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ELECTROCHEMICAL OXIDATION OF ARSENIC

By

Michael William Sanville

THESIS

Submitted to
Northern Michigan University
In partial fulfillment of the requirements
For the Degree of

MASTER OF SCIENCE

Graduate Studies Office

2007

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This thesis by Michael W. Sanville is recommended for approval by the student's Thesis Committee and Department Head in the Department of Chemistry and by the Dean of Graduate Studies.

Committee Chair: Dr. Eugene Wickenheiser Date

First Reader: Dr. Lesley Putman Date

Second Reader: Dr. Mark Paulsen Date

Department Head: Dr. Suzanne Williams Date

Dean, College of Graduate Studies: Dr. Cynthia Prosen Date

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NAME: SANVILLE MICHAEL WILLIAM
(Last) (First) (Middle)

DATE OF BIRTH: NOVEMBER 07 1977
(Month) (Day) (Year)

ABSTRACT

Arsenic is a semi-metallic element found naturally in the environment, but its concentration may be elevated as a result of industrial applications including leather and wood treatment, pesticides, burning and refining petroleum fuels, and manufacturing metals. Arsenic can be more easily removed from aqueous solutions when in the oxidized arsenate, As(V), form compared to the arsenite, As(III), oxidation state.

The goal of this research project was to evaluate the use of electrochemical oxidation as a means of converting arsenite to arsenate in aqueous solutions. An electrolytic cell was created using platinum electrodes and a DC power source to oxidize arsenic in solution. Experimental parameters like pH, conductivity, and electrode size versus solution volume were used to evaluate the potential of the electrochemical oxidation method.

The results showed the increase in electrode area per solution volume increased the oxidation rate. Of the parameters evaluated in this research, the increase in conductivity resulted in the largest increase in oxidation rate. It was also concluded that HPLC was the best method for detection of arsenic. This research defines parameters that make it feasible to use electrochemical oxidation to oxidize As(III) to As(V).

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This thesis follows the format proscribed by the ACS Style Guide.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
AES	Atomic Emission Spectrometry
aq	aqueous
As	Arsenic
AsB	Arsenobetaine
ASV	Anodic Stripping Voltammetry
atm	pressure in atmospheres
AU/mV	Attenuation/millivolt
CA	Chronoampermetry
CCSA	Constant Current Stripping Analysis
CSV	Cathodic Stripping Voltammetry
DC	Direct Current
DMA	Dimethylarsenic
E	Cell potential
EDTA	Ethylene Diaminetetraacetic Acid Tetrasodium Salt Hydrate
EPA	Environmental Protection Agency
GC-MS	Gas Chromatograph-Mass Spectrometry
GF-AAS	Graphite Furnace Atomic Absorption Spectrometry
h	hour
HG	Hydride Generation
HG-AAS	Atomic Absorption Spectrometry with Hydride Generation
HMDE	Hanging Mercury Drop Electrode
HPLC	High Performance Liquid Chromatography
HPLC-USN-N2-MIP-MS	High Performance Liquid Chromatography-Ultrasonic Nebulizer-High Power Nitrogen-Microwave Induced Plasma- Mass Spectrometry
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
l	liquid
M	Molarity (moles/liter)
m/z	mass per charge
mAmp	milliamp
MCL	Maximum Contaminant Level
min	minute
mL	milliliter
mm	millimeter
MMA	Monomethylarsenic
MS	Mass Spectrometry
N	Efficiency
ng	nanogram

nm	nanometer
ppb	parts per billion
ppm	parts per million
psi	pounds per square inch
scfh	Standard Cubic Feet per Hour
SPME	Solid Phase Microextraction
SWCSV	Square Wave Cathodic Stripping Voltammetry
TBA	Tetrabutylammonium Bromide
TN	Thermospray Nebulizer
UV/VIS	Ultra Violet/Visible
V	Volts
σ	conductivity
ΔG	Free energy
λ	Wavelength
μL	microliter
$\mu\text{S}/\text{sec}$	microsiemens/second
μV	microvolt

INTRODUCTION

The purpose of this research project is to evaluate the use of electrochemical oxidation as a means of converting arsenite to arsenate in aqueous solutions. While both forms of arsenic are found in native water supplies, As(V), arsenate, is more easily removed when compared to As(III), arsenite.

Trace concentrations of Arsenic, a semi-metallic element, are found in both soil and water. Concerns about arsenic are due to toxicity and its ability to enter drinking water supplies. Natural sources of arsenic are released into the environment through forest fires, volcanic activity, and erosion of rocks (6). Arsenic does occur naturally in the environment, but elevated levels also occur as the result of industrial applications including leather and wood treatment and pesticides (1, 2). Other sources of contamination include burning fossil fuels, refining petroleum, and manufacturing metals (3, 4, 5). A major concern about arsenic contamination is that arsenic cannot be transformed into a non-toxic material but rather it must be transformed to an arsenic compound that is less toxic (7).

Arsenic is a known carcinogen, and long term exposure to arsenic has been implicated in bladder, lung, skin, kidney, liver and prostate cancers (6, 8). Short-term exposure to arsenic can lead to blindness, partial paralysis, nausea, vomiting, diarrhea, numbness in the hands and feet and discoloration or thickening of the skin (6). The detrimental health effects of arsenic have led the United States Environmental Protection Agency (EPA) to stiffen the arsenic standard for drinking water. In 1975, the EPA set the maximum contaminant level (MCL) for arsenic in drinking water at 50 ppb (7). The new

standard for arsenic in drinking water, 10 ppb, was adopted on January 22, 2001. These standards include total arsenic concentration, and do not distinguish between the different chemical forms of arsenic. All community water systems were required to be in compliance with this new standard by January 23, 2006 (9). This new regulation affects water supply systems that serve 15 locations or 25 residents year round and also affects non-community water systems that serve at least 25 people for more than six months (6). Arsenic is also a concern in countries other than the USA. The national standards for several countries located around the world are reported in Table 1.

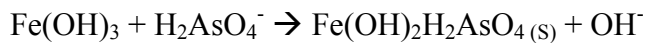
Table 1: Current national standards for arsenic in drinking water (10, 11).

Country	Standard ($\mu\text{g/L}$)
Australia	7
European Union, USA, Japan, Jordan, Laos, Mongolia, Namibia, Syria, Vietnam	10
Canada	25
Bahrain, Bangladesh, Bolivia, China, Egypt, India, Indonesia, Oman, Philippines, Saudi Arabia, Sri Lanka, Zimbabwe	50

Chemical Species

Arsenic occurs in valence states of -3, 0, +3 (As(III)) and +5 (As(V)) (12). The As(III) and As(V) are the most abundant forms with As(III) having the higher toxicity and higher mobility (13). Arsenic forms both organic and inorganic species. The inorganic species include hydrides, halides, oxides, acids and sulfides. The two main arsenic states differ as As(III) generally exists as arsenious acid (H_3AsO_3) and As(V) consists primarily as $\text{H}_2\text{AsO}_4^{-1}$ and HAsO_4^{-2} (7). It is possible to have the oxyanions of As(V) present as four different species of H_3AsO_4 , $\text{H}_2\text{AsO}_4^{-1}$, HAsO_4^{-2} and AsO_4^{-3} when

solution pH is at <2, 3-6, 8-10, and >12 respectively (14). The As(V) species are generally considered to be lower-risk although there is some concern because it is possible for bacteria to reduce As(V) (15). Organic forms of arsenic are also found in groundwater and soil including monomethylarsenic acid, dimethylarsenic acid, trimethylarsine oxide and trimethyl arsine (7). In the environment, arsenate is often immobilized on the surface of iron oxides as shown in the following equation (16).



Arsenic removal is difficult because the chemical form and valence state of arsenic can change in the environment. Some of the factors that affect the change are pH, complexation with other ions, microbial activity and oxidation-reduction potential. The absorption of arsenic on clays and other materials in the environment can also affect the mobility of arsenic.

Arsenic Removal Methods

In 2001, when the new standard for arsenic in drinking water was adopted, the EPA discussed the best available methods for the removal of arsenic from drinking water. These methods include ion exchange, activated alumina, reverse osmosis, nanofiltration, electrodialysis reversal, coagulation assisted microfiltration, modified coagulation/filtration, modified lime softening, greensand filtration, conventional iron and manganese removal along with other emerging methods (9). A brief description of several of these methods will be discussed. The methods the EPA identified to fulfill the requirements for arsenic removal and their arsenic removal efficiencies are listed in Table 2.

Table 2: Arsenic removal efficiency using standard drinking water treatment technologies, stated as maximum percent removal by mass (9).

Treatment Technology	Maximal Percent Removal
Ion Exchange (sulfate \leq 50 mg/L)	95%
Activated Alumina	95%
Reverse Osmosis	> 95%
Modified Coagulation/Filtration	95%
Modified Lime Softening (pH > 10.5)	90%
Electrodialysis Reversal	85%
Oxidation/Filtration (20:1 iron: arsenic)	80%

Precipitative Method

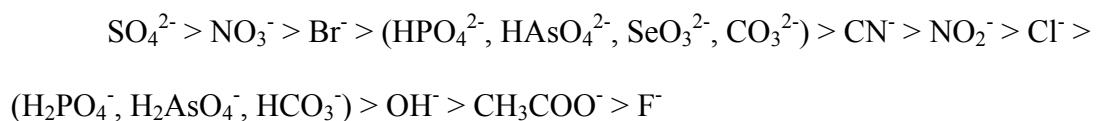
There are several types of precipitative processes that have been used to remove arsenic. One method commonly used by water treatment facilities is coagulation/filtration. This technique alters the properties of suspended matter to result in an agglomeration of particles that will settle out via gravity or by air flotation to remove the arsenic solids from solution. The removal of arsenic using this process is more successful when As(V) is present, because it forms a less soluble precipitate. When the As(III) is present, it must be oxidized to As(V) to facilitate removal by coagulation with alum, ferric chloride, or ferric sulfate. Coagulation technology has been used to remove greater than 90 percent of As(V). The precipitate forming ability of iron and aluminum decreases when the pH is greater than 7.6 causing decreased removal of As(V). Under acidic conditions the formation of a FeAsO_4 precipitate is favorable (17).

Adsorptive Method

Arsenic can be removed through adsorption on activated alumina. Clifford and Lin found activated alumina is prepared by dehydration of $\text{Al}(\text{OH})_3$ at high temperatures forming alumina oxide (18). The removal is accomplished by exchanging arsenic ions for hydroxide ions on the surface of the alumina as water is passed over the bead-filled column. In this method, arsenic removal is optimum at a pH range from 5.5 to 6.0 according to Singer and Clifford (18). The oxidation state of arsenic is also important in the adsorptive processes. Arsenate is more easily adsorbed than arsenite because arsenate is an anion at the specified pH while arsenite is fully protonated. Other considerations for this approach are the need to regenerate the column, the possibility for media fouling that reduces the number of adsorption sites and the need to control the pH. The adsorptive process also creates a concentrated arsenic solution during the column regeneration step which requires additional treatment prior to disposal.

Ion Exchange

The ion exchange resin method displaces an ion on a solid phase with an ion in the water. This approach may be advantageous for the removal of arsenic because the pH needed for optimal removal is approximately the same pH of most arsenic contaminated groundwater sources. The order of adsorption preference for an anion exchange resin is as follows (18):



The arsenic ion with the highest affinity for this type of resin is HAsO_4^{2-} because of its negative two charge allowing the HAsO_4^{2-} to exchange with hydroxide ions on the surface of the column. In this method, the presence of iron decreases the amount of arsenic removed because iron forms a neutral complex with arsenic; therefore reducing affinity to the column according to Clifford (18). When utilizing this method, the potential for resin fouling and regeneration of the column must also be considered.

Membrane Processes

Membrane processes involve passage of some particles while blocking the passage of others through a semi-permeable barrier. Some processes utilize pressure to increase the separation rate. The different types of pressure driven membrane methods include microfiltration, ultrafiltration, nanofiltration and reverse osmosis; these separation methods differ by the pore size of the membrane. Microfiltration and ultrafiltration are not the most viable techniques for the removal of arsenic from groundwater; however nanofiltration is reliable in the removal of arsenic from groundwater with a removal percentage of 90 percent (18). Unlike ion exchange and precipitation, nanofiltration can also remove both As(V) and As(III).

Reverse osmosis, which employs pressure to facilitate purification, can also be an effective way to remove arsenic from groundwater. Reverse osmosis is efficient at removing dissolved arsenic species which are often found in groundwater, however, reverse osmosis can be difficult for water scarce regions because of the volume of water required for regeneration (18). Another problem associated with the use of reverse osmosis is the concentrated ionic solution produced which requires further processing

prior to disposal. Reverse osmosis is another method requiring pre-oxidation of As (III) to As(V) for optimal removal.

Pre-Treatment Oxidation

As mentioned earlier, the two most common forms of arsenic in water are As(V) and As(III). The As(V) species that are most likely to occur within the pH range 4 to 10 are negatively charged (i.e. HAsO_4^{2-} and H_2AsO_4^-) and the As(III) species occurring in this pH range is neutral (i.e. H_3AsO_3). The neutrality of arsenite makes its removal more difficult using the common methods based on precipitation, ion exchange, and microfiltration. A solution to this problem is to use some means to oxidize As(III) to As(V) prior to arsenic removal.

Most surface water sources like river and lake water that contain arsenic have the majority of the contaminate in the As(V) oxidation state due to available oxidizing species such as dissolved oxygen. These surface sources of water do not require a pre-oxidation step, but most groundwater sources which draw from deep aquifers contain predominantly As(III) and therefore require a pre-oxidation step. Many arsenic containing groundwater sources are found in rural parts of the United States where their treatment of drinking water is minimal when water is obtained from wells. The new arsenic maximum contaminate level (MCL) of 10 ppb will put many of the small rural communities out of compliance with respect to arsenic concentrations. Due to the small size of the communities and cost of the full treatment facilities, the cost and ease of operation will be determining factors in how the new arsenic limits are met. For filtration, flotation, ion exchange, and precipitation based separation methods, one step in

the removal process will be the pre-oxidation of the As(III) in groundwater to the ionic As(V) forms.

There are several methods used to oxidize As(III) to As(V). Some of the methods include the use of oxidizing agents such as chlorine, potassium permanganate, and ozone. Other methods include photo-oxidation by UV lamp or natural sunlight in the presence of oxygen and Fe(III) which significantly increase the rate of oxidation (18, 19). Dissolved oxygen from the air or from air bubbled through the water sample can also be used to oxidize As(III) to As(V).

Electrochemistry

A technique which has recently gained notoriety uses electrochemistry to remove ionic species, particularly metal ions from aqueous solutions (20). The method uses a DC power supply with an anode and cathode to either electrodeposit, precipitate, or oxidize arsenic found in water sources (20, 21, 22). The arsenic removal technique is used in the treatment of waste streams from industrial processes and for the purification of chemical solutions. The use of iron electrodes has been found to remove >99% of arsenic in arsenic contaminated water sources (22). With little scientific data reported about the electrochemical method referred to as electrocoagulation, this research project investigates the parameters affecting the oxidation of arsenic in electrolytic cells.

The two main types of electrochemical cells are galvanic cells and electrolytic cells. In a galvanic cell energy is spontaneously released by the cell. The galvanic cell has a positive cell potential (E) and a negative change in free energy (ΔG). Batteries are common everyday examples of galvanic cells. In contrast, an electrolytic cell is a

nonspontaneous cell, opposite of the galvanic cell. The electrolytic cell requires an energy input and has a negative cell potential (E) and a positive change in free energy (ΔG). The cell types are summarized in Table 3.

Table 3: Electrochemical cell types

Cell Type	Cell Potential (E)	Free Energy (ΔG)	Reaction Type
Galvanic	+	-	Spontaneous
Electrolytic	-	+	Nonspontaneous
Dead Battery	0	0	Equilibrium

Arsenic Analysis Techniques

Multiple determination methods have been developed for the speciation and quantification of arsenic levels over the past 45 years. The most common analysis techniques include spectrophotometry and electrochemistry (12). The research in this project employed primarily spectrophotometric methods and also attempted the use of gas chromatography-mass spectrometry. Many of the analysis techniques require a pre-analysis derivatization step (e.g. hydride generation), and separation techniques for speciation of the arsenic compounds are also frequently used, such as gas or liquid chromatography. Therefore, the methods are normally a hyphenated combination of steps.

The spectrometry methods commonly used in the determination of arsenic species include UV/VIS, atomic absorption spectrometry (AAS), and graphite furnace atomic absorption spectrometry (GF-AAS). The use of atomic absorption spectrometry with hydride generation (HG-AAS) using atomic flame adsorption allows determination of

arsenic in the concentration range of 1 to 20 ppb (23). Although HG-AAS is very sensitive, it has been found to be subject to error if organic forms of arsenic are found in the sample solution (24). The detection limits of UV/VIS arsenic determinations were not reported in the literature.

Analysis methods based on inductively coupled plasma (ICP) atomization include ICP-mass spectrometry (MS) and ICP-atomic emission spectrometry (AES); each of these have been used in other multi-hyphenated methods (i.e. ICP-MS). One example of a multi-hyphenated analysis method is high performance liquid chromatography-ultrasonic nebulizer-high power nitrogen-microwave-induced plasma-mass spectrometry (HPLC-USN-N₂-MIP-MS), which reports an As(V) detection limit of 0.46 ppb (25). Another method using HPLC-ICP-thermospray nebulizer (TN) reported arsenic detection limits in the range of 0.04-0.12 ppb (26). A third method reported the simultaneous determination of As(V), monomethylarsenic (MMA), dimethylarsenic (DMA), As(III), and arsenobetaine (AsB) using a multi-mode ion exchange column as part of the HPLC method followed by ICP-MS. This method gave a range of detection limits with the lowest being 0.02 ppb for arsenobetaine and the highest limit of 0.4 ppm for monomethylarsenic (27).

