

POTABLE WATER TREATMENT USING
ELECTROLYTICALLY GENERATED
COPPER AND SILVER IONS

By

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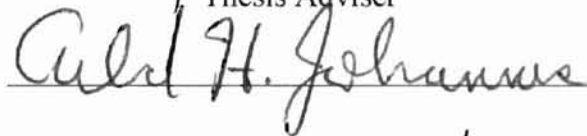
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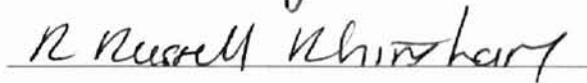
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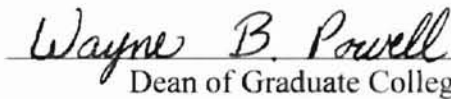
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PREFACE

Ion generation performance for a prototype batch delivery device that was designed to generate copper and silver ions is evaluated. The device was a first attempt at manufacturing a device that could be used in potable water treatment applications. Recommendations for future designs and specific applications are presented. A literature review of current disinfection technologies being used today is included.

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NOMENCLATURE

a_e	volume specific electrode area (electrode area divided by treatment volume)
a_i	activity
c	total molar concentration (moles/liter)
c_{eq}	total equivalent concentration (equivalents/liter)
DBPs	disinfection by-products
E	electrode potential (volts or millivolts)
E°	standard half-cell electrode potential (volts or millivolts)
F	Faraday's constant (coulombs/mole electrons)
I	electrical current (amps)
i	current density (total current divided by electrode area)
ISA	ionic strength adjuster
k_m	mass transfer coefficient (volume/[time (electrode area)])
n_{eq}	total number of equivalents
R	ideal gas constant (energy/mole K)
T	temperature (K)
v^i	stoichiometric coefficient of ion in half cell reaction
z	stoichiometric coefficient of electrons in half cell reaction

CHAPTER I

INTRODUCTION

Maintaining good public health, relies upon a water supply that is free from harmful bacteria and other microbes. Since the introduction of large-scale disinfection, mainly chlorination, the quality of drinking water improved significantly along with public health. Yet today, in developing countries, disease and sickness caused by contaminated water supplies is a common occurrence. There is a need to provide simple and effective disinfection methods to help curtail this problem.

Chlorination has been the disinfectant choice of use since the early 1900s. It provides an effective treatment for a wide variety of microbial species. Unfortunately, research has shown that there are several negatives associated with chlorination. The main concern with using chlorine disinfectants is the formation of disinfection by-products (DBPs), specifically, trihalomethanes. This has prompted research into other disinfection methods.

Another problem with chlorination disinfection is portability. Chlorine compounds cannot be stored for extended periods of time (Burch et al., 1998). This requires dependable delivery of disinfection chemicals, which may not be possible in remote locations or in emergency situations.

Several metal ions have been shown to have bactericidal properties. Two such metals are copper and silver. The ions of these two metals have been shown to have

disinfection capacities for several different microbial species (Landeem et al., 1989). Several devices have been developed to treat swimming pools using electrolytically generated copper and silver ions. Current devices that have been designed have a risk to the consumer for over exposure of copper and silver ions. Typical designs rely upon the user to determine the treatment time. Most often, the user uses a copper test kit to determine the concentration in solution. Several devices are discussed in the next section. This risk needs to be reduced to acceptable levels before these types of devices can be considered viable options to current disinfection methods.

Problem Defined

As more information becomes available on the harmful effects of DBPs, it is apparent that better disinfection strategies need to be implemented. New regulations imposed by the Safe Drinking Water Act Amendments of 1996 requiring the reduction of DBPs are being enforced. It is becoming increasingly difficult for water utilities to meet these regulations (Kuo et al., 1999). Either technology needs to incorporate downstream removal strategies of these harmful by products, or use a disinfectant that does not form DBPs.

Copper and silver ions are ideal as disinfectants in relation to chlorine. There are no DBPs formed when used by themselves. Concentrations considered for potable water disinfection, 80 ppb silver and 800 ppb copper, are below limits set by the EPA for drinking water. The lowest limits that the EPA recommends for copper and silver concentration are 1000 ppb and 100 ppb respectively (EPA, 1999). These are the National Secondary Drinking Water Regulations set by the EPA, which are not

enforced. The National Primary Drinking Water Regulations, which are enforced, limit copper to 1300 ppb. Silver is not considered a primary contaminant. Primary contaminants are those contaminants found to adversely affect human health when concentrations are above levels regulated by the EPA. Secondary regulations are listed for cosmetic reasons (odor, skin discoloration, taste, etc.).

The main problems with using copper and silver ions, as reported in the literature, are the relatively low kill rates and performance variability over various microbial species. The low kill rates make disinfection difficult on a large scale distribution system, and the variability makes it difficult to determine the optimum contact time. However, research has shown that copper and silver ions can be combined with low level concentrations of other disinfectants to achieve performances similar to current disinfection methods. This would lower DBPs released by the low-level disinfectant, while still maintaining water quality.

Devices have been developed to generate ions electrolytically. Chak et al. (1987) designed a device to put silver into flowing water. Water flows between electrodes in parallel that have a specified composition of copper and silver. Water that flowed out of the device contained a certain level of copper and silver ions. The device was simple and took into account temperature and pH effects. The user could connect the device to an ordinary house water faucet. The system was designed to operate in three different modes: drinking water, sterilization, and bypass mode. The user selected the treatment cycle on an electronic touch pad. The device did not have online monitoring capabilities. Matsuo et al. (1988) developed a similar treatment device. The apparatus generated silver ions and included the ability to adjust the pH of the silver