition potential of -1000 mV, conditions which are similar to those used in this study. However, Salaun's determination of As(III), which was carried out at natural pH, showed a complete loss of the As peak with 4 ppm Triton-X in the analysis cell – a full order of magnitude lower than the concentration used in this study. This difference in the effect of Triton-X additions on Salaun's As(III) and total inorganic As methods is presumably largely due to the difference in pH used for the As(III) and total inorganic As determinations. This suggests that the lower pH electrolyte used for

total inorganic Arsenic determination could reasonably be surmised to have the effect of reducing Triton-X interference, probably by reducing its ability to complex the analyte metal, as has been seen to happen to As with naturally occurring organics [55]. However, other work by Salaun *et al.* [23] also indicates that generation of hydrogen gas at the working electrode, under similar analysis conditions to those used in this study, could also have a cleaning effect on the working electrode, and thus reduce the effect of the Triton-X interference.

It should be noted that both Salaun *et al.* [18] and this study used a very high deposition overpotential for total As determination. Studies on other metals determined by voltammetry have been shown to overcome lack of response of organo-metallic complexes by application of larger overpotential in the deposition step [18, 54, 56, 57]. It seems reasonable to assume that deposition potential could also have some effect on organic interferences for total As. It is also possible that the Cl_2 and other oxidizing radicals generated at the counter electrode during the deposition step [18] could aid in breaking down some inorganic interferences and help reduce their effects. However, it must be noted that, in contrast with other researchers who determined As(III) in HCl medium at much less negative potentials such as -300 mV [30], Salaun *et al.* [18] used a more negative deposition potential for As(III) than for total inorganic As, so deposition potential alone could not have been a significant factor in that case.

Salaun *et al.* [18] also noted broadening of the As peak with higher Triton-X concentrations, similar to observations in this study. Those authors attribute this to the Triton-X causing increased irreversibility of the electrode process. In this study, high concentrations of Triton-X analysed in 0.25M HCl electrolyte solution containing no As, also gave a broad peak in the As region. This may have been due to some component of the Triton-X reagent giving an oxidation peak, coincidentally in the As region. While some contamination of the Triton-X reagent used with some other metal such as Bi cannot be ruled out (Sb would be oxidised to the electro-inactive Sb(V) form by Cl_2 generated at the counter electrode [23]), this would not explain the reduction in this Triton-X peak after the addition of $KMnO_4$. This does not refute the irreversibility of the electrode process explanation proposed by Salaun *et al.* but does suggest that other factors may also contribute to the peak broadening seen with Triton-X and As containing solutions that warrants further investigation. A brief investigation into the effect of $KMnO_4$ into this is described in the Appendix 2 as it was beyond the scope of this study.

4.2 Individual Treatments for Interferents

4.2.1 Cu Treatment Methods

Both methods for the removal of Cu effects on the As peak, electrolytic removal and ion exchange resin, were shown to be successful. However, despite the potential advantages in selectivity of the electrolytic Cu removal method and the successful results obtained the successful use of this apparatus required considerable amount of practice and dexterity. Most of these tests were in fact complete failures, despite consistent sample matrix and Cu deposition parameters. Trial and error determined that careful removal of the gold foil electrode was required to prevent the loss of deposited Cu back into the sample solution. Some minor modifications had to be made to the Cu removal apparatus to allow the gold foil to be removed without first, or simultaneously, removing the reference and/or counter electrode. Presumably, removal of either the reference or counter electrode from the sample solution first caused a loss of the potential applied to the gold foil electrode and thus loss of deposited Cu back into the sample solution.

In contrast to electrolytic removal, Cu removal using ion exchange resin was very straightforward, with the only complication in the single interferent tests arising when the resin was not conditioned before use. This required soaking overnight in deionised water as per the manufacturer's instructions. The reliability, ease of use, rapid analysis, very low cost, and disposable equipment made the resin method the obvious choice for the removal of Cu effects on the As peak (and for progress to Phase 3) and supports previous studies that have also shown resin removal of Cu interference for As determination by ASV to be effective [58, 59]. Apart from the resin approach, other researchers tend to focus on novel electrodes [26, 60] or Cathodic Stripping Voltammetry (CSV) methods [26, 61], which rely on deposition of As as a Cu complex, to resolve Cu interference in As determination. There may be some application for electrochemical removal of Cu in other applications (perhaps removal of Cu for Zn, Sn or Mn analysis on Hg film), but in the applications envisaged in this project, there were no significant advantages seen when compared to the ion exchange resin method.