Some of the available electrochemical analysis methods used to determine arsenic concentrations include cathodic stripping voltammetry (CSV), chronoamperometry (CA), constant current stripping analysis (CCSA), anodic stripping voltammetry (ASV), and square wave cathodic stripping voltammetry (SWCSV). These methods are reported to have detection limits for As(III) and As(V) ranging from 0.005 ppb to 3 ppb with most under 1 ppb (12). Another electrochemical method using CSV on a hanging mercury

drop electrode (HMDE) is used to analyze environmental water samples. The detection limit for As(III), As(V), MMA, and DMA is 0.3 ppb with a linear detection range from 2.5 ppb to 190 ppb (28).

There are many methods available for the detection of arsenic in aqueous solutions. Many of the methods report detection limits at concentrations less than 1 ppb of arsenic. The majority of the methods require specialized analysis equipment to complete arsenic determinations. The optimization of methods performed in this research project will attempt to simplify arsenic analysis.

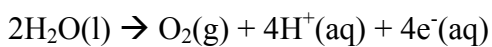
This study will investigate the pre-oxidation of arsenic in an electrolytic cell. The oxidation of As(III) by DC power will be investigated by monitoring the effects of variations in solution characteristic including pH, conductivity (σ), solution volume, and concentration. The results of the oxidation experiments will be measured using HPLC, GF-AAS, HG-AAS, and GC-MS.

With very little scientific data reported about the electrochemical oxidation of arsenite, this research project investigates the parameters affecting the oxidation of arsenic in electrolytic cells. The available reduction half-reactions of the arsenic experimental solutions are summarized in Table 4. The half-reactions found in Table 4 are discussed below as the reactions pertain to the anode and cathode for this research project:

E_{anode} :

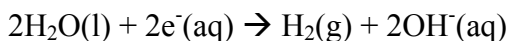
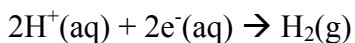


The arsenite will be the first species oxidized in the electrolytic cell.



After all of the arsenite is oxidized, the next half-reaction at the anode will be the oxidation of water. The oxidation half cell potential E° for water is -1.23 V.

E_{cathode} :



The first reduction reaction will be favored due to the higher E° value as reported in Table 4.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

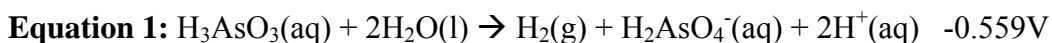


Table 4: Reduction Potentials Half-Reactions of species found in solution:

Reduction Half-Reactions	E° (V)
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{H}_3\text{AsO}_4(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^-(\text{aq}) \rightarrow \text{H}_3\text{AsO}_3(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	0.559
$2\text{H}^+(\text{aq}) + 2\text{e}^-(\text{aq}) \rightarrow \text{H}_2(\text{g})$	0
$\text{H}_2\text{AsO}_4^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^-(\text{aq}) \rightarrow \text{H}_3\text{AsO}_3(\text{aq}) + 3\text{OH}^-(\text{aq})$	- 0.08
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^-(\text{aq}) \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	- 0.83

The electrolytic cell reaction is therefore as displayed in Equation 1. The balanced equation shows a cell potential of -0.559V. The cell is a nonspontaneous reaction requiring an energy input of 0.559 V for a 1 M solutions of each species at 298 K and 1 atm to oxidize arsenite. Equation 1 and the half-reaction equations demonstrate the experimental chemistry that serves as the basis for this research.

MATERIALS AND METHODS

Materials

Standard arsenic solution in 10% nitric acid certified 1000 ppm +/- 1% was obtained from Fisher Chemicals. Solid arsenic acid anhydride was manufactured by Fisher Certified Reagents. The arsenous oxide was produced at 100.03% purity by Thorn Smith. Fisher Chemical Company also supplied o-phosphoric acid 85%, ferric chloride, aluminum chloride, and sodium acetate trihydrate. The sodium borohydrate 98% and ethylene diaminetetraacetic acid tetrasodium salt hydrate (EDTA) were received from Sigma. Potassium phosphate was obtained from Baker's Analyzed. Aldrich produced the tetrabutylammonium bromide (TBA). Dr. David Kingston graciously supplied a conductivity standard of potassium chloride. Sodium carbonate monohydrate crystal was obtained from Flinn Scientific Inc. Sodium bicarbonate and potassium hydrogen phalate (primary standard) were obtained from Acros Organics. The matrix modifier, nickel nitrate, was received in hydrated flake form from Mallinckrodt. The carrier and purge gases, nitrogen and argon, were supplied locally by Intrastate Welding.

Equipment

The Spectronic Genesys 2 and Shimadzu UV 3101PC scanning ultraviolet/visible spectrophotometers were used to optimize the detection wavelength for the arsenic ions. Samples were analyzed using plastic cuvetts in the Spectronic Genesys 2. The Shimadzu UV 3101PC instrument was used with a matched set of quartz cuvetts.

High performance liquid chromatography (HPLC) analysis was completed using a Varian Vista Series HPLC, Model 5500 with a Varian 4270 Integrator. An Alltech, Allsep anion 7 μm 150 mm x 4.6 mm anion exchange column was used for chromatographic separation.

The atomic absorption determinations were detected using a Perkin Elmer HCA-800 and AAnalyst 300 with a Perkin Elmer AS-72 auto-sampler. The Perkin Elmer AAS analysis equipment included a graphite furnace.

Gas chromatograph-mass spectrometry (GC-MS) were conducted using a Finnigan Trace DSQ Mass Spectrometer, equipped with direct probe, Trace GC ultra gas chromatograph, and AS3000 autosampler.

The electrolysis reactions were completed using the apparatus displayed in Figure 1. The arsenic solutions were held in a 300 mL beaker like glass container with a sealable cover and no pouring spout. Two Fisher Scientific Platinum Electrodes, 2.5 mm x 10.0 mm flag electrodes were used as the anode and cathode. The cover of the container was altered allowing the two platinum electrodes to pass through it, and be submerged in the arsenic solution. Glass shafts protected the copper wires which connect to the platinum flags, preventing moisture exposure and oxidation of the copper and copper-platinum interface. Bored number 5 rubber stoppers were used to seal the penetrating hole through the glassware cover. Thin gauge wires with alligator clips were used to attach the electrodes to the DC power source. An Elenco Precision: Variable Regulated Power Supply Model XP-656 was used to generate the DC potential required for the oxidation reaction. The oxidation vessel was placed on a Corning Model PC-220, 0-10 stirrer/hotplate. The experimental chamber was placed on a stirrer hotplate.

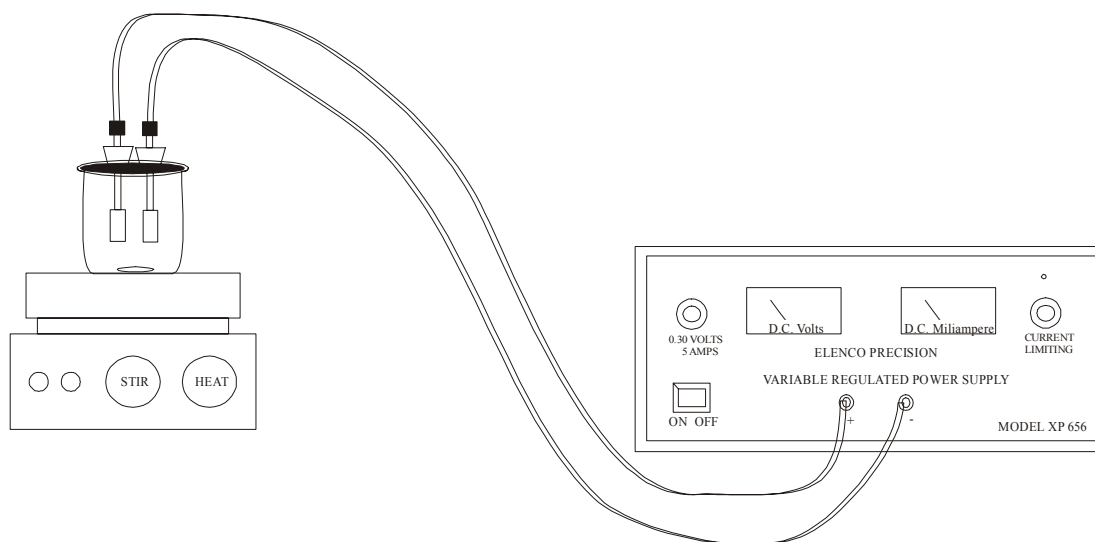


Figure 1: Electrochemical oxidation apparatus

Procedures

HPLC Mobile Phase Detection Optimization

The mobile phase buffers were analyzed neat and with 100 ppm arsenic in solution using the Spectronic Genesys 2 (200-400 nm) and the Shimadzu UV 3101PC scanning spectrophotometer (190-250 nm) using water and buffer as blanks, respectively. The wavelength with maximum absorbance were used for UV/VIS detection on the HPLC.

A 0.10 M tetrabutylammonium bromide (TBA) 0.20 M potassium phosphate adjusted to pH 5.5 with sodium hydroxide was made in 1 L stock solutions. The buffer was made by adding 32.239 g of TBA and 27.218 g of KH_2PO_4 to a 250 mL beaker. The beaker was filled to 175 mL with dH_2O and the pH was adjusted to 5.5 with 0.1 M NaOH. The mixture was transferred to a 1 L volumetric flask and the flask was filled to the line with dH_2O .

A 12 mM phosphate solution was made using neat H_3PO_4 adjusted to pH 5.5 with 6 M NaOH. A 1.371 g aliquot of H_3PO_4 was added to a 30 mL beaker followed by 20 mL of dH_2O . The pH was adjusted to 5.3 using approximately 50 drops of 6.0 M NaOH. The mixture was then transferred to a 1 L volumetric flask and filled to the base of the neck with dH_2O . The pH was adjusted to 5.5 using 0.1 M NaOH and the flask was filled to the line with dH_2O .

A 12 mM acetate buffer at pH 5.5 was made from 0.994 mL of acetic acid and 0.8165 g of sodium acetate. The aliquots were added to a 1 L volumetric flask and filled to the base of the neck with dH_2O . The pH was adjusted to 5.5 using 0.1 M NaOH and the volumetric flask was filled to the line.

Arsenic Oxide Preparation:

Arsenous oxide standard solutions were prepared by first drying the As_2O_3 for three hours at 105°C , and then transferring it to the desiccator for storage. For a 1,000 ppm As(III) standard solution, 0.132 g of arsenous acid was weighed into a 20 mL glass vial. Next, 10 mL of 6 M NaOH were added and mixed until all the white powder dissolved. Gentle heating was used to aid in the dissolving of the oxide. The solution was diluted with ~50 mL of 12 mM phosphate solution before the pH was adjusted back to 5.5 with concentrated HCl. After the pH was adjusted to 5.5 the solution was transferred to a 100 mL volumetric flask and filled to the line with 12 mM phosphate solution.

Arsenic pentoxide, As_2O_5 , was used to make the 1,000 ppm As(V) standard solution. The 12 mM phosphate solution pH 5.5 was used in a volume of ~ 50 mL to

dissolve 0.1549 g of arsenic pentoxide. The pH of the solution was adjusted to pH 5.5 with concentrated NaOH and 0.1 M HCl. The mixture was then transferred to a 100 mL volumetric flask and filled to the line with 12 mM phosphate solution with a pH of 5.5.

Spectrophotometric Detection of Arsenic Using Alizarin Red S:

Another method of detection was investigated using sodium 1,2-dihydroxyanthraquinone 3-sulphonic acid, alizarin red S, in a buffer solution to determine arsenic concentration in solution. It was reported that the alizarin will react to allow spectrophotometric determination of arsenic at λ_{max} 520 nm under slightly acidic conditions, pH 5.4-6.1 (29). Scans of 100 μL alizarin red S in 12 mM phosphate solution pH 5.5 with 100-ppm As(V) and without As(V) present were used to determine the validity of this method.

Arsenic Stability in Storage:

The storage stability of the As(III) and electrolysis solutions were tested to measure the usable shelf life of the samples. The arsenic standard electrolysis solutions were analyzed by HPLC. The samples were tested for As(III) concentrations at the time of solution make-up or electrolysis. Those concentrations were then compared to results from later analysis done on the same samples stored for 24 and 48 hours at 4°C.

The standard solutions were also left at room temperature for 2.5 hours to simulate the time required to make the electrolysis solution along with the actual electrolysis reaction time. These samples were then analyzed after the prescribed time using the method described for HPLC sample analysis.

Another HPLC investigation was performed to assure the long term storage viability for the As(III) standard solutions. The concentrated, 1000 ppm, As(III) standard solution was made and then stored for 960 hours at 4°C. This solution was analyzed using the HPLC protocol to test for As(III) stability and the appearance of As(V) in solution. For these tests, the 1000 ppm As(III) solution was diluted to 50.9 and 101.7 ppm to fit the working analysis range of the HPLC column and UV/VIS detector.

The electrolysis sample solutions were tested for storage stability as well, after 24 and 48 hours of storage. The tests were performed using the AAS protocol. This was just a preventative investigation in the case an electrolysis sample could not be analyzed at the time of oxidation.

Electrochemical Oxidation of Arsenic:

The electrolysis reactions were carried out in a 300 mL glass container with the two platinum electrodes submerged approximately halfway between the surface of the solution and the bottom of the container. The electrolysis volume was held constant at 110 mL for all concentrations. The pH and conductivity were measured after reaction solution make-up prior to the start of electrolysis, and they were also measured 3 or 4 times during electrolysis while samples were being collected. The voltage and amperage were also measured at the same time samples were collected. The As(III) standard solution was diluted to the desired concentration using the buffer required for each specific analysis method, i.e. HPLC 12 mM phosphate solution and AAS 12 mM acetic acid/sodium acetate buffer. The required conductivity was obtained by addition of NaCl to the electrolysis solution. At predetermined sample intervals, for example 0, 60, 120,

180, and 240 min, the DC power unit would be turned off. The cover and platinum electrodes would be removed and a 1.0 mL sample would be collected using the 1000 μ L fannpipette. The samples would be stored in a properly labeled 10 mL glass vial, and stored at 4°C until analysis. At the sample collection time, the pH and conductivity would be measured with the respective probes. The sampling would be completed as quickly as possible to prevent any oxidation due to oxygen in the air contacting the electrolysis solution.

HPLC Analysis of Arsenic Solutions:

The sample and guard columns were conditioned by running approximately 1 L of mobile phase through the columns. The mobile phase was initially prepared with 0.10 M tetrabutylammonium bromide (TBA) and 0.20 M potassium phosphate, and then adjusted to pH 6.0 with concentrated phosphoric acid.

The samples were analyzed using a 20 μ L sample added manually to the injection loop. The 12 mM phosphate solution pH 5.5 was located at location A, and the method was set to pump 1 mL/min of 100% A. The column operating temperature was set to 40°C. The recorder signal from the HPLC software was set at 0.1 AU/mV. The Varian 4270 integrator attenuation was set to 32, and the peak evaluation was internally adjusted to 120. The integrator used thermal paper to produce the chromatograms, and included a table of peak area when requested by pressing the results tab.

A 1.0 mL syringe was used to inject the arsenic samples. The syringe was triple rinsed with dH₂O and dried between samples.

HPLC Anion Exchange Column Regeneration:

The HPLC column was producing reduced retention times for both As(V) and As(III), therefore the Alltech regeneration procedure was used to assure peak resolution and identification would remain consistent. Table 5 shows the regimen used to regenerate the column.

Table 5: Anion Exchange Column Regeneration Procedure

Step	Material	Volume
1	12 mM Phosphate solution	20 mL
2	18 mM Phosphate solution	20 mL
3	HPLC Water, 0.45 µm filter	20 mL
4	0.1 M EDTA	20 mL
5	HPLC Water, 0.45 µm filter	20 mL
6	Acetonitrile	20 mL
7	HPLC Water, 0.45 µm filter	20 mL

Glassware Cleaning:

All glassware was washed with soap and tap water in the sink, and then rinsed with deionized water. Second, the glassware was placed in a covered plastic container filled with 7% phosphoric acid, and remained there for a minimum of twenty-four hours. Third, the glassware was transferred to a second 7% phosphoric acid bath for a minimum of twenty-four more hours. Finally, the glassware was transferred to a deionized water bath for a minimum of twenty-four hours.

Atomic Absorption Spectrometry Graphite Furnace Analysis:

Arsenic standard curves and unknown sample analysis were analyzed using the Perkin Elmer AAS with AA WinLab software to interface the instrument. The recommended HGA analytical conditions for arsenic included a monochromatic wavelength of 193.7 nm, slit width of 0.7 nm, matrix modifier of 0.02 mg nickel as nickel nitrate, pretreatment furnace temperature of 1300°C, and an atomization temperature of 2300°C. These conditions were used as a starting point of optimization. The matrix modifier was made-up as a 0.0342 M nickel nitrate solution and placed in location 61 of the AAS autosampler for logistics of addition to each analysis. At this concentration 10 µL of matrix modifier was added to each arsenic analysis. After optimization of the arsenic absorbance signal, the conditions used for analysis were slit width of 2.0 nm, pretreatment furnace temperature of 700°C, and an atomization temperature of 2100°C.

An example of the furnace program used for arsenic analysis using the AAS follows in Table 6. The temperatures and times were adjusted throughout the experiments based on performance. Certain conditions like furnace replacement, decreased signal, and PMT overloads made it mandatory to re-optimize the system. This always mandated small changes in the furnace program.

Table 6: AAS Furnace Program

Temperature (°C)	Ramp Time (sec)	Hold Time (sec)	Air Flow (scfh)	Description
150	10	50	250	Water Flash
700	1	30	250	Organic Flash
20	1	15	250	Rest
2100	0	10	0	Analysis
2400	1	5	250	Clean Out

The arsenic samples were analyzed using injection volumes of 10 μL . This volume and the 10 μL matrix modifier volume gave a total injection volume of 20 μL . The injection made a small, ~ 0.8 mm, droplet on the floor of the graphite furnace. A greater injection volume of 20 μL arsenic sample and 10 μL matrix modifier was used for several trials. The 30 μL injection gave a larger, ~ 1.1 mm, droplet on the graphite furnace. The larger volume was used after a decrease in signal during analysis. Later, the injection volume was again returned to the 20 μL total volume initially used.

The auto-sampler was used to make the standard curve dilutions. A concentrated arsenic sample was placed in the auto-sampler along with a diluent vial of 6 mM acetic acid/sodium acetate. The arsenic standard and diluent contained 0.327 M acetic acid, which was necessary for the borohydride analysis of the unknown arsenic samples. The concentrations were recorded in a standard dilution chart. Table 7 shows an example standard concentration chart with the diluent location specified as A/S (auto-sampler) location 1 on another screen of the method listed.

Table 7: Method As040812 Standard Dilution Concentrations

ID	Concentration (ppb)	A/S Location	Stock Vol (μL)	Dil Vol (μL)
Calib Blank	Blank	1	10	0
As(III) 98.23	98.23	2	1	9
As(III) 294.7	294.7	2	3	7
As(III) 491.2	491.2	2	5	5
As(III) 687.6	687.6	2	7	3
As(III) 982.3	982.3	2	10	0

The AA WinLab software program produced standard curves for the calibration data collected from auto dilution analysis. The standard curves were plots of the average blank corrected signal recorded for each sample concentration, and included a correlation coefficient for the linear fit of the data. These standard curves were reproduced using Origin 5.0. The five actual data points were used in these plots giving a more representative correlation coefficient for the data set.

Hydride Generation of Arsenic:

Arsenic samples were prepared for hydride generation using 1.1 mL autosampler vials from the Perkin Elmer AAS. The total solution volume of 700 μL and volume of sodium borohydride (1%) of 300 μL remained constant through all reduction reactions. The reduction of the arsenic species by hydride generation was performed in the presence of 40 μL of 6.036 M acetic acid giving a calculated pH of 2.36. The sodium borohydride was added using 3 injections of 100 μL taking ~60 seconds for total addition due to bubble formation during the borohydride addition. The solution was purged with

nitrogen during sodium borohydride addition and for an extended time afterwards to reach a total purge time of 150 seconds. The flow rate of the nitrogen gas was adjusted with a needle valve to bubble once every 2 seconds. The samples were taken directly from the purge fume hood to the Perkin Elmer AAS for immediate analysis. Five replicates of each sample were analyzed on the AAS.

Arsine collection for GC-MS Analysis:

The same experimental solutions were used to analyze arsine gas formation using the GC-MS. These solutions included 300 μL standard arsenic solution in 6 mM acetic acid/sodium acetate buffer, 40 μL 6.036 M acetic acid, 60 μL 6 mM acetic acid/sodium acetate buffer, and 300 μL 1% sodium borohydride for a total solution volume of 700 μL . All materials except the sodium borohydride were added to a 50 mL narrow neck glass container with a rubber cap. The cap was penetrated by three needles; the first was an open syringe needle used as a vent, the second was a 1.0 mL syringe used to add the 300 μL of 1% sodium borohydride, and the third was the Supelco fiber assembly with a 100 μm polydimethylsiloxane coating. The sodium borohydride was added slowly to the container, 300 μL over a 30 second period, to prevent excess bubbling. The coated fiber was exposed for varied amounts of time (30 sec to 30 min) to optimize arsine adsorption, while minimizing contamination. The fiber was then drawn back into its needle housing, removed from the rubber stopper, and inserted into the manual inject of the GC-MS. There, the fiber was re-exposed in the 200° C pre-column chamber for 1 minute. The fiber was removed from the GC-MS during the sample analysis, but after the run the fiber

was place back in the pre-column chamber for a 9 minute clean off exposure before the next analysis.

RESULTS AND DISCUSSION

The experimental results and procedures discussed below were completed to evaluate the potential use of electrochemistry as a means of converting arsenite, As(III), to arsenate, As(V), in drinking water acquired from groundwater sources. Considerable preliminary ground work was required prior to the evaluation of electrochemical oxidation of arsenite to arsenate. Reaction solutions and analysis methods had to be evaluated prior to optimizing the electrochemical oxidation apparatus. First, experimental solutions were evaluated based on electrochemical oxidation potential, buffering ability, and UV/VIS detection. Next, analysis methods such as, High Performance Liquid Chromatography (HPLC), Gas Chromatograph-Mass Spectrometry (GC-MS), and Atomic Absorbance Spectrometry (AAS) were evaluated using varied experimental parameters. The evaluation of the arsenic oxidation was completed by varying experimental parameters including stirring, pH effects, ionic solution strength, and plate surface area experiments.

Optimization of Experimental Solutions

In order to properly and consistently analyze the electrochemical oxidation of arsenite to arsenate it was necessary to establish appropriate experimental solutions. The experimental solution had to be compatible with the electrochemical oxidation procedure while providing buffering capacity to prevent pH change. It was also necessary for the buffer solution to be compatible with the UV/VIS detector, HPLC column, and AAS graphite furnace flame ionization detector.

Since the first stage of the investigation was designed to use HPLC with an UV/VIS detector to separate As(III) and As(V) in an aqueous solution, it was important to find an acceptable mobile phase solution to carry the arsenic through the HPLC column that would not interfere with the detection of arsenic in the UV/VIS range. The electrochemical oxidation reaction produced protons as a product during the reaction as shown in Equation 1 on page 12. The mobile phase was required to resist large changes in pH due to the electrochemical oxidation taking place in the test chamber. Therefore, buffering solutions were tested as possible mobile phases. Several buffering solutions found in the literature were mixed with experimental arsenic and analyzed to assure the buffer would not interfere with arsenic analysis.

In order to choose a pH where arsenite was a fully protonated non-ionic molecule and arsenate was a deprotonated ionic molecule; the alpha plots of arsenite and arsenate were compared. As Figure 2 displays, the arsenious acid, As(III), was fully protonated at a $\text{pH} < 7.5$. Figure 3 shows the arsenic acid, As(V), was ionic with at least one proton removed at $\text{pH} > 4.5$. From the alpha plots, the optimized experimental pH was determined to be 5.5. The pH of 5.5 gave representative conditions of groundwater sources where the As(III) was fully protonated and the As(V) was an ion.

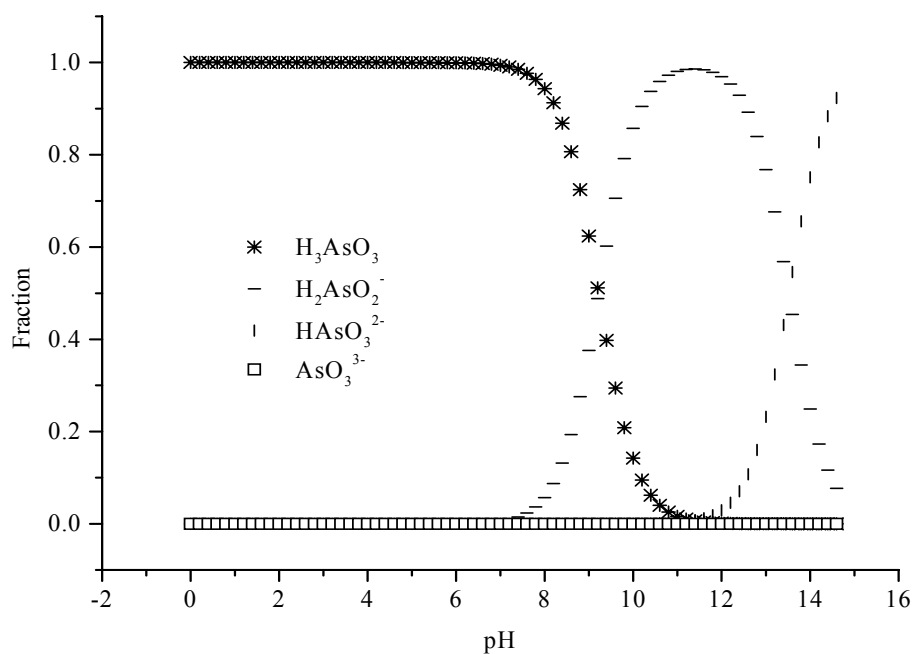


Figure 2: H_3AsO_3 alpha plot calculated from arsenous acid K_a values.

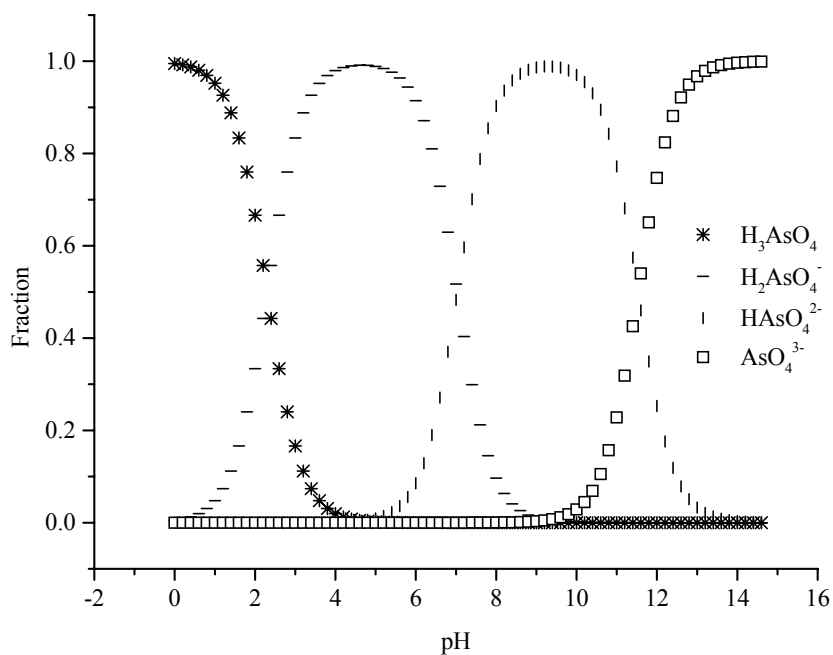


Figure 3: H_3AsO_4 alpha plot calculated from arsenic acid K_a values.

After the experimental pH of the arsenic solution was determined, the optimal wavelength of UV/VIS analysis had to be determined and evaluated for possible interference from molecules in the buffer solution. The first buffered mobile phase contained 0.10 M tetrabutylammonium bromide (TBA) and 0.20 M potassium phosphate adjusted to pH 5.5 with concentrated phosphoric acid (TBA buffer). The TBA buffer had peaks in the 208-220 nm range when analyzed using the Spectronic Genesys 2 scanning spectrophotometer with a water reference solution, these peaks would not interfere with arsenic analysis in the lower UV range of < 200 nm.

The standard arsenic solutions were made up in the TBA buffer. The sample buffer was tested using the Spectronic Genesys 2 scanning spectrophotometer to determine the wavelengths where arsenic in the samples would be detectable. The pure TBA buffer was used as a reference, while an arsenic solution containing 100.0 ppm of As(V) was used as the test solution. The Genesys 2 spectrum displayed detectable peaks at < 205 nm and 217 nm as displayed in Figure 4. The peak at 217 nm was larger than the peak which ended at 200 nm, but it could be possible the majority of the 200 nm peak was actually found in the UV range less than 200 nm. Since the UV/VIS detector on the Varian Vista 5500 HPLC had an ultraviolet detection which read from 190 nm, the 190 nm to 200 nm range of the spectrum was investigated to determine if there was a wavelength with a greater absorbance reading than 217 nm. As previously mentioned, the TBA buffer also had a relatively large peak at 217 nm.

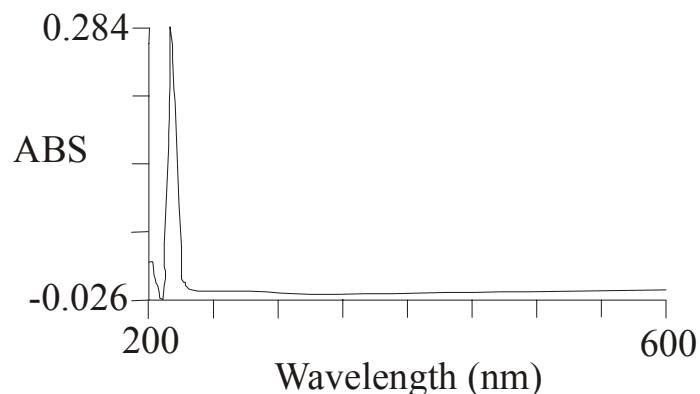


Figure 4: Spectrogram of 100.0 ppm arsenate in TBA buffer analyzed on Spectronic Genesys 2 spectrophotometer.

Since the Genesys 2 spectrophotometer has a lower wavelength limit of 200 nm in the UV range, the Shimadzu UV 3101PC spectrophotometer was used to scan the UV/VIS range between 190 nm and 400 nm. The same reference solution containing 100.0 ppm of As(V) in the TBA buffer and the neat TBA buffer as a reference were scanned for the trial. The results of the scan showed that 190 nm was the optimum wavelength in the UV/VIS range for analysis of arsenic in the TBA buffer solution. The absorbance peak for 100.0 ppm As(V) at 217 nm was ~0.25 absorbance units and the absorbance peak at 190 nm was greater than 3 absorbance units. The optimized wavelength and increase in absorbance significantly enhanced the detection limit of arsenic in solution, which allowed HPLC investigations to be performed at arsenic concentrations ranging from 5-100 ppm.

An additional buffer was analyzed using the Shimadzu UV 3101PC scanning spectrophotometer to determine if the phosphate solution would interfere with arsenic absorbance in the UV range. The new buffer was 0.12 M potassium phosphate solution adjusted to pH 5.5 with concentrated phosphoric acid. The phosphate solution was used as a reference solution for analysis of a 50.7 ppm As(V) solution made in the 0.12 M

phosphate solution at pH 5.5. The 50.7 ppm As(V) absorbance scan gave an absorbance peak over 2.1 absorbance units in the UV range from 190 to 200 nm. Therefore, the phosphate solution would not interfere, was suitable for use, and provided ~25% greater sensitivity when compared to the TBA buffer.

Two buffer solutions were deemed acceptable for future experiments. The TBA buffer was initially used as the buffer for electrochemical oxidation and as a HPLC mobile phase. In later trials, a phosphate solution at pH 5.5 was used as the oxidation solution and mobile phase for the HPLC analysis.

Arsenic Determination Using Alizarin Red S

Post-column derivitization has been employed for the detection of metals and semi-metals in many applications (29). The method has been used with metals to increase sensitivity during analysis. Ahmed and Hassan reported the use of 1, 2-dihydroxyanthraquinone-3 sulphonic acid sodium salt at pH 5.4-6.1 (alizarin red S) as an indicator to detect As(V) in solution with a linear absorbance correlation when compared to concentrations from 0.1 ppm to 18 ppm arsenic (29). To investigate the possible use of alizarin red S by post column derivatizing, alizarin red S was added to a sample of 100.0 ppm As(V) and the solution's UV/VIS spectrum was collected. An absorbance peak with a significant peak height would indicate the alizarin red S would chelate arsenic and allow analysis by post-column derivitization.

Figure 5 shows the results collected using the Spectronic Genesys 2 spectrophotometer to compare absorbance intensities for the 100.0 ppm As(V) solution in the TBA buffer with alizarin red S compared to the TBA buffer with 100.0 ppm As(V).

Both samples were analyzed using the TBA buffer as the reference solution. The spectra showed the TBA buffer/arsenic/alizarin red S absorbance at the specified 520 nm wavelength was only 0.04 absorbance units larger than the TBA buffer/arsenic. When these two samples were compared at 214 nm, in the range of buffer and arsenic absorbance, the buffer/arsenic/alizarin solution gave a peak with absorbance 0.10 absorbance units larger. Also, the peaks size at 214 nm was 3.6 absorbance units versus only 0.4 absorbance units at 520 nm. The peak heights at 520 nm for both solutions, with and without alizarin, were equal; therefore the alizarin red S interaction with arsenic was not a viable means to analyze arsenic concentration.

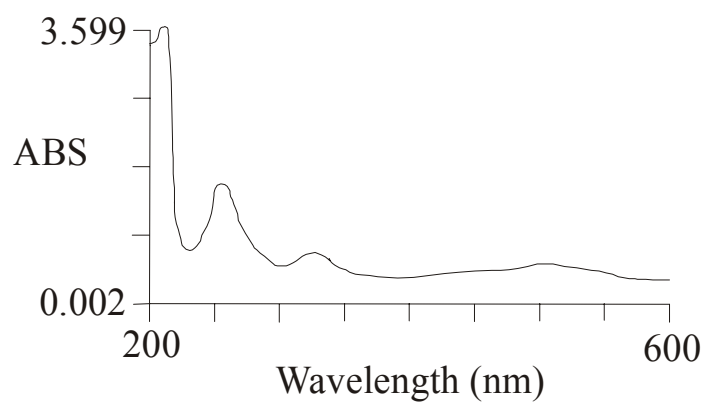
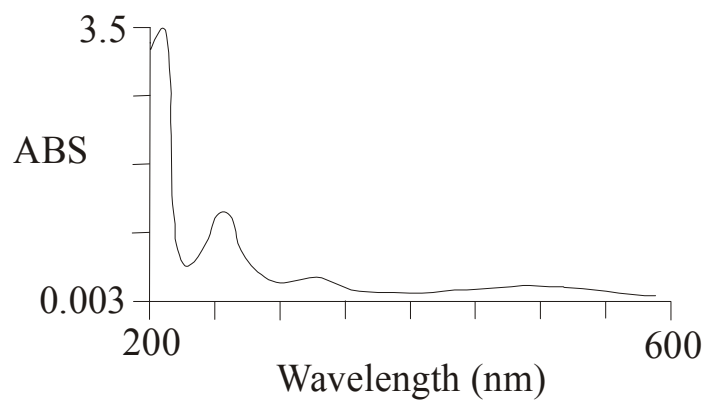


Figure 5: Spectrogram (top) of 100.0 ppm arsenate in TBA buffer analyzed on Spectronic Genesys 2 spectrophotometer. Spectrogram (bottom) of 100.0 ppm arsenate in TBA buffer with 10.0 μL of alizarin red S analyzed on Spectronic Genesys 2 spectrophotometer.