4.2.2 Sulfide Treatment Methods

Sulfide interference in As determination by ASV is largely ignored in the literature, despite having been shown to interfere [31]. In this literature search, sulfide was only found as a tested interferent for ASV when comparing it to the Gutzeit method based kits described in Section 1.2.2, for which sulfide is a known interferent [62]. That study found no interference from sulfide for the ASV method at the tested level of 10 ppm, but no details are given for the analytical parameters or reagents used. In this study, chemical oxidation with $KMnO_4$, UV digestion, ozone pretreatment and even sample purging with air were all completely successful for removing sulfide interference, and no one treatment could be considered more successful than another for the removal of

sulfide in As detection. While it could be argued that UV digestion should have been chosen for sulfide pretreatment, since it was the only successful pretreatment method for the organic interference and therefore its use for sulfide would remove an unnecessary pretreatment method, chemical oxidation of the sample with $KMnO_4$ was selected for sulfide. There were two reasons for this. Firstly, UV digestion equipment is expensive and not easily used in the field, so is likely to be considered an unnecessary or unaffordable option for many users given that many researchers have successfully analysed As in the field by ASV without the need for UV digestion [18, 26, 27]. Thus, a more affordable pretreatment option for sulfide interference is likely to be required. Secondly, $KMnO_4$ was not only the simplest and cheapest method, but also improved the As response of clean test solutions by increasing peak size for As, making it worthy of consideration for use in As analysis even when sulfides are known not to be present.

There was also evidence that $KMnO_4$ can be used as an indicator of significant sulfide or organic contamination, since an organic free test solution would change to a clear pink / purple colour upon addition of $KMnO_4$, and retain that colour until after the repeat analyses had been carried out but sulfide or Triton-X contaminated solutions would lose this colour and become clear again within minutes. Although this should be tested with other organic interferents, it seems likely to be helpful in identifying the presence of such an interferent. Without it, organic contamination could go unnoticed if sample validation by spiking with As is not carried out. Brief testing on the utility of $KMnO_4$ without UV digestion for sulfide and organically contaminated samples was carried out and is discussed in the Appendix.

4.2.3 Organic Treatment Methods

UV digestion is a common method of sample pretreatment for voltammetric analysis [19, 33]. UV digestion is often supplemented by addition of H_2O_2 to help generate these radicals, but this option was rejected in this study due to the adverse effects of H_2O_2 described in Section 2.1.2. One observation with UV digestion was that the sample was heated to 38 degrees C during the digestion process and required approximately 40 minutes to cool to the room temperature of 24 degrees C to avoid errors associated with sample temperature described in Section 1.4.2. This cooling time brought the total pretreatment time for UV digestion to almost 2 hours including the automated cleaning cycle of the UVI4000 digester used. As expected, due to its widespread use in literature and standard methods [23, 24, 33, 34], UV digestion was highly successful in pretreating the samples containing Triton-X. Unfortunately, the ozone, chemical oxidation and ultrasonication methods were not completely successful, and so UV digest was the only defensible choice of pretreatment for organic contamination in this study.

While ozone was shown to remove the Triton-X background peak and return some response for As, the recovery was still lower than the 25% cut-off point when compared to the interferent free test solution. While it is possible that longer pretreatment times with ozone could have resulted in acceptable responses for As, the time required for pretreatment must be taken into consideration, and the time required for even the promising, but inadequate, ozone results was longer than that required for the completely successful UV digestion, even allowing for sample cooling.

Although $KMnO_4$ also failed to remove the Triton-X interferent at the concentrations studied here, there was evidence that it could be used to reduce the peak broadening and/or background peaks produced by high levels of Triton-X, thus reducing the chance that this background peak might be mistaken for As by an inexperienced operator. This, in conjunction with the lack of a colour change in the Triton-X test samples when $KMnO_4$ was added, at least aids in identification of the presence of organic interferences. This lack of a colour change is presumably due to reduction of the purple coloured MnO_4^- ions to the brown MnO_2 and possibly colourless Mn^{2+} ions upon reaction with components of the Triton-X reagent, since some slight brown stains were visible on the analysis cups when they were emptied after the analysis. Since $KMnO_4$ failed to resolve Triton-X interference, further investigation was beyond the scope of this study, however a brief investigation is described in the Appendix 2.