Arsenic Analysis Instrumentation

Many analytical methods are available for the determination concentration and speciation of arsenic in aqueous solutions, as mentioned earlier. Since the methods available at Northern Michigan University for the arsenic experiments were High Performance Liquid Chromatography (HPLC), Gas Chromatography-Mass Spectrometry (GC-MS), and Atomic Absorption Spectrometry-Graphite Furnace (GF-AAS), these methods were used to evaluate arsenic concentrations and speciation.

HPLC was initially used to determine arsenic speciation and concentration. HPLC is a method of chromatography which uses liquid as a mobile phase. The mobile phase carries the samples of interest through a relatively short column at elevated pressure. HPLC is known for using reverse phase columns because the technique is frequently used to separate non-polar molecules; however, arsenate was in an ionic form, therefore a standard phase ionic column was used for the separation of As(III) and As(V).

Arsenic standard and experimental solutions were analyzed using the Varian Vista 5500 High Performance Liquid Chromatography (HPLC) along with the Varian 4270 Integrator. The method of operation was tested and optimized based on several runs of the arsenic and buffer solution through the HPLC column. The wavelength was set at 190 nm based on arsenic absorbance spectrum. A multi-mobile phase method was considered, but the operation of the HPLC with the single buffer mobile phase gave acceptable retention times and good resolution between the arsenic species of interest. The mobile phase flow rate was established at 1.0 mL/minute, which created a pressure in the column of 160-200 psi. This pressure was reasonable at approximately one-half the maximum pressure rating of the column.

The efficiency (N) in plates/meter and symmetry of the HPLC chromatogram peaks were calculated soon after the parameters of operation were established allowing for future monitoring of column performance. The number of theoretical plates refers to the number of arsenic and HPLC column packing interactions occur in a defined length of column. If a decrease in peak quality was observed, then corrective action could be taken in the form of column regeneration or troubleshooting any problems with the system. The efficiency and symmetry of the peaks in the HPLC chromatograms for the new column were as follows:

$$\text{Efficiency (N)} = 5.54 (T/W_{1/2})^2 * 1000/L$$

$$\text{Efficiency (N)} = 55 \text{ plates/m}$$

T = Retention Time

W_{1/2} = Peak width at ½ peak height

L = Column Length (mm)

$$\text{Symmetry} = (A + B)/2B$$

$$\text{Symmetry} = 1.45$$

A = distance from peak centerline to peak descending line at 10% peak height

B = distance from peak centerline to peak ascending line at 10% peak height

The preliminary HPLC runs with As(V) indicated the UV/VIS detector at 190 nm could collect a peak at concentrations as low as 1 ppm. The retention time for As(V) and As(III) were tested to assure the new column and mobile phase buffer would separate the two species of arsenic. The As(V) was found to consistently elute at 5.60 to 5.70 minutes, while the As(III) had a retention time of 1.80 to 1.95 minutes. Standard curves were established for both arsenic species of interest.

The As(V) solutions from 3.98 ppm to 255.3 ppm were used to establish a standard curve. The sample solutions were tested in ascending order to prevent residual arsenic from the high concentrations affecting the lower concentration arsenic analysis. A typical example of one of the 127.6 ppm As(V) chromatograms is shown in Figure 6. The standard curve for As(V) in the TBA buffer is displayed in Figure 7.

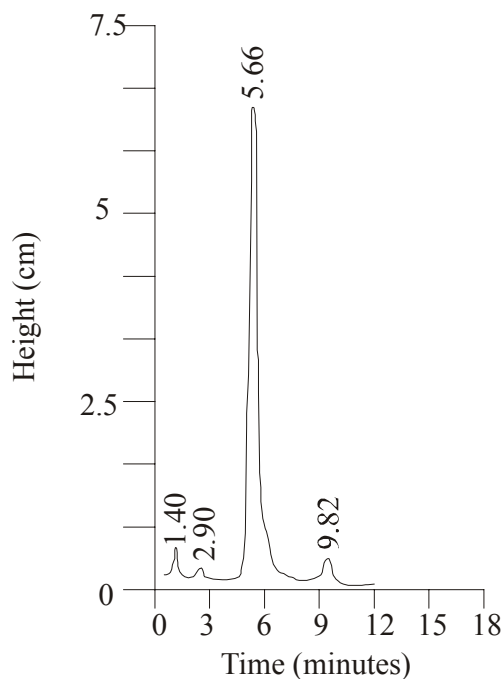


Figure 6: Chromatogram of 127.6 ppm arsenate (5.66 min) sample in TBA buffer analyzed using the Varian 5500 HPLC and Varian 4270 Integrator at $\lambda = 190$ nm. Peak height measured using the settings listed in methods section page 19.

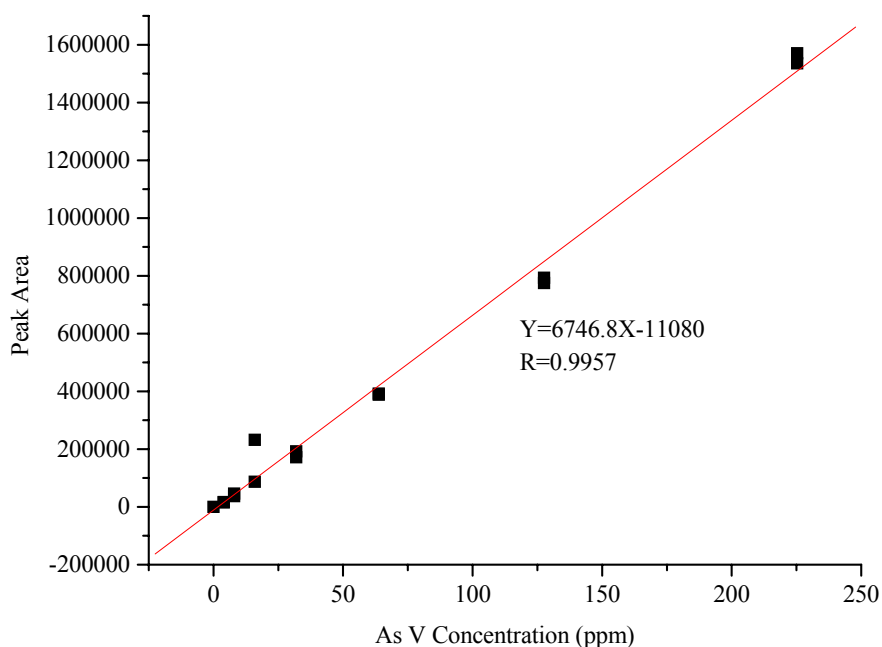


Figure 7: Arsenate standard curve (peak area absorbance @ 195 nm) analyzed in TBA buffer using the Varian 5500 HPLC and Varian 4270 Integrator.

The As(III) solutions from 5.65 ppm to 361.7 ppm were used to establish a standard curve. Again, the sample solutions were analyzed in ascending order to prevent residual arsenic from the high concentrations affecting the lower concentration analysis. An example of one of the 45.21 ppm As(III) chromatographs is shown in Figure 8. The standard curve for As(III) in the TBA buffer is displayed in Figure 9.

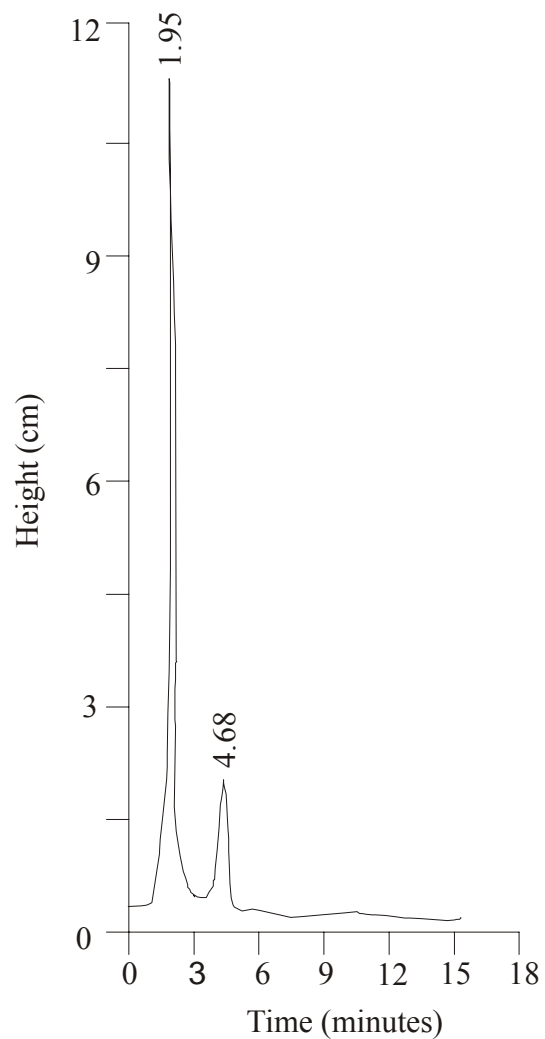


Figure 8: Chromatogram of 45.21 ppm arsenite (1.95 min) sample in TBA buffer analyzed using the Varian 5500 HPLC and Varian 4270 Integrator at $\lambda = 190$ nm. Peak height measured using the settings listed in methods section page 19.

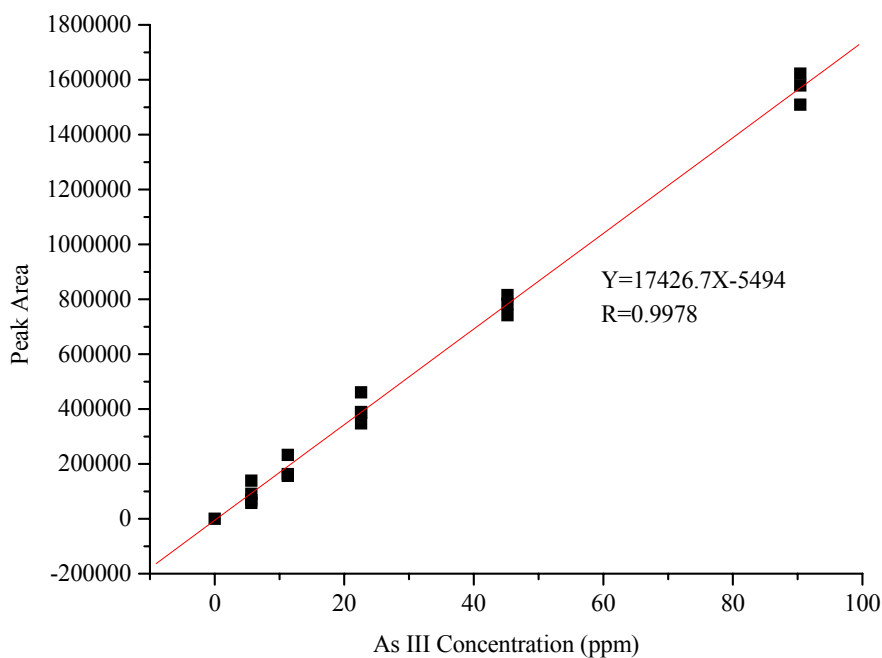


Figure 9: Arsenite standard curve (peak area absorbance @ 195 nm) in TBA buffer analyzed using the Varian 5500 HPLC and Varian 4270 Integrator.

The detection limits of the two arsenic species were determined using an average from 10 noise peaks. Noise peaks collected from the standard curve spectrograms were used to determine the detection limit of arsenic. Noise peaks were defined as baseline peaks of irregular shape which the Varian 4270 Integrator detected and integrated. The average area of ten noise peaks was used to calculate a ppm concentration based on the arsenic standard curve equations. The ppm concentration was multiplied by 3 to determine the detection limits, and the concentration was converted to mass for a minimum mass detection limit in 20 μ L samples. The resulting detection limits for the HPLC analysis showed arsenite had a detection limit of 3.48 ppm or 69.6 ng and arsenate had a detection limit of 7.10 ppm or 141 ng.

Arsenic Storage Stability

The As(III) standard solutions were found to be stable during storage. There was no noticeable decrease in As(III) concentration during the 24, 48, and 960 hour storage test periods. More importantly, there was no sign of As(V) presence on the HPLC chromatograms at retention time 5.65 minutes even at elevated As(III) concentrations. Since the As(V) detection limit is 7.10 ppm or 141 ng, less than this amount of As(V) was present in the stored As(III) solutions. Table 8 shows the As(III) absorbance values for times 0, 24, 48, and 960 hours. Based on the results obtained during the storage stability experiments, the arsenite samples could be stored up to 960 hours or 40 days as long as the samples were stored between 4° and 7° C.

Table 8: Arsenate oxidation stability analyzed after 0, 24, 48, and 960 hours.

Concentration (ppm)	Run	Time = 0 hr		Time = 24 hr		Time = 48 hr		Time = 960 hr	
		Area As (III)	Area As (V)	Area As (III)	Area As (V)	Area As (III)	Area As (V)	Area As (III)	Area As (V)
22.6	1	347520	0			363401	0	374624	0
	2	386187	13205	364669	1192	368126	0	369471	15241
	3	388872	0	390778	11826				
	Ave	374193	4402	377724	6509	365764	0	372048	7621
45.2	1	782894	7580	769034	10946	706592	0	756412	9885
	2	815215	6811	742187	0	673382	0	729641	13279
	3	741975	3130						
	Ave	780028	5840	755611	5473	689987	0	743027	11582

HPLC Column Regeneration

After completing the As(V) and As(III) standard curves along with numerous other arsenic samples using the anionic HPLC ion exchange column, the retention times for As(V) started to decrease. There was concern as the As(V) peak started to approach

the As(III) peak, so the column was regenerated using the column manufacture's suggested method. After regenerating the column, the retention time for As(V) was extended beyond the original As(V) retention of 5.6 minute to 5.8 minutes. This indicated the buffer solution used as the HPLC mobile phase was probably playing a role in the degradation of the ion exchange column.

Since the TBA buffer limited the number of HPLC runs between regenerations, a new buffer was needed. The new mobile phase for the HPLC would need buffering capacity to prevent large pH changes during electrochemical oxidation while having less anionic charge to prevent fouling of the HPLC ion exchange column.

Following the regeneration of the Alltech Allsep Anion 7u column, the 0.12 M potassium phosphate solution adjusted to pH 5.5 with concentrated phosphoric acid buffer was used as the carrier liquid in the HPLC trials and buffer during electrochemical oxidation. The new buffer was previously analyzed to assure it would allow proper analysis of arsenic.

The retention times of As(III) and As(V) were tested using HPLC with the phosphate solution at pH 5.5 as the mobile phase to assure proper separation prior to experiments to establish standard curves for both arsenite, As(III) and arsenate As(V). As shown in Figure 10 and Figure 12, the retention times for As(III) and As(V) in the phosphate solution were 1.80 and 4.40 minutes, respectively. Therefore, the 0.12 M phosphate solution at pH 5.5 worked as a mobile phase for the separation of As(III) and As(V).

The HPLC operation was then tested and optimized based on several runs of the arsenic and buffer solution through the column. The wavelength was set at 190 nm based

on the arsenic absorbance spectra. Operation of the HPLC with the single buffer mobile phase gave acceptable retention times and good resolution between species of interest. The new 0.12 M phosphate mobile phase flow rate was at 1.0 mL/min, which established a pressure in the column of 90-120 psi. There was a decrease in pressure when compared to the original buffer mobile phase. The pressure was at less than one-half the maximum pressure rating, 400 psi, of the column.

The efficiency (N) in plates/meter and symmetry of the HPLC chromatogram peaks were calculated to compare to the same calculations from previous arsenic HPLC chromatograms. If a decrease in performance was observed, then corrective action could be taken in the form of column regeneration or troubleshooting any problems with the system. The efficiency and symmetry following column regeneration and the implementation of a new buffer were as follows:

$$\text{Efficiency (N)} = 34 \text{ plates/m}$$

$$\text{Symmetry} = 1.25$$

When comparing the efficiency of the arsenic peaks in the two buffer solutions, the TBA buffer had a better efficiency of 55 plates/m compared to 34 plates/m for the phosphate solution. The phosphate solution gave better symmetry when compared to the TBA buffer, 1.25 versus 1.45, respectively. The arsenic peaks from both buffers were of high quality making them easy to analyze.

Again standard curves for As(III) and As(V) were determined by HPLC using the new 0.12 M phosphate solution at pH 5.5. The retention times for As(III) and As(V) decreased when compared to the previous times using the original buffer. The new retention times were sufficient for speciation of the two arsenic species. The standard

curves for both species were determined for an arsenic concentration range from approximately 12 ppm to 100 ppm.

An example of one of the 101.7 ppm As(III) chromatograms produced by the Varian 5500 HPLC and Varian 4270 Integrator can be observed in Figure 10. The standard curve for As(III) in the potassium phosphate solution is displayed in Figure 11.

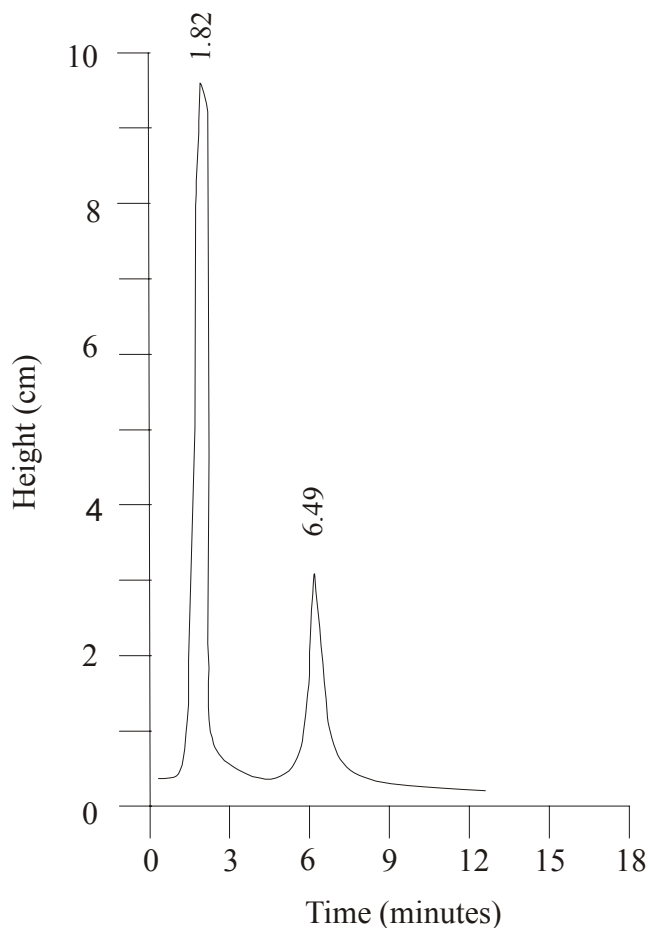


Figure 10: Chromatogram of 101.7 ppm arsenite (1.82 min) sample in 0.12M potassium phosphate solution at pH 5.5 analyzed using the Varian 5500 HPLC and Varian 4270 Integrator at $\lambda = 190$ nm. Peak height measured using the settings listed in methods section page 19.