Ultrasonic agitation of the sample in the analysis cell was initially tested using Cu to avoid the issues of gas formation on the surface of the working electrode associated with the pH and working electrode potentials required for As analysis. Even this simpler analysis proved unusable, however, due to peaks resembling Pb and Cu appearing in blank solutions and an increasing Cu peak in Cu standard solutions. It should be noted that after several runs, the sample solution being analysed was heated to almost 60 degrees C by the horn, so this would at least partly explain the increase in the Cu peak seen with repeat runs of a single Cu standard solution. This temperature increase would also be expected to have a significant positive effect on As response without some kind of temperature control. As noted in Section 1.4.2, voltammetric response is generally considered to increase in the order of 1 to 2% for each degree C increase in temperature [24]. This alone makes this method, at least with the equipment available, unsuitable for the in-cell use that was originally envisioned.

Tests with putting the analysis cup in a water bath to overcome the temperature increase proved unsuccessful in controlling the sample temperature, possibly because the ultrasonic horn tip was closer to the working electrode than either of them were to the cooled edges of the analysis cup, reducing the effectiveness of the bath cooling at the working electrode surface. It should be noted that this in no way invalidates previous work by researchers such as Compton *et al.* [21, 32,

40, 41, 42] who proposed that it was the generation and implosion of micro-bubbles on the working electrode surface that was breaking down organics only in the immediate vicinity of the working electrode, rather than in the solution as a whole, as the mechanism for overcoming organic interference. Attempting to reproduce Compton`s apparent success would have required a complete redesign of the analysis cell to place the ultrasonic horn directly opposite the working electrode, as well as some kind of temperature control system such as a large water bath.

4.3 Mixed Treatment Testing for Multiple Interferents

A real sample contaminated with any of the 3 chosen interferents used in this study could also contain one or both of the other two interferences. For this reason, it was intended to assess the combined pretreatment methods for samples containing more than one interferent. Performance in removing the interferents of interest, ease of use and widespread applicability were considerations in the choice of methods for the mixed treatments. Therefore, when more than one pre-treatment method was successful in removing a given interferent, the simplest of the successful pretreatment methods was chosen. It should also be noted that, at this phase of the study, the gold film working electrode was used instead of the solid gold electrode, since it is specifically specified in the USEPA method for detection of As [7]. However, since $KMnO_4$ was a designated pretreatment method for this phase, further tests were carried out to ensure that the damage seen with the 3 step rinse to the gold film working electrodes described was not a result of the $KMnO_4$ component, and this successfully demonstrated that $KMnO_4$ alone does not damage the gold film electrode.

4.3.1 Copper, Sulfide and Organic Contaminated Sample Treatment

While it could be argued that UV digestion obviated the need for $KMnO_4$ oxidation since UV also removed sulfide interference, the ease of $KMnO_4$ addition and extra utility both in increasing voltammetric response and as a visible indicator of residual organic contamination seemed to make it a worthwhile addition. However, in this case the $KMnO_4$ was only added after the Cu removal resin step, since addition of $KMnO_4$ before the resin step caused the solution to turn a creamy colour after the resin, rather than the pink colour typically seen with $KMnO_4$ treated solutions. It is thought that the $KMnO_4$ caused some damage to the structure of the resin beads, as well as release some kind of organic compound into the sample itself.

Results of this combined pretreatment method were successful, although it was only carried out on three artificial solutions, so further validation work is warranted, particularly since no other references combining these pretreatments for determination of As by ASV could be found. Table 3.14 shows the results for three test solutions containing 7 ppb As, Triton-X, sulfide and Cu after the mixed

pretreatment described above. To highlight the effectiveness of the mixed pretreatment methods chosen and tested in this study, the data shown in Table 3.14is presented below, in Table 4.1, in the form of percent recovery with respect to a clean 7 ppb As standard measured immediately beforehand. The percent recovery (R) being calculated from the following equation, where H_S is the peak height of the clean stock solution and H_T is the peak height of the contaminated and pretreated test solution.

$$R = (H_T / H_S) \times 100 \qquad \text{(Equation 4.1)}$$

Table 4.1 Final results summary. Shown is response compared to previously analysed clean 7 ppb As solution expressed as % recovery for treated samples containing all three interferents.

Solution	Mean Peak Height (μA)	% Recovery (R)
Mixed interferent & treatment test 1	14.30	106%
Mixed interferent & treatment test 2	11.45	90%
Mixed interferent & treatment test 3	11.20	105%

The difference in responses (μA) between the three samples can be attributed to thin gold film deterioration during the long delay between measuring each sample, due to the approximately 2 hour long total sample pretreatment times.

To ensure a low As response in any real samples is due to a low total inorganic As concentration rather than some interference, it is proposed that all samples also be measured with a 7 ppb spike after the normal analysis. This proposed analysis procedure is described in further detail in Section 5.2.

5 Conclusions and Future Work

5.1 Conclusions

The impact of three key interference types, copper, sulfide and organics, on arsenic analysis by ASV were investigated, as well as a number of different pretreatment methods to resolve them both individually and in combination. Despite the failure of some of the newer pretreatment methods, a successful and usable combination of pretreatments was found in UV digestion, ion exchange resin and addition of $KMnO_4$ to the sample solution. Although it was only tested on artificial sample solutions rather than real natural waters, this combination of treatments was found to both reliably remove all three interferences and provide some increase in instrument performance due to the addition of $KMnO_4$. However, future work will now need to be done to test this combined treatment method on real samples.

The use of $KMnO_4$ not only successfully removed interference from sulfide, a key interferent under investigation, but became part of the intermediate cell cleaning step without which the study would have been much harder to complete due to residual contamination effects from the organic and sulfide interferences. $KMnO_4$ addition even helped to reduce some effects of the organic interference, which was more difficult to remove. Although this only reduced the Triton-X background peak, which could be mistaken for As, it is still helpful in identifying the presence of such an interferent. Without it, organic contamination could go unnoticed if sample validation by spiking with As is not carried out. Also, there is a chance that a very high level of some organics in a sample could be mistaken for As by inexperienced operators. The absence of this Triton-X peak when $KMnO_4$ is added also allows spiking an unknown sample with As for either easier identification of organic interference or standard addition analysis as described below in the recommended procedure for the analysis. Such spiking of unknown samples is a common quality control measure in standard methods such as USEPA 7063.

Despite the broad use of solid gold electrodes used in this study, gold film electrodes were generally found to be more sensitive, stable and easy to use, and are therefore recommended in the current investigations. The only drawback of gold film electrodes is their greater physical and chemical fragility, particularly if high levels of sulfide or organic interference remain in analysed samples, or if a NaOH cleaning step is required to remove such contamination. However, if such contamination is found, cleaning the cell with 1M NaOH, followed by deionised water and finally a solution of 0.2M HCl with 0.0001M $KMnO_4$ was shown to be an effective remedy. This, followed by a further deionised water rinse and fresh gold film plate was successful in removing such contamination effects several times during the course of this work.

In retrospect, a higher stock test solution concentration may have produced more stable results, since the 7 ppb solutions used in this study were quite close to the stated detection limit of 2 ppb for the solid gold electrode method. However, As will generally be analysed with respect to the regulatory limits, which is 7 ppb in Australia according to the guideline value in the Australia and New Zealand water quality guidelines [10]. Since this will be the concentration range of interest to most users, the possibility of reduced interference effects at higher concentrations of As must be considered and so analysing As at the 7 ppb level in this study still seems the most appropriate choice.

5.2 Recommended Treatment Methods and Procedures

Since levels of organic interference that can cause a significant effect on As determination are expected to be relatively uncommon in natural water, due to the lack of UV digestion required in determination of As by ASV in other studies [18, 26, 27], it seems reasonable to assume that use of the relatively expensive UV digestion system is unlikely to be needed in most cases. With this in mind, a second sample analysis procedure without the use of UV digestion was briefly investigated and is discussed in the Appendix. However, other studies indicate that organics can be present in natural samples at levels which may cause interference with voltammetric determination of As [63] and the aim of this project was to evaluate a pretreatment method for samples containing all 3 interference types. Therefore, the following method is proposed for sample pretreatment before determination of total inorganic As by ASV.

Electrode Preparation and Calibration.

1. Prepare the reference and working electrodes in accordance with the manufacturers specifications and procedures
2. Prepare a solution of 0.0001M $KMnO_4$ in 0.25M HCl. Analyse this as a blank directly two times, using the parameters given in Figure 2.3.
3. Rinse the analysis cell three times with deionised water
4. Prepare a fresh solution of 0.0001M $KMnO_4$ and 10 ppb As standard in 0.25M HCl. Analyse this as a standard directly three times, using the parameters given in Figure 2.3. Ensure the peak height is stable to within 10%.
5. Rinse the analysis cell three times with deionised water.

Method – Mixed Pretreatment of Samples with Sulfide, Copper and Organic Contamination.