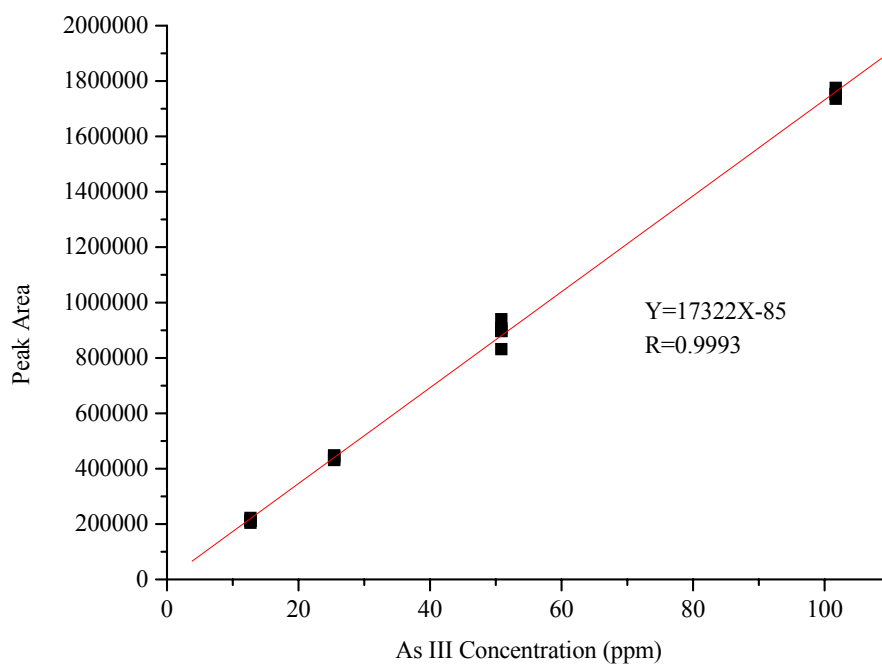


Figure 11: Arsenite standard curve (peak area absorbance @ 190 nm) in 0.12 M potassium phosphate solution at pH 5.5.

An arsenate standard curve was made in the buffer containing 0.12 M potassium phosphate adjusted to pH 5.5 with concentrated phosphoric acid. An example of the 49.93 ppm arsenate chromatogram produced by the Varian 5500 HPLC and Varian 4270 Integrator can be observed in Figure 12. The standard curve for As(V) in the potassium phosphate solution at pH 5.5 is displayed in Figure 13.

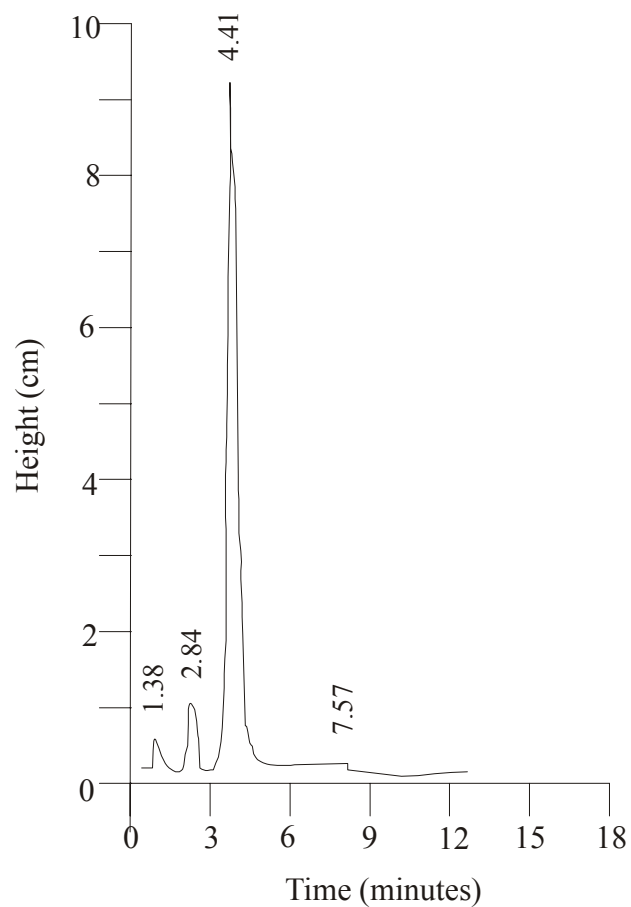


Figure 12: Chromatogram of 49.93 ppm arsenate (4.41 min) sample in 0.12 M potassium phosphate solution at pH 5.5 analyzed using the Varian 5500 HPLC and Varian 4270 Integrator at $\lambda = 190$ nm. Peak height measured using the settings listed in methods section page 19.

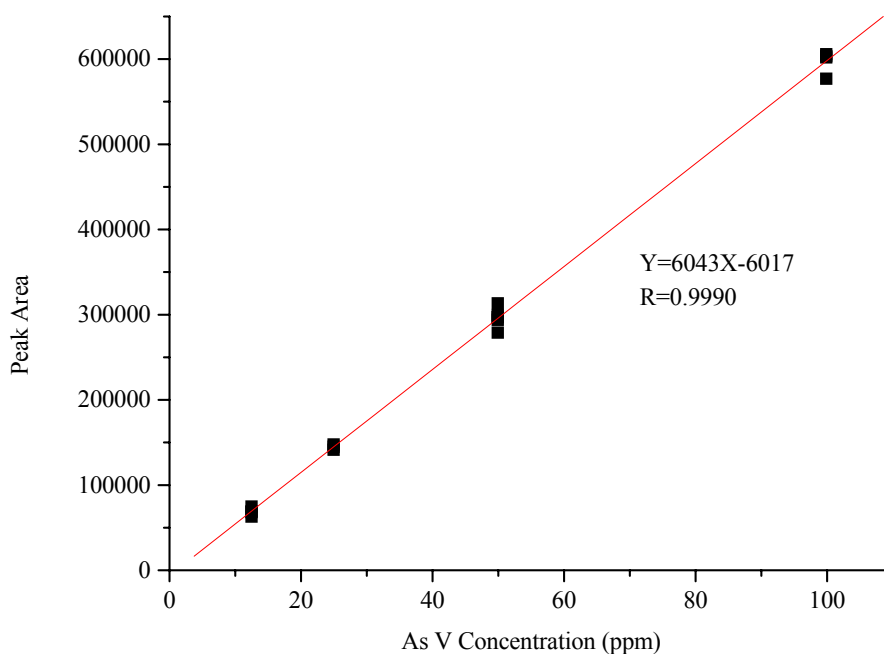


Figure 13: Arsenate standard curve (peak area absorbance @ 190 nm) in 0.12 M potassium phosphate solution at pH 5.5 analyzed using the Varian 5500 HPLC and Varian 4270 Integrator.

The experimental HPLC data collected for both arsenite and arsenate standard curves exhibited linear correlations with R-values greater than 0.999. It was also determined that the arsenite was stable in storage for up to 40 days when stored in a refrigerated climate. With this information, it was time to evaluate the electrochemical oxidation of arsenite to arsenate.

Electrochemical Oxidation of Arsenic: HPLC

An electrolytic cell was established to investigate the use of electrochemistry as a means of converting As(III) to As(V). The cell was created using platinum as the anode and cathode with the voltage supplied to the system by a DC power source. Since

arsenate is more easily removed from potential drinking water sources than arsenite, the oxidation of arsenite to arsenate is beneficial. With an established HPLC analysis method for each species, the arsenic oxidation can be evaluated based on variables in the electrolytic cell.

The variables of interest when evaluating the electrochemical oxidation of arsenite include the plate surface area to solution volume ratio, solution ionic strength, and pH. The oxidation rate will be dependent on how the variables of interest affect the overpotential of the reaction solution. Overpotential is when the voltage required by an electrolytic cell is larger than the calculated electrochemical potential required by the cell. One source of overpotential occurs at the surface of the electrode where ions of the opposite charge impede the electrode surface preventing the exchange of electrons and this is affected by the concentration of ions in solution.

The use of DC potential to electrochemically oxidize arsenite to arsenate was investigated following the standardization of the HPLC procedures. The apparatus used in the electrochemical oxidation experiments included platinum electrodes connected to copper wires within sealed glass tubes, a 300 mL glass reaction chamber with custom cover, and Elenco Precision Model XP 656 DC power source, as shown in Figure 1.

The first experiment using the Pt electrodes in the electrochemical oxidation apparatus was performed to evaluate the potassium phosphate solution and assure no peaks appeared following the DC current. A volume of 120 mL of 0.12 M potassium phosphate solution at pH 5.5 was placed in the glass container. The conductivity of the buffer was tested and determined to be 956 $\mu\text{S}/\text{cm}$. The power source was turned on and adjusted to 10 volts and 5 mA for the experiment. Samples of the electrochemical

oxidation were collected every hour, including time zero, for six hours. All seven of the 1 mL sample aliquots were tested using the HPLC for separation of possible contaminant peaks and detected at 190 nm. None of the chromatograms displayed any significant peaks following the electrochemical oxidation of the buffer solution. Figure 14 shows the chromatogram of the phosphate solution following 3 hours of electrochemical oxidation. The very small peaks in Figure 14 are representative of the peaks observed at the other 6 sample times. There was no consistent change in peak height or area associated with the time of electrochemical oxidation. The 0.12 M potassium phosphate solution at pH 5.5 was not expected to interfere with the analysis of arsenite and arsenate following the oxidation experiments.

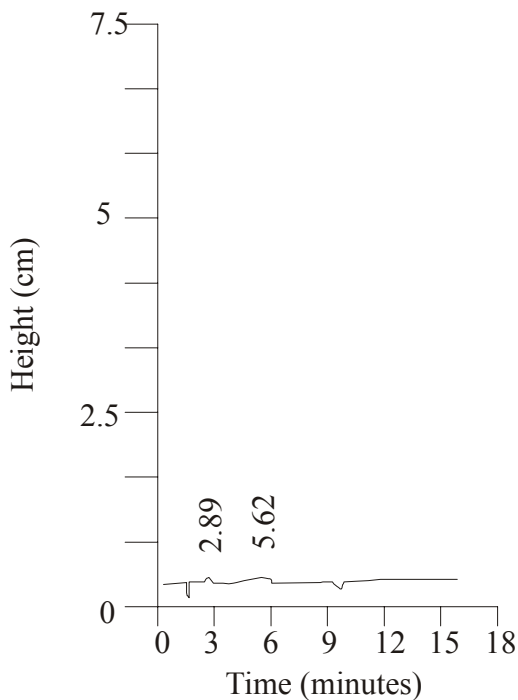


Figure 14: Chromatogram of 0.12 M phosphate solution at pH 5.5 following 3 hours of electrochemical oxidation analyzed using the Varian 5500 HPLC and Varian 4270 Integrator at $\lambda = 190$ nm. Peak height measured using the settings listed in methods section page 19.

A baseline experiment was performed to evaluate the viability of the electrochemical oxidation of arsenite to arsenate in the phosphate solution at pH 5.5. A 101.7 ppm arsenite solution made up in phosphate solution was oxidized for 240 minutes using the apparatus displayed in Figure 1. The initial solution was found to have a conductivity of 2,570 $\mu\text{S}/\text{cm}$ and pH of 5.5. Samples of the experimental solution were collected every hour for analysis by HPLC. A comparison was made every hour to evaluate the progress of the oxidation by comparing the change in peak height of arsenite at 1.81 minutes to the arsenate peak height at 4.35 minutes. The progression of the oxidation reaction is displayed in Figure 15.

The electrolytic cell created a noticeable decrease in the arsenite peak found at 1.82 minutes in Figure 15. The arsenate peak grew incrementally at each sample time during the electrochemical oxidation of arsenite. The results showed the electrolytic cell will oxidize arsenic in an aqueous solution as theory predicted, and the HPLC method works for determination of As(III) and As(V) peaks following the transformation from one form to the other during electrochemical oxidation.

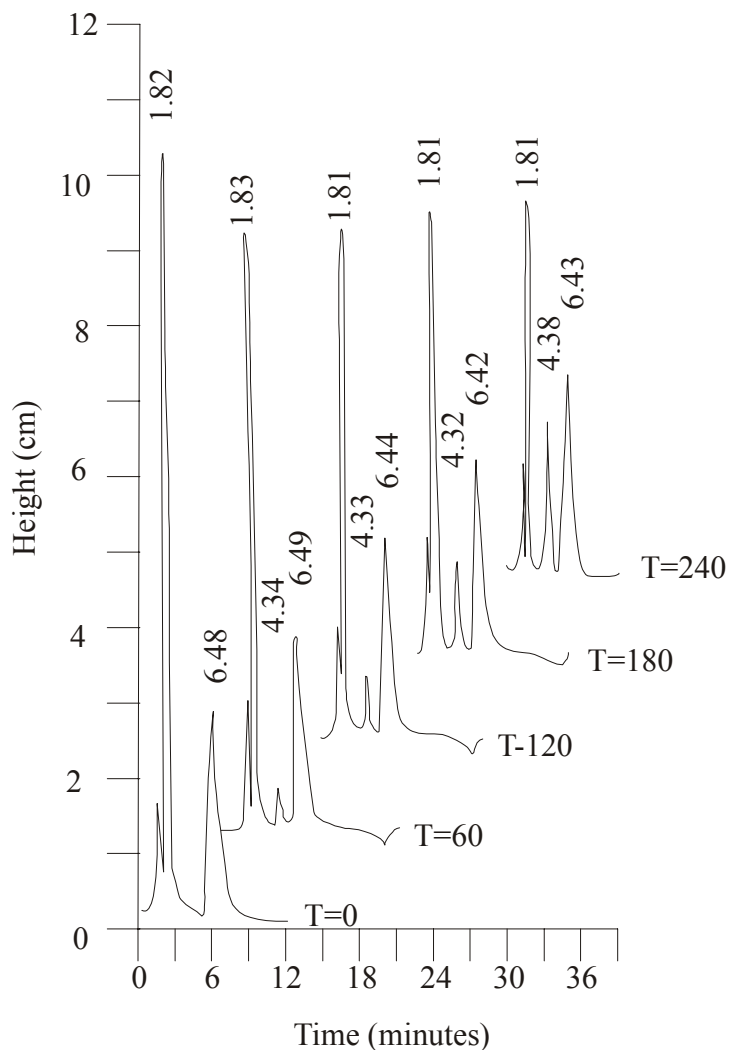


Figure 15: Chromatograms of 101.7 ppm arsenite sample in 0.12 M phosphate solution at pH 5.5 following 0, 60, 120, 180, and 240 minutes of electrochemical oxidation analyzed using the Varian 5500 HPLC and Varian 4270 Integrator at $\lambda = 190$ nm. The arsenite peaks elute at T=1.81 minutes and the arsenate peaks elute at T=4.35 minutes. Peak height measured using the settings listed in methods section page 19.

Oxidation Rate: Conductivity

Since the experimental approach was proven to work, it was necessary to adjust variables to optimize the oxidation system. Experiments were then performed to determine how the conductivity of the test solution affects the oxidation rate of the arsenite in solution. The arsenite experimental solution was made up using the standard 1,000 ppm As(III) solution made from dissolving the arsenic oxide with strong base and then neutralizing with strong acid. The arsenite solution was diluted to the experimental concentration of 91.7 ppm As(III) with the 0.12 M phosphate solution at pH 5.5. The conductivity of the arsenite experimental solution was found to be approximately 2,500 $\mu\text{S}/\text{cm}$. From the baseline conductivity level of 2,500 $\mu\text{S}/\text{cm}$, the conductivities were raised using NaCl to 3,800 $\mu\text{S}/\text{cm}$ and 5,100 $\mu\text{S}/\text{cm}$ to compare the rates of oxidation at elevated conductivity levels.

The four hour electrochemical oxidation of the 91.7 ppm As(III) solution at 2,500 $\mu\text{S}/\text{cm}$ was done at 10 volts and 17 mA, with an initial pH of 5.3. Samples were collected for analysis every 30 minutes. The pH of the experimental solution along with the conductivity, voltage, and amperage were recorded at each 30 minute sample collection. The data along are recorded in Table 9. The same procedure was followed for $\sigma = 3,700 \mu\text{S}/\text{cm}$. An increase in amperage (20 mA) was observed due to the increased conductivity. The data along with the arsenite and arsenate concentrations are recorded in Table 10. Once again, the procedure was followed for $\sigma = 5,100 \mu\text{S}/\text{cm}$. The amperage increased to 22 mA due to the increased conductivity. The data along with the arsenite and arsenate concentrations are recorded in Table 11.

Table 9: Electrochemical oxidation solution characteristics during 2,500 $\mu\text{S}/\text{sec}$ trial.

Time (min)	Conductivity ($\mu\text{S}/\text{sec}$)	pH	Voltage (volts)	Amperage (mAmp)
0	2570	5.28	10	17
60	2540	5.23	10	18
120	2540	5.05	10	18
180	2510	4.85	10	18
240	2550	4.63	10	18

Table 10: Electrochemical oxidation solution characteristics during 3,700 $\mu\text{S}/\text{sec}$ trial.