1. UV digest an appropriate volume of sample for analysis in accordance with the manufacturer's procedures. Allow the UV digested sample solution to cool to room temperature.

2. Treat the UV digested sample with acetate buffer to 0.01M and treat with the Cu removal resin for 5 minutes.
3. Add 200μL of 0.01M $KMnO_4$ to every 20 mL of UV digested sample and stir. If the pink colour does not remain after 5 minutes, add further aliquots of $KMnO_4$ until the solution keeps a pink colour for 5 minutes.
4. Acidify the sample to 0.25M with HCl.
5. Analyse the sample directly two times, using the parameters given in Figure 2.3. Ensure the peak height is stable to within 10%.
6. Spike the sample solution in the analysis cell with the same amount of As used in the calibration standard. Ensure that the peak height of the spiked sample solution minus the peak height of the sample is within 25% of that seen for the clean calibration standard.

5.3 Future Work

The first priority for future work will be to validate the combined pretreatment procedure shown in Section 5.2 on real samples and compare results to ICP-MS laboratory data. Of all of the pretreatment methods investigated in this study, the addition of $KMnO_4$ stands out for its simplicity and variety of potential future applications. Further work based on this is already being carried out with Professor Yoko Fujikawa of Kyoto University. This will include testing of real groundwater and drinking water samples in Japan, Vietnam and possibly other countries in support of As remediation projects already underway at Kyoto University, which should further validate the work carried out in this study.

One particular concern with real samples is the possibility that oxidation at neutral pH of Fe(II) and Mn(II), which can be present in some real samples, could result in the loss of some As in the sample by co-precipitation. Since Fe and Mn by themselves are not considered to be significant interferences in the determination of As by ASV with this instrument [28, 29], they were not investigated as part of this study, but this possibility should be investigated. One possible solution could be to carry out the UV digestion at low pH and then raise the pH back to 4.5 with acetate buffer. A key reason this resin was chosen was that it functions at pH4.5, to which is much easier to buffer than neutral pH. This may require some method of bringing the UV digested sample`s Eh back to a less oxidising value to ensure Fe oxides don`t form at pH 4.5 however.

Due to the high cost and inconvenience of using UV digestion compared to the other pretreatment methods, along with the lower probability of the type of organic contamination represented by Triton-X being present in natural water samples at concentrations high enough to cause interference [18, 43], the possible utility of combined $KMnO_4$ and resin treatment of samples containing only sulfide and Cu contamination seems worthy of further investigation. This was briefly investigated in side tests described in the Appendix, but further work is needed.

Other uses for $KMnO_4$ which are currently under investigation are increasing sensitivity of solid gold electrodes for methods demanding very low detection limits, such as Hg, and recovery of gold electrode surfaces that have been passivated by strong negative potentials and/or strong HCl solutions.

Ozone was only partially successful in treating the Triton-X interference and so could not be chosen as the pretreatment method for organic contamination in Phase 3 of this study. However, there are still possible applications. Firstly, it does seem possible that further improvements to the ozone digestion equipment could make this efficient enough for As applications in the test matrix used in this study. Secondly, it does seem likely that a similar system could be useful in treating less strongly organically contaminated samples for other voltammetric methods, which may be less resistant to organic interference because they don't use such low pH electrolytes or large overpotentials in the deposition step. If successful, use of ozone pretreatment could become a much more affordable pretreatment method for organically contaminated samples than the relatively expensive UV digestion systems commercially available. It would also remove the need to carry Hg containing lamps into the field, thus reducing risks of accidental environmental contamination.

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7 Appendices

7.1 Appendix 1. Copper and Sulfide Contaminated Sample Treatment

Due to the lower probability of the type of organic contamination represented by Triton-X [18, 43] and the significantly higher cost and inconvenience of using UV digestion compared to the other pretreatment methods, a brief side investigation was carried out on copper and sulfide interferences with only ion exchange resin and $KMnO_4$ pretreatments. Testing of these two treatments required test samples of 7 ppb As contaminated with both sulfide and Cu at the concentrations determined in Phase 1. These were initially carried out at neutral pH, although tests at pH4.5 with acetate buffer were also successfully carried out. Initially, the resin treatment was carried out first, to avoid possible adverse effects of the $KMnO_4$ on the resin, with the HCl and $KMnO_4$ being added after the resin step, just prior to analysis. However, this approach proved unsuccessful, with a significant loss of As seen, as shown in Figure 7.1.

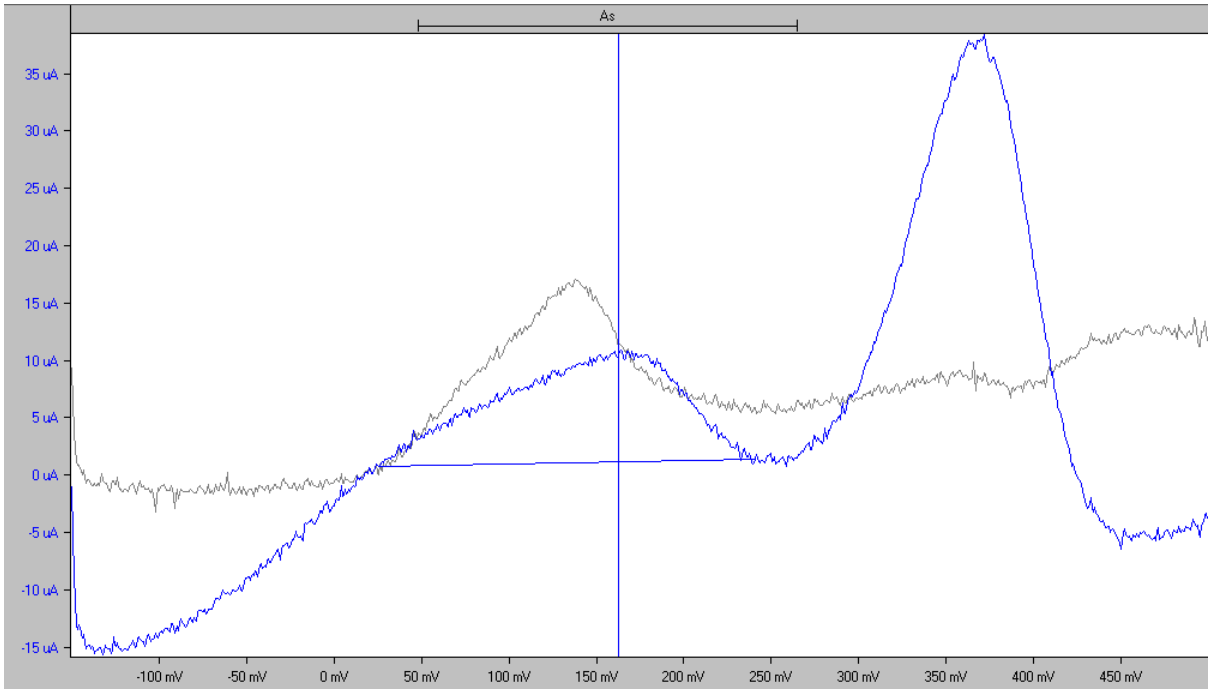

Figure 7.1 Voltammograms showing clean 7 ppb As solution (grey) and 7 ppb As with 4 ppm S & 60 ppb Cu after resin then $KMnO_4$ treatment (blue). Residual Cu peak visible between +300 mV and +450 mV. Vertical axis is Current (µA) and horizontal axis is Potential (mV).

It was found that the $KMnO_4$ had to be added to the sample both before and after the resin step. If $KMnO_4$ was not added before the resin step, then Cu removal was less effective and a reduced response for As was seen. This reduced effectiveness of Cu removal was presumed to be due to sulfide combining with the Cu, thus making it unavailable for the ion exchange process. While the loss

of As response could be said to be attributable to the higher level of residual Cu, comparison of the data with initial Cu interference tests don`t support this conclusively, as the relative size of the residual Cu and As peaks is similar to ratio`s seen in Phase 1, where change in the As response was less than the 25% threshold. It is thought that some of the As may have combined with the sulfide and precipitated in the resin column and / or the 0.45 micron filter used after the resin.

When $KMnO_4$ was added to the sulfide/Cu/As test sample before it was treated with the resin, the pink residual $KMnO_4$ colour in the sample was lost in the resin column and the sample emerged from the column a creamy colour similar to the resin itself. Both to stay consistent with the general method and as a test for the nature of this creamy sample colouration, further $KMnO_4$ was added to the sample after the resin. The first spike of $KMnO_4$ did not keep the sample pink for the previously defined 5 minutes and so a further spike was added, which did stay pink for the 5 minute period. The sample was then acidified and successfully analysed, with the As response being within an acceptable range of the clean standard, with a typical response shown in Figure 7.2. It is thought that the $KMnO_4$ caused some damage to the structure of the resin beads, causing them to lose some effectiveness, and hence remove Cu a little less effectively, as well as release some kind of organic compound into the sample itself. Here it should be noted that the experience of previous tests with $KMnO_4$ and Triton-X was useful, as it was already known that loss of colour after a $KMnO_4$ spike could indicate the presence of organic contamination.