Time (min)	Conductivity ($\mu\text{S}/\text{sec}$)	pH	Voltage (volts)	Amperage (mAmp)
0	3770	5.33	10	20
60	3790	5.38	10	20
120	3800	4.85	10	20
180	3820	4.48	10	20
240	3840	4.12	10	20

Table 11: Electrochemical oxidation solution characteristics during 5,100 $\mu\text{S}/\text{sec}$ trial.

Time (min)	Conductivity ($\mu\text{S}/\text{sec}$)	pH	Voltage (volts)	Amperage (mAmp)
0	5070	5.29	10	22
60	5060	4.26	10	22
120	5140	3.63	10	22
180	5005	4.80	10	22
240	4970	5.65	10	22

The graph displaying concentration versus time for arsenite and arsenate at $\sigma = 2,500 \mu\text{S}/\text{cm}$ is shown in Figure 16. The graph displaying concentration versus time for arsenite and arsenate at $\sigma = 3,700 \mu\text{S}/\text{cm}$ is shown in Figure 17 and the graph displaying

concentration versus time for arsenite and arsenate at $\sigma = 5,100 \mu\text{S}/\text{cm}$ is shown in Figure 18.

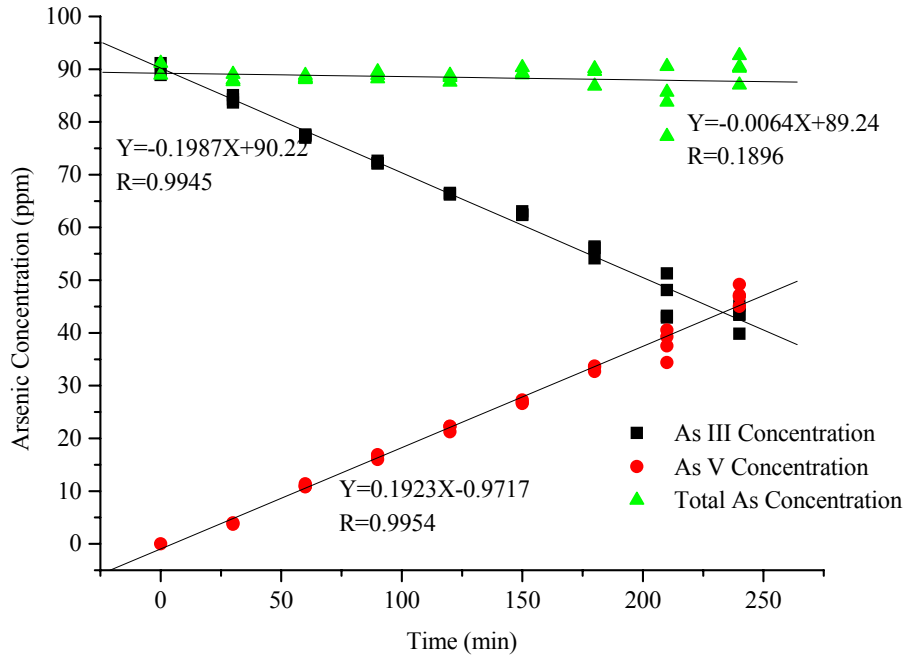


Figure 16: Graph displaying electrochemical oxidation of arsenite $\sigma = 2,500 \mu\text{S}/\text{sec}$.

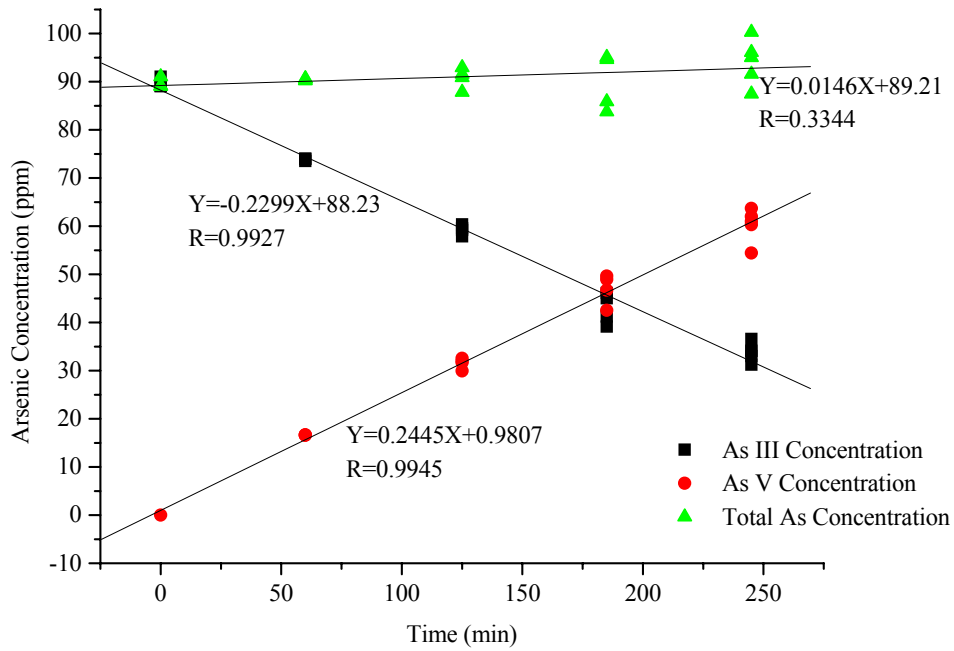


Figure 17: Graph displaying electrochemical oxidation of arsenite $\sigma = 3,700 \mu\text{S}/\text{sec}$.

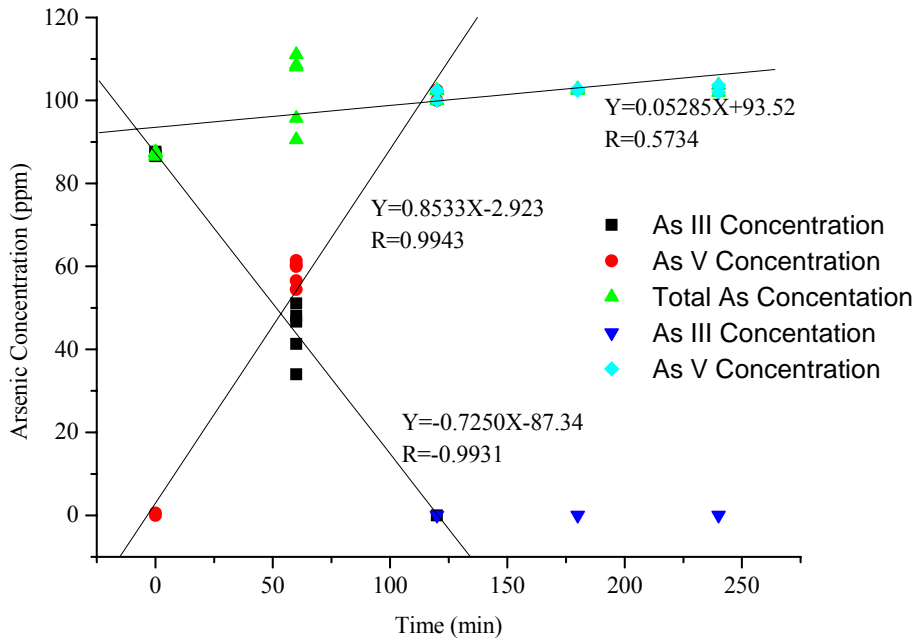


Figure 18: Graph displaying electrochemical oxidation of arsenite $\sigma = 5,100 \mu\text{S}/\text{sec}$. Note: two symbols for arsenite and arsenate are found in the graph legend. The oxidation was complete by $t = 120 \text{ min}$.

Samples of the solution with a conductivity of 5,100 $\mu\text{S}/\text{cm}$ and a pH of 5.5 were collected and analyzed at times 0, 60, and 120 minutes. A comparison was made every hour to evaluate the progress of the oxidation by comparing the change in peak height of arsenite at 1.88 minutes to the arsenate peak height at 4.3 minutes using HPLC. The progression of the oxidation reaction was displayed by offsetting the chromatograms for each sample set in Figure 19.

The rate of arsenite oxidation was dramatically affected by the conductivity of the test solution. A comparison of oxidation rates was made based from the conductivity data by comparing the slopes of the arsenite lines recorded in ppm/min. The rates (ppm/min) of arsenite concentration lines for the 2,500 $\mu\text{S}/\text{cm}$, 3,700 $\mu\text{S}/\text{cm}$, and 5,100 $\mu\text{S}/\text{cm}$ conductivity experiments were 0.199, 0.223, and 0.725 (ppm/min), respectively. As shown in Figure 20, the increase in oxidation rate is not linear when compared to conductivity, because the conductivity in this reaction was approximately doubled from 2,500 $\mu\text{S}/\text{cm}$ to 5,100 $\mu\text{S}/\text{cm}$ and the corresponding oxidation rate increase was 3.6 times faster. The increase in ionic strength or conductivity has a result of decreasing the affect of overpotential. The solution with increased conductivity allows enhanced movement of ions in solution resulting in increased transfer of electrons at the electrode surface.

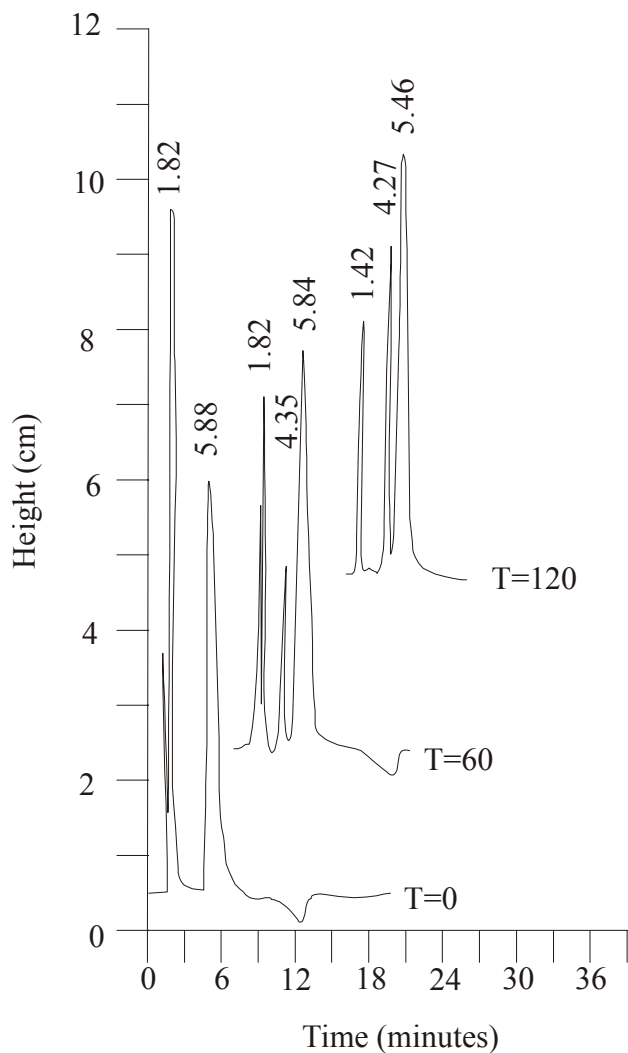


Figure 19: Chromatograms of 101.7 ppm arsenite sample in phosphate solution at 5,100 $\mu\text{S}/\text{cm}$ conductivity following 0, 60, and 120 minutes of electrochemical oxidation analyzed using the Varian 5500 HPLC and Varian 4270 Integrator at $\lambda = 190 \text{ nm}$. The arsenite peaks elute at $T = 1.82$ minutes and the arsenate peaks elute at $T = 4.3$ minutes. Peak height measured using the settings listed in methods section page 19.

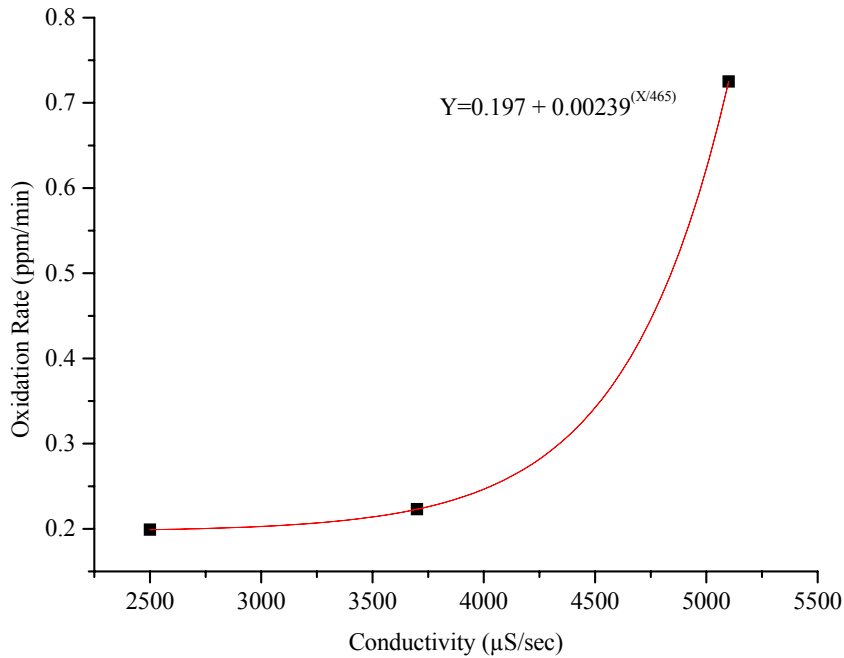


Figure 20: Graph of As(III) oxidation rate versus solution conductivity.

The results of the varied conductivity experiment were compared to the conductivity of local Upper Peninsula water sources to see how the range tested in the laboratory compared to actual water treatment applications. The sample water sources were collected from a variety of water types including surface lake water, surface river water, well water, and municipal city water. The surface lake water was collected from Lake Michigan at Van Cleeve Park in Gladstone, Michigan. The surface river water was collected from the Escanaba River at the Cornell access site on County Road 426. The well water was collected from a 78 feet deep well located at 11967 County 426 E Road in Cornell, Michigan, and municipal water from the City of Gladstone collected at 840 Clark Drive Gladstone, Michigan. The conductivity of the four water samples was recorded in Table 12. As Table 12 shows, the conductivities of the water samples were

significantly less than conductivities measured in the experimental arsenic solutions, which would decrease the oxidation rate of arsenic based on the conductivity results.

Table 12: Conductivity of Native Waters

Water Source	Conductivity ($\mu\text{S}/\text{cm}$)
City of Gladstone water	363
Lake Michigan water	282
Well water	765
River water	563

Electrochemical Oxidation of Arsenic: pH

While investigating the oxidation rates of arsenic with varied solution conductivities, the pH of the test solutions became a variable of interest. The pH of the experimental arsenic solution decreased during oxidation. The pH change can be explained by referring to the oxidation/reduction equation listed as Equation 1, which shows that when arsenite is oxidized to arsenate, protons are a product of the reaction. Therefore, the oxidation reaction of arsenite lowered the pH as displayed in Table 9, 10, & 11. The pH results from the experiment performed at $\sigma = 5,100 \mu\text{S}/\text{cm}$ showed an interesting result. The pH at time zero was 5.3, similar to the pH at the other conductivities. By the time the oxidation had reach 120 minutes, where all the measurable arsenite had been converted to arsenate, the pH was down to 3.6. This result seems logical due to the rapid oxidation of arsenite and the corresponding protons that were produced with the reaction, but as the experiment continued for the next 120 minutes, the pH increased to 4.8 in the 180 minute sample and 5.6 in the 240 minute sample. No signs of a reverse reaction or reduction were evident by the re-appearance of

arsenite on the chromatogram. The pH trends of all three conductivities are displayed on the graph in Figure 21.

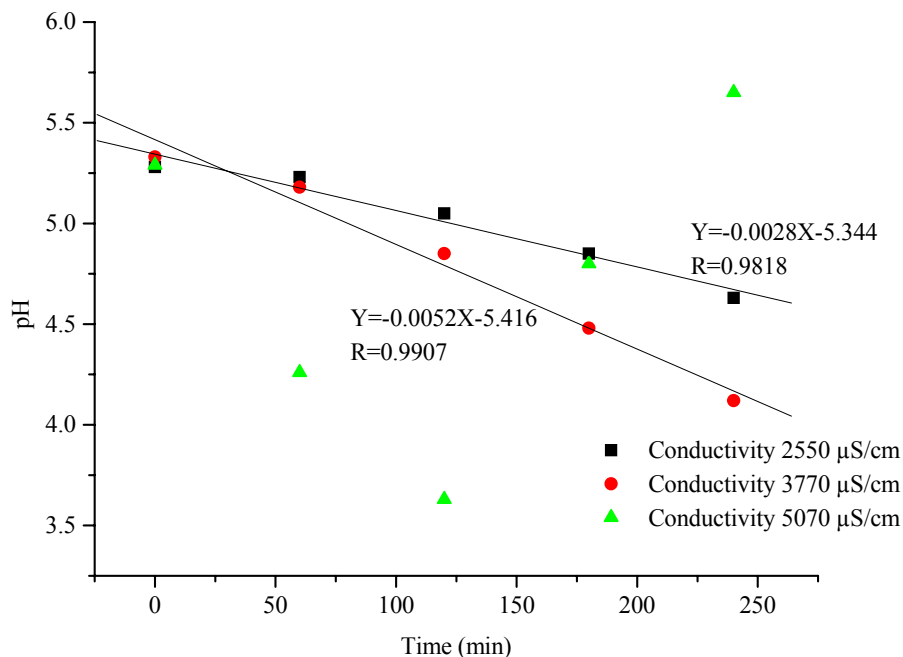
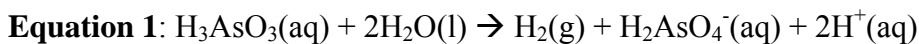


Figure 21: Graph of pH variation during varied conductivity oxidation trials.