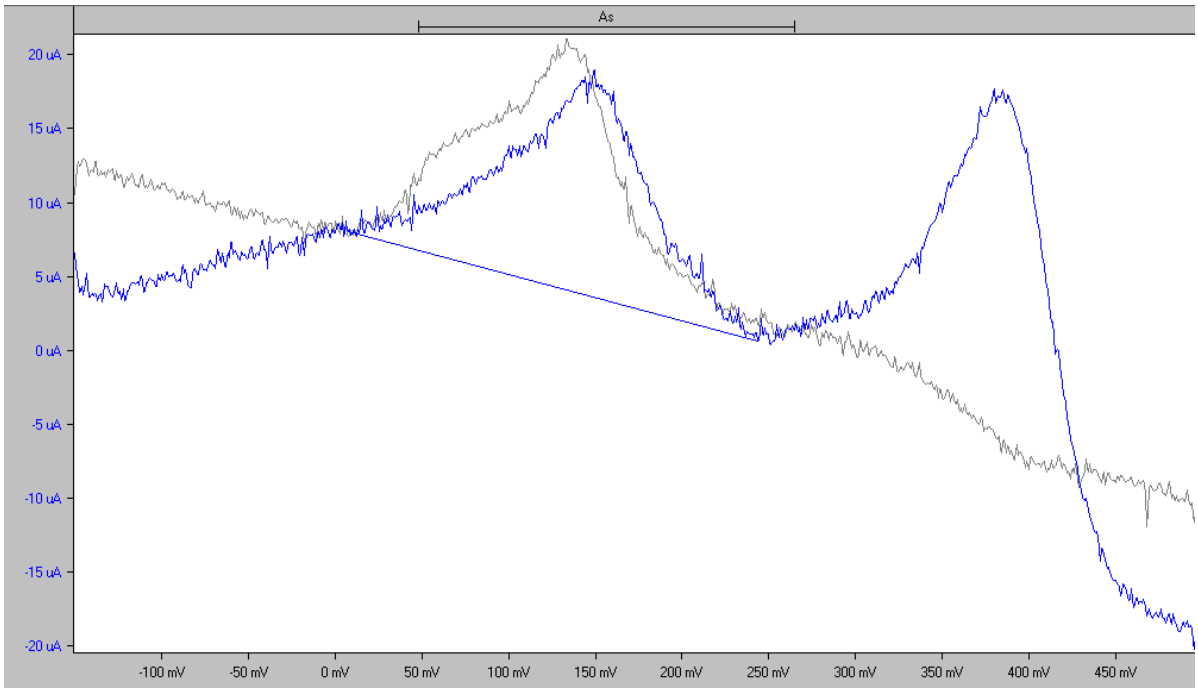

Figure 7.2 Voltammograms showing clean 7 ppb As solution (grey) and 7 ppb As with 4 ppm S & 60 ppb Cu after $KMnO_4$ addition, then resin treatment, followed by further $KMnO_4$ addition. Vertical axis is Current (µA) and horizontal axis is Potential (mV).

To ensure a low As response in real samples is due to a low total inorganic As concentration rather than some inorganic interference, two tests are proposed. Firstly the addition of $KMnO_4$ as described in Section 3.2.5, along with a 5 minute waiting time to ensure the test solution retains its pink colour, and subsequent further additions of $KMnO_4$ if it doesn`t. Secondly, it is proposed that all samples also be measured with a 7 ppb spike after the normal analysis. This proposed analysis procedure is described in further detail below.

Method – Pretreatment of Samples without UV Digestion.

1. Add 200μL of 0.01M $KMnO_4$ to every 20 mL of sample. If the pink colour does not remain after 5 minutes, add further aliquots of $KMnO_4$ until the solution keeps a pink colour for 5 minutes.
2. Treat the sample with acetate buffer to 0.01M and treat with the Cu removal resin for 5 minutes.
3. Take the sample from the resin column and add 200μL of 0.01M $KMnO_4$ for every 20 mL of sample. If the pink colour does not remain after 5 minutes, add further aliquots of $KMnO_4$ until the solution keeps a pink colour for 5 minutes.
4. Acidify the sample to 0.25M with HCl
5. Analyse the sample directly two times, using the parameters given in Figure 2.3. Ensure that the peak height is stable to within 10%.
6. Spike the sample solution in the analysis cell with the same amount of As that was used in the calibration standard. Ensure that the peak height of the spiked sample solution minus the peak height of the sample is within 25% of that seen for the clean calibration standard.

7.2 Appendix 2. Effect of $KMnO_4$ on Triton-X Interference

Given the relative ease and cost of this method compared to ozone or UV oxidation, a brief investigation was undertaken as to the effect of $KMnO_4$ pretreatment on lower concentrations of Triton-X which, although difficult to distinguish from peak data alone, do have a visible effect on the As peak. In this test, 0.00125% Triton-X was added to the 7 ppb As stock solution, giving the peak broadening effect reported in Section 3.1.3.3 and by Salaun *et al.* [18]. This was then compared to both a clean 7 ppb As solution and a solution with 7 ppb As, 0.00125% Triton-X and 200µL 0.01M $KMnO_4$. The peaks for all 3 solutions, plus a further clean test solution analysed at the end of the test, can be seen in Figure 7.3, indicating that addition of $KMnO_4$ is likely to have a beneficial effect on samples contaminated with much lower levels of organics than the 0.005% v/v Triton-X cut off point used in this study.

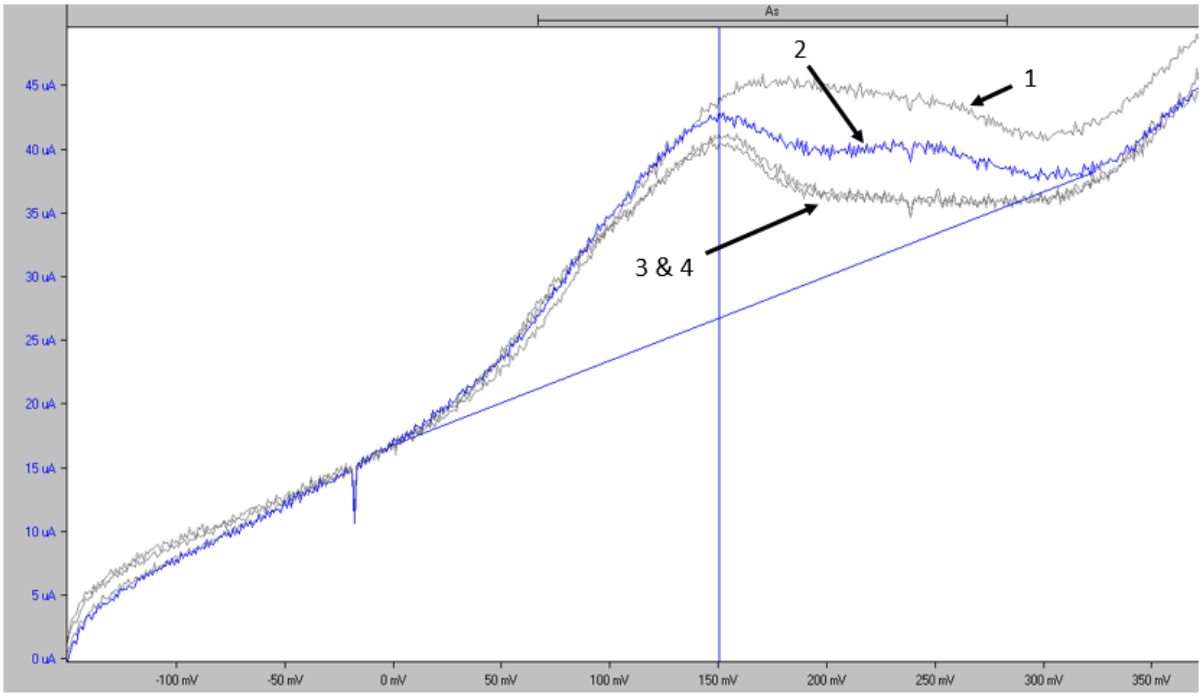

Figure 7.3 Stock 7 ppb As solution with 0.00125% Triton-X (1). 7 ppb As solution with 0.00125% Triton-X and 200µL 0.01M $KMnO_4$ (2). Clean 7 ppb As solutions measured before and after the two contaminated solutions (3&4). Vertical axis is Current (µA) and horizontal axis is Potential (mV).

So, although $KMnO_4$ treatment by itself is not a sufficient pretreatment for organic contamination, it may have a use in confirming whether a visible peak is actually As or an organic contaminant.