Oxidation rate: Electrode Size/Solution Volume

The electrochemical oxidation of arsenite in the apparatus displayed in Figure 1 was used to complete experiments to scale the oxidation reaction by comparing the volume of arsenic solution to the surface area of the oxidizing electrodes; since only one size of electrode was available for the experimental apparatus, the volume of solution was varied to establish the variable. The surface area of the electrodes was measured and

calculated to be 50.0 mm^2 . Two experimental solutions of volume 82.5 mL and 137.5 mL were made up at 92.5 ppm As(III), pH 5.3, and $\sigma = 2,600 \text{ }\mu\text{S/cm}$. The rate of reaction was related to the ratio of arsenic solution volume in mL per mm^2 of Platinum electrode surface area (mL/mm^2). The test solutions had ratios of $1.65 \text{ mL}/\text{mm}^2$ and $2.75 \text{ mL}/\text{mm}^2$ respectively. The samples were oxidized for 4 hours at 10 volts and 17 mA with samples collected for analysis every 60 minutes. A plot of concentration versus time for the two sample solutions is shown in Figure 22. The rates are $0.119 \text{ ppm}/\text{min}$ ($1.65 \text{ mL}/\text{mm}^2$) and $0.161 \text{ ppm}/\text{min}$ ($2.75 \text{ mL}/\text{mm}^2$) for the reduction of As(III) during the oxidation.

A comparison of oxidation rates was again made based on the conversion rate of arsenite to arsenate in the experimental solution. The $2.75 \text{ mL}/\text{mm}^2$ arsenite experimental solution oxidation rate was 1.35 times faster than the $1.65 \text{ mL}/\text{mm}^2$ experimental solution. When ratios of the volume to surface area and extent of oxidation were compared, the results showed a 67% increase in electrode surface area created only a 35% increase in oxidation rate. The results showed that an increase in electrode size does not create a proportional increase in oxidation rate. The smaller than expected increase in oxidation rate could be explained based on the effect of overpotential. It is possible the increase in plate size compared to solution volume could be masked due to limited movement of ions in solution and limited exchange of electrons at the surface of the electrodes both because of overpotential. Oppositely charged ions built up on the surface of the electrodes could prevent electron exchange; therefore requiring a larger than expected potential to oxidize the arsenite.

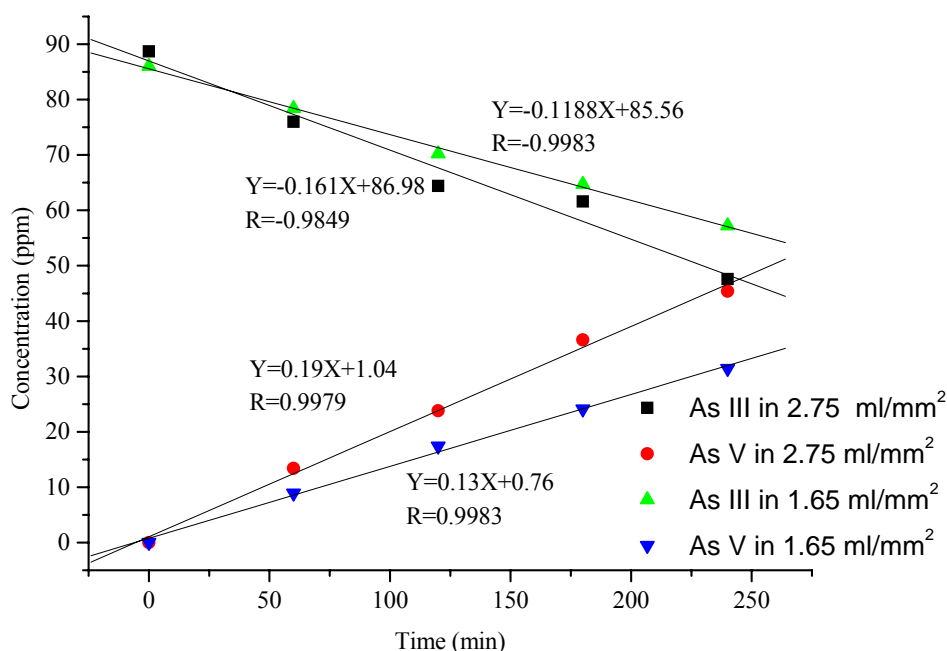


Figure 22: Graph of As(III) and As(V) concentrations during oxidation reaction with varied solution volume vs platinum plate surface area conducted at conductivity at conductivity $\sigma = 2,500 \mu\text{S}/\text{sec}$.

The electrochemical oxidation of the arsenite sample solutions analyzed by HPLC appeared to have a fairly accurate mass balance for total arsenic; however some variations in the data were observed. The results of the varied conductivity experiments performed at $2,500 \mu\text{S}/\text{cm}$ and $3,700 \mu\text{S}/\text{cm}$ conductivity, which appeared in graphs Figure 16 and Figure 17 had total arsenic concentration of approximately 90 ppm just below the starting concentration of 91.7 ppm arsenic. The total arsenic in both solutions remains fairly constant during the entire 240 minute oxidation experiment. The high conductivity solution of $5,100 \mu\text{S}/\text{cm}$ did not display the same consistent arsenic concentration results. The total arsenic concentration as recorded by HPLC analysis increased as the electrochemical oxidation reaction proceeded. The initial 91.7 ppm

arsenite solution produced HPLC peaks which correlated to approximately 88 ppm As(III) as calculated from the As(III) standard curve. When the arsenite was oxidized to arsenate at sample time, 120 minutes, the total arsenic concentration measured as As(V) correlated to a concentration of approximately 102 ppm arsenic. This makes it very difficult to draw conclusions, as it relates to mass balance, based on the HPLC results. First, it appears there may be a slight loss of arsenic during the electrochemical oxidation, but after reviewing the high conductivity arsenic sample it shows an increase in arsenic concentration. Therefore, further investigation was required prior to drawing any conclusion pertaining to the mass balance of arsenic during electrochemical oxidation of arsenite to arsenate because of the contradictory results.

Mass Balance of Arsenic during Oxidation

The use of gas chromatography (GC) coupled to mass spectrometry (MS) could be used to evaluate arsenic in its gas phase, to evaluate if any arsenic was converted to arsine during the electrochemical oxidation. The GC portion of the analysis instrument would work similar to the liquid chromatography column, but the gas column is much longer. The column separates molecules based on their vapor pressure and solubility in the mobile phase.

An experiment using GC-MS to monitor the mass balance of arsenic during electrochemical oxidation was investigated next. In order to monitor the mass balance of arsenic, the headspace of the electrochemical oxidation apparatus in Figure 1 would be monitored. A possible means of losing arsenic from the closed system would be through the gas phase. The gas phase of the reaction vessel could be monitored using a Supelco

SPME (solid phase microextraction) fiber assembly to collect any arsine gas in the headspace. The fiber could then be placed in the GC-MS and heated to release the arsine gas into the GC column for separation followed by analysis using the MS (30).

Many variations in the borohydride reaction and GC-MS method were used, but no arsine peak was ever identified by the GC-MS method. If arsine gas was present, peaks would be present at 75, 76, 77, and 78 m/z with the major peak at 76 m/z (30). No peak of any size was ever identified in the mass to charge ratio of interest. Since the method did not work properly with high concentrations of arsine, it was not used in the oxidation experiments in an attempt to identify trace amounts of arsine. The mass balance of the oxidation reaction could not be monitored using the GC-MS method since the SPME arsine determination method did not seem to be a viable method.

Electrochemical Oxidation of Arsenic: GF-AAS

The use of graphite furnace (GF)- atomic absorption spectrometry (AAS) allowed the investigation of electrochemical oxidation of arsenic to move from parts per million concentrations to parts per billion concentrations, which made the experimental parameters closer to the realistic concentrations found in natural water sources. GF-AAS experiments also allowed for more mass balance investigations to determine if the electrochemical oxidation method of oxidizing arsenic causes loss of arsenic. Arsenic concentrations were determined using graphite furnace analysis on the AAS. When analyzing arsenic using GF-AAS, a matrix modifier was required to ensure proper atomization during analysis to prevent polymerization and peak broadening. The specified matrix modifier for arsenic was nickel nitrate added at 0.02 mg per analysis.

The matrix modifier was automatically added to each sample analysis using the auto sampler. The optimized operating parameters for arsenic analysis can be found in Table 6 in the methods section.

Once the operating parameters of the GF-AAS analysis were optimized, it was time to create standard curves for arsenic concentrations. The first standard curve was created to determine the functional range of arsenic analysis by GF-AAS. The curve was created between approximately 100 ppb and 1000 ppb in increments of 100 ppb. Figure 23 displays the GF-AAS results recorded during analysis of the arsenic samples. The standard curve became nonlinear at around 600 ppb of arsenate. This experiment determined the upper limit of effective arsenic analysis using the AAS graphite furnace method. Future experiments were completed in the linear range of the curve.

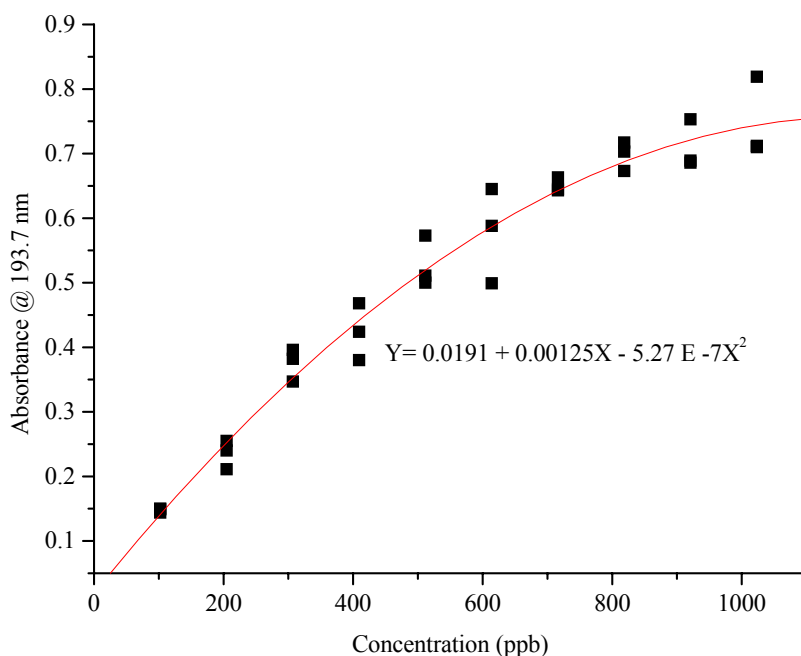


Figure 23: Arsenate standard curve in potassium phosphate solution at pH 5.5 analyzed by GF-AAS.

With the high end limit of the arsenic analysis using GF-AAS analysis determined, it was necessary to determine the low arsenic limit for GF-AAS analysis. Therefore, an experiment was conducted using solution containing between 20 and 100 ppb of arsenic. The samples were varied in 20 ppm increments and tested using the GF-AAS method above. The results contained excessive random error, therefore a standard curve was not created below 100 ppb arsenic. It was determined that the repeatable range of arsenic analysis using GF-AAS was between 100 and 600 ppb.

Since speciation of arsenic was a focal point, arsenite and arsenate samples were used to create standard curves by the GF-AAS method to check for any discrepancies between the species. Both As(III) and As(V) standard curves are plotted in Figure 24 for the comparison of species. As Figure 24 showed, both species have the same absorbance at a given concentration when using GF-AAS analysis.

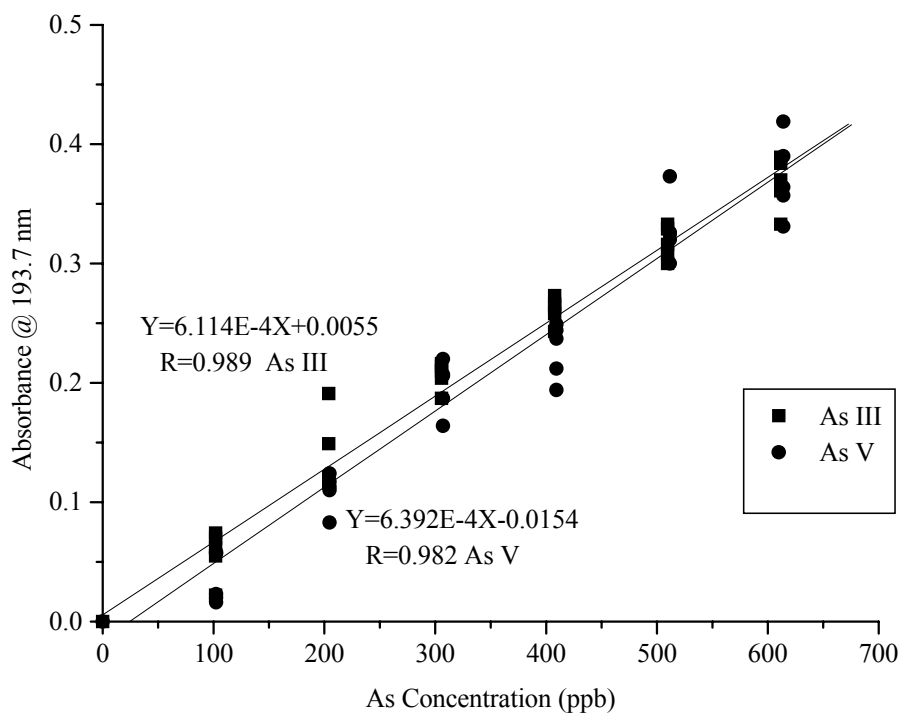


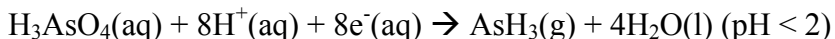
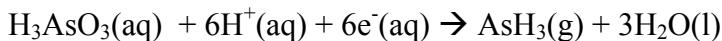
Figure 24: Arsenite and arsenate standard curves in 0.12 M potassium phosphate solution at pH 5.5 analyzed by Graphite Furnace Atomic Absorption Spectrometry.

Electrochemical Oxidation of Arsenic: HG-AAS

The next GF-AAS analysis included the reduction of arsenite to arsine gas using sodium borohydride for hydride generation (HG) as the reducing agent. Concentrations of As(III) and As(V) were investigated to verify if the species could be selectively determined by HG-AAS analysis following hydride generation procedures as described by Anderson et al (31, 32) and Hinners (24). At a pH between 2 and 6, arsenite can be reduced to arsine gas removing it from solution. The arsenate remains in solution for analysis and detection by HG-AAS analysis. Only fully protonated arsenic species are reduced by the borohydride method; therefore the solution pH must be less than 2 for the

arsenate reduction to arsine to occur (33). The pH of the oxidation solutions was buffered at 5.5 allowing the reduction of arsenite only. Samples were first analyzed by GF-AAS for total arsenic including both arsenite and arsenate. Then, the hydride generation reaction was designed to remove arsenite from solution, leaving only arsenate for detection during analysis. The arsenite concentration was then determined by subtracting the arsenate concentration from the total arsenic concentration, $As(III) = \text{Total As} - As(V)$.

The strategy used for selective reduction by hydride generation to selectively speciate As(III) and As(V) oxidation states in solution was built upon the following reaction scheme:



To test the procedure, a 1% sodium borohydride solution was made for analysis of the arsenic samples. Arsenic solutions containing 1 ppm arsenite in the 12 mM phosphate solution at pH 5.5 were used for initial investigations of the hydride generation reactions. The arsenite solution was diluted to 463 ppb by the addition of the borohydride reducing agent to test for As(III) removal from solution. The test solution was degassed and analyzed by HG-AAS to find virtually no reduction in arsenic concentration. The concentration of arsenic was reduced from 463 ppb to an average of 431 ppb in 10 samples. It was determined that As(III) was not reduced to arsine gas in the phosphate solution.

Next, the same procedure was followed with an additional step to purge any arsine from solution. A nitrogen purge line was added to the hydride generation vial to off gas any arsine formed during the reaction. The result of the nitrogen bubbling line was to reduce the initial concentration of arsenic, 333 ppb, down to an average of 238 ppb detected by HG-AAS after 15 minutes of nitrogen purge. Still, this was not the response expected based on reported previously reported results. The hydride generation procedure was not producing the expected decrease in As(III) concentration.

In an attempt to improve the hydride generation, 2 M acetic acid was added to achieve a 0.5 M acetic acid concentration in the reaction vial lowering the pH. The vial was again purged with nitrogen following borohydride addition. The concentration of arsenite in the vial as determined by HG-AAS was reduced from 429 ppb to an average of 286 ppb in five samples. It appeared something was interfering with the hydride generation of the arsenic solution.

The 0.12 M phosphate solution at pH 5.5 was tested next by the borohydride method with no arsenic added to the solution. An equal volume of phosphate solution, which in previous experiments contained arsenic, was mixed with acetic acid and sodium borohydride solution followed by a nitrogen purge. The sample was analyzed using the AAS graphite furnace method. The phosphate solution sample containing no arsenic was analyzed to contain an arsenic concentration of 89 ppb, the results were too inconsistent with phosphate.

To further investigate the potential problems created by the phosphate solution, arsenic samples were prepared for analysis in distilled water. A standard solution of arsenite in water was diluted down to an experimental concentration of 446 ppb using

acetic acid and the sodium borohydride solutions. Following the reaction, the vial was purged with nitrogen for 45 minutes prior to GF-AAS analysis. The results of five tests gave an average arsenic content of 424 ppb, when extrapolated from the arsenic standard curve in phosphate solution. This would not be accurate because the phosphate solution standard curve was used for concentration calculations, but the reduction in arsenic still did not appear significant.

A standard curve was created with an arsenite solution made up in deionized water to see if there was a significant arsenic reduction when compared to analysis done in the phosphate solution at pH 5.5.

The arsenite solution in water was again mixed with 0.5 M acetic acid and 1% sodium borohydride. The reaction vial was purged with nitrogen for 240 minutes to remove any arsine gas that may have formed. The test solution was analyzed using the GF-AAS method, and the arsenic concentration was found to be 23.6 ppb arsenic. The removal rate of arsenite from solution was 94.5% arsenic removal. The hydride generation method finally produced similar results as previously presented in the literature.

The HG-AAS analysis of arsenite was optimized using a new buffer solution. The buffer was a 12 mM acetate solution at pH 4.75. The new buffer was used for electrochemical oxidation reactions and HG-AAS optimization and analysis. The HG-AAS analyses were performed by mixing 400 μL of arsenite solution in 12 mM acetate buffer with 300 μL of 1% sodium borohydride. The mixture was then purged for 5 minutes with nitrogen prior to analysis.

With the hydride generation method working for arsenite removal, it was necessary to test the effect the hydride generation had on the concentration of arsenate in solution. Once again, a standard solution of arsenate was made up in deionized water for analysis. The solution was diluted to 429 ppb with the reaction solutions of 0.5 M acetic acid and 1% sodium borohydride. Following the reaction the vial was purged with nitrogen for 60 minutes. The results showed a final arsenate concentration of 253 ppb, a 41.0% loss of arsenate from solution. This significantly affected the ability to speciate arsenic using the AAS graphite furnace method, since some of the arsenate was reduced to arsine gas.

With the positive results for arsenite removal by reduction to arsine gas determined above, it was time to optimize arsenite removal parameters while trying to preserve arsenate concentrations in solutions. Standard arsenite and arsenate solutions were made up at 1.040 and 1.023 ppm, respectively. The standard arsenic solutions were diluted to create new standard curves for both species in the 100 to 500 ppb range. The standard curves were determined with each set of experiments due to variation in the AAS results with identical solutions on different days.

The arsenic solutions were analyzed to optimize the nitrogen purge time which would allow for maximum removal of arsenite by reduction to arsine gas while preserving the majority of the arsenate. The experiment was done by combining 400 μL of the standard arsenite solution listed above in 12 mM acetate buffer, and 300 μL of 1% sodium borohydride. This created an arsenite concentration in the test vials of 446 ppb. The nitrogen purge time was then varied for 5, 10, and 20 minutes to see what effect it had on the rate of arsenite reduction and removal from solution. The nitrogen purged

experiments for each time were completed three times and each sample was then analyzed five times by the GF-AAS. The results of one set of trials along with the average were recorded in Table 13. The nitrogen purge times of 5-20 minutes gave similar results of approximately 80-90% arsenite removal. Illustrating, a short nitrogen purge time would effectively remove arsenite from solution.

Table 13: Change in concentration of arsenite (446 ppb) following sodium borohydride reduction with varied nitrogen purge times analyzed by AAS Graphite Furnace.

Sample	5 minute (ppb)	10 minute (ppb)	20 minute (ppb)
1	30.43	61.78	39.93
2	82.79	82.01	67.57
3	75.85	57.21	100.50
4	58.74	100.60	80.90
5	100.80	17.00	105.10
Average	69.70	63.70	78.80

Since arsenite could be removed by borohydride reduction followed by 5 minutes of nitrogen purge, the reduction time required to remove arsenate from solution also required examination. The standard arsenate solution prepared above was also tested for reduction to arsine gas using the same procedure as above. The experiment was completed by combining 400 μ L of the standard arsenate prepared in 12 mM acetate buffer, and 300 μ L of 1% sodium borohydride in an auto sampler vial for the HG-AAS. This created an arsenate concentration in the test vials of 438 ppb. The nitrogen purge time was varied between 5, 10, and 20 minutes to see what affect it had on the rate of arsenate reduction and removal from solution. The nitrogen purged experiments were once again completed three times and each sample was then analyzed five times by the

GF-AAS. The results along with the averages are recorded in Table 14. The arsenate removal rate increased with extended nitrogen purge times. This may have been the result of extended contact time between arsenate and sodium borohydride, where the borohydride caused a decrease in pH forming the protonated arsenate species. The protonated arsenate could then be reduced to arsine and removed from solution. The results showed approximately 1.1% arsenate removal after 5 minutes of nitrogen purge, 2.8% removal after 10 minutes of purge, and 18.4 % removal after 20 minutes of nitrogen purge.

Table 14: Change in concentration of arsenate (438 ppb) following sodium borohydride reduction with varied nitrogen purge times analyzed by AAS Graphite Furnace.

Sample	5 minute (ppb)	10 minute (ppb)	20 minute (ppb)
1	374.0	454.5	391.9
2	427.0	436.0	400.3
3	389.8	364.3	302.8
4	494.4	406.1	290.8
5	434.9	421.0	362.0
Average	424.0	416.4	349.6

The results showed with a 5 minute nitrogen purge after sodium borohydride reduction that 83.7% of the arsenite in solution was removed while only 1.1% of the arsenate was removed. These results were very encouraging when the averages are taken from larger sample sets, but when the range of the data sets was investigated some questions arose. The arsenite concentration calculated from the standard curve in the 5 sample data set ranged from 30 ppb to 100 ppb arsenic remaining. The range of the data was fairly large since the difference between the high and low account for over 15% of

the total arsenic in the original solution. The results could have been due to the random reading of arsenic concentrations below 100 ppb, but when the arsenate samples were further investigated they were found to have similar if not larger amounts of variation. The results of the arsenate analysis gave an arsenic concentration range from 374 ppb to 494 ppb. The 120 ppb range found in the results gave a variation over 27% of the initial arsenic concentration in solution, and two of the sample results gave arsenic concentrations approximately 50 ppb over the initial concentration. These results were also recorded in the linear range of the standard curve, therefore more repeatable results were expected. The overall trend of the average results appeared to match the expected results.

Electrochemical Oxidation of Arsenic: HPLC and AAS

The electrochemical oxidation of arsenite to arsenate was examined using the oxidation apparatus displayed in Figure 1. A standard 91.2 ppm arsenite solution was made in 0.12 M acetic acid/acetate buffer at pH 5.5 for the purpose of oxidation. This solution was oxidized like previous solutions, but the analysis of the solution was performed by both HPLC and GF-AAS to allow comparison and repeatability of the two methods. The experimental solution for GF-AAS was diluted 1:100 with 12 mM acetate buffer followed by combining 300 μL of the diluted experimental solution, and 400 μL of 1% sodium borohydride in an auto sampler vial. Then, the solution was purged for 5 minutes with nitrogen gas prior to analysis. The total concentration of arsenic at the time of analysis was 398 ppb, which fit the linear portion of the arsenic standard curves. The concentration was then converted back to ppm for reporting in Table 15 by multiplying

the calculated concentration in ppb by 228.3, a volume correction from the 1:100 and 300:700 dilutions. The analyses by HPLC were performed using the neat experimental solution.

The electrochemical oxidation of the 91.2 ppm arsenite solution was carried out for 90 minutes. The conductivity of the arsenite solution was increased to 5,100 $\mu\text{S}/\text{cm}$. Samples from the solution were collected every 30 minutes for analysis. The results of the analyses are recorded in Table 15.

The overall trend of the results from both analyses methods matches the expected advancement of the oxidation reaction. The HPLC results from time 0 minutes were as expected when compared to previous HPLC analysis results. All arsenic in solution was found as arsenite with no readable arsenate peak. The results of the AAS analysis at time 0 minutes showed over 25% of the arsenic as the arsenate species. This raised questions to the accuracy of the GF-AAS analysis. Past experiments using HPLC had repeatedly identified trace amount of arsenate in analyzed samples with fairly accurate mass balances. The analysis methods showed oxidation rates of 0.75 ppm/min and 0.82 ppm/min for AAS and HPLC, respectively. These oxidation rates were slightly greater than the rate (0.725 ppm/min) previously reported for the 5,100 $\mu\text{S}/\text{cm}$ conductivity level. Also, both analyses methods showed a complete conversion from arsenite to arsenate at the 90 minute sample.

The AAS results presented an issue, since the As(III) concentration was calculated from the As(V) concentration subtracted from the total arsenic and the total arsenic was less than the As(V) recorded by 7.7 ppm; it was not possible to calculate an As(III) concentration. Inconsistencies similar to this were experienced throughout the

entire AAS graphite furnace experiments. The results compiled by the AAS graphite furnace method may not be concrete based on the inconsistencies in data compiled by many trials using the GF-AAS and the lack of correlation between the results from the two analysis methods.

Table 15: Comparison of the electrochemical oxidation of 91.2 ppm arsenite at 5,100 $\mu\text{S}/\text{cm}$ conductivity when analyzed by GF-AAS versus HPLC.

Time	AAS			HPLC		
	As(III)* (ppm)	As(V) (ppm)	Total As (ppm)	As(III) (ppm)	As(V) (ppm)	Total As (ppm)
0	55.1	20.3	75.4	90.7	0.0	90.7
30	40.2	36.0	76.2	54.1	42.4	96.5
60	10.0	59.8	69.8	41.1	58.0	102.1
90	~	78.5	70.8	0.0	101.0	101.0

* As(III) determined by Total As – As(V)

The mass balance of total arsenic was inconsistent between GF-AAS and HPLC results. The calculated mass of total arsenic by AAS ranged from 69.8 ppm to 76.2 ppm, where the mass calculated from the HPLC results ranged from 90.7 ppm to 102 ppm arsenic. The initial arsenite concentration added to the oxidation chamber was 91.1 ppm. The results from the HPLC analysis were much closer to the expected arsenic levels. The largest arsenic concentration measured by GF-AAS was over 16% lower than the original arsenic concentration. A consistent mass balance was not recorded during any of the three analysis methods.

CONCLUSION

The removal of arsenic from drinking water has become very important. In 2001, the EPA set forth new regulations that decreased the acceptable level of arsenic contamination to less than 10 ppb. The importance of this research was to determine if electrochemical oxidation could be used to as a method to facilitate the removal of arsenic. Most of the current arsenic removal methods preferentially remove As(V) when compared to As(III). Electrochemical oxidation was evaluated to determine if it was a feasible method to convert arsenite into a more easily removed species, arsenate. This research could provide a means of pre-oxidation of arsenite, which would allow the utilization of current methods for the removal of arsenic from drinking water. The experimental results showed electrochemical oxidation is a viable method for pre-oxidation of arsenite to arsenate.

The analysis of arsenic by UV/VIS spectrophotometers found that both arsenic species of interest, arsenite and arsenate, could be detected at wavelengths less than 200 nm with the majority of the analyses performed at 190 nm. These experiments were used to determine the appropriate wavelength for detection of arsenite and arsenate for the HPLC.

In addition to UV/VIS analysis, post-column derivatization was evaluated as a possible means of analyzing the two arsenic species. The UV/VIS spectrophotometer was again used to analyze the arsenic sample that had been mixed with an indicator solution containing alizarin red S. The alizarin red S and arsenic were reported to complex giving a detectable visible peak at 520 nm. Evaluation of the method did not

show any noticeable peaks in the specified UV/VIS range of the spectrum. Therefore, post-column derivatization was determined to be an ineffective method to evaluate arsenic concentrations and speciation, and was not used in follow-up experiments.

The HPLC with an UV detector was used for analysis because it gave excellent consistency determining the concentrations of arsenic. The HPLC was also effective at separating the arsenic species. Both arsenite and arsenate gave linear standard curves in the range from 5 ppm to 100 ppm with R^2 values >0.998 . The detection limits for the HPLC analysis for arsenite was 3.48 ppm or 69.6 ng, while arsenate was 7.10 ppm or 141 ng. The standard curve gave a working range which allowed for the detection of arsenite as the concentrations decrease and also detected the arsenate concentrations as they increase during the oxidation reaction. These experiments proved UV detection would be a viable means of analyzing arsenic samples.

The rate of oxidation was monitored to investigate the affect of conductivity (σ) on the conversion of arsenite to arsenate. The rate of oxidation significantly increased when the conductivity of the arsenic solution was increased. The results showed when the conductivity was doubled from 2,500 $\mu\text{S}/\text{cm}$ to 5,100 $\mu\text{S}/\text{cm}$; the oxidation rate increase 3.6 times from 0.199 to 0.725 ppm/min. The results proved conductivity has a significant effect on the electrochemical oxidation of arsenic in an aqueous solution.

With results concluding the oxidation of arsenic was significantly affected by conductivity of the water source, groundwater and surface water samples were analyzed to determine how natural water source conductivities would compare to the experimental solutions. River, lake, and well water samples were analyzed to determine comparative conductivity levels. The conductivity results from the water sources ranged between 363

and 765 $\mu\text{S}/\text{cm}$. The analyzed conductivity values collected from the natural water sources were significantly less than the experimental conductivities between 2,500 and 5,100 $\mu\text{S}/\text{cm}$. Based on the equation in Figure 20, the rate of oxidation would be 0.197 ppm/min for the $\sigma = 765 \mu\text{S}/\text{cm}$ water sample, which is a similar rate to what was found in the $\sigma = 2,500 \mu\text{S}/\text{cm}$ solution.

During electrochemical oxidation reaction, the pH decreased even in the 12 mM acetate buffer solution as the arsenite was converted to arsenate. The half-reactions were balanced and showed protons were produced during the oxidation accounting for the pH change. As the speed of the electrolytic reaction increased a corresponding decrease in pH occurred. During the $\sigma = 5,100 \mu\text{S}/\text{cm}$ oxidation, the pH decreased to 3.6. The pH of 3.6 corresponded with the time at which all arsenite was converted to arsenate. The pH of the solution returned over the next 120 minutes to the initial pH of 5.6. These experimental results are important in the evaluation of electrochemical oxidation as a future method for the pre-oxidation of arsenic for removal from drinking water because current processes or infrastructure may be pH dependent.

The electrochemical oxidation reaction was again evaluated by comparing the volume of arsenic solution to the surface area of the oxidizing electrodes. Two test solutions with arsenic volume to Pt plate area ratios of 1.65 mL/mm² and 2.75 mL/mm² were oxidized and analyzed. The rates of arsenite oxidation were 0.119 ppm/min at 1.65 mL/mm² and 0.161 ppm/min at 2.75 mL/mm². Therefore, a 67% increase in plate area only produced a 35% increase in oxidation rate. The increase in plate area did increase the oxidation rate, but not nearly to the extent an increase in conductivity increases the oxidation rate of arsenite.

The use of GC-MS was evaluated as a means of determining the mass balance of arsenic throughout the electrochemical oxidation experiments. Arsenic species were never detected during the GC-MS experiments. The Supelco SPME would not properly extract arsine gas from the head space of experimental solutions. Therefore, no conclusive evidence was collected to evaluate if the electrochemical oxidation of arsenic produces any gaseous arsenic forms.

The evaluation of GF-AAS as a means of investigating arsenic concentration gave linear standard curves in the range from 100 ppb to 600 ppb with R^2 values >0.964 . The HPLC standard curves R^2 values >0.998 had a better linear fit than the GF-AAS curves. The GF-AAS was capable of detecting much lower concentrations of arsenic when compared to the HPLC analysis method.

The HG-AAS method of arsenic speciation using NaBH_4 was found to be inconsistent. For example, an arsenite sample containing 446 ppb arsenite should have been reduced to near 0 ppb arsenite following the addition of excess 1% borohydride solution. When five samples were analyzed the results showed a range from 30.4 ppb (6.7%) to 105 ppb (24%) arsenic remaining. The method failed to reduce all of the arsenic and also displayed large variations in the concentration of arsenic remaining. Therefore, the HG-AAS method did not provide the precise data expected for the lower concentrations of arsenic found in aqueous solutions.

The comparison of HPLC and GF-AAS analysis methods gave similar arsenic oxidation rates, but inconsistent mass balance data. The oxidation rate of arsenite (91.2 ppm) to arsenate in a $\sigma = 5,100 \mu\text{S}/\text{cm}$ was determined to be 0.75 and 0.82 ppm/min when analyzed by GF-AAS and HPLC, respectively. The mass balance of arsenic

collected four times from the same solution was determined by both HPLC and GF-AAS. The HPLC analysis gave a total arsenic concentration range of 90.7 to 102.1 ppm arsenic, while the GF-AAS analysis gave a range of 69.8 to 76.2 ppm. Both analysis methods showed variations in concentration and lack of evidence whether the amount of arsenic in solution was affected by the electrochemical oxidation.

At the time research investigating the electrochemical oxidation of arsenic concluded, several new questions have arisen providing opportunities for new research projects. Topics of interest include; further mass balance investigations, additional pH studies, evaluation of additional oxidation methods, and experiments with alternative metal electrodes.

The results provided evidence of a consistent decrease in pH during the electrochemical oxidation. Additional pH experiments could be conducted to evaluate the extent of pH change in a non-buffered experimental solution. Also, the pH of a representative flow through electrochemical cell would give representative data pertaining to the actual application of electrochemical oxidation of arsenic in a water treatment plant.

The reported research investigated the oxidation of arsenic using electrochemical potential. Future research could compare the use of alternative oxidation technologies, such as ozonation, bubbling of oxygen, or addition of an oxidizing agent like chlorine to aqueous arsenic samples. These experiments could be conducted as a multidiscipline project to evaluate oxidative ability along with cost analysis.

The platinum electrodes were used in the reported research to reduce variables during oxidation and arsenic removal in the experiments. Electrodes made of alternative

materials would allow for further investigations into the removal of arsenic from aqueous solutions. Many of the methods designed to remove arsenic from aqueous solutions include some type of precipitation by cationic metals such as iron or aluminum. Experiments investigating the use of iron or aluminum electrodes could provide a means of oxidizing arsenite in solution and provide metal cations for precipitation. Future research in this area may provide more scientific data to help determine the feasibility of using electrochemical oxidation as the preferred method of the pre-oxidation of arsenite for application in water treatment facilities. Some current research has been published on this topic (22).

Current methods for the removal of arsenic from drinking water require arsenic to be in the As(V) form to best facilitate removal. The results showed the increase in electrode area per solution volume increased the oxidation rate. Of the parameters evaluated in this research, the increase in conductivity resulted in the largest increase in oxidation rate. It was also concluded that HPLC was the best speciation method for separation of arsenic species. This research defines parameters that make it feasible to use electrochemical oxidation to oxidize As(III) to As(V).

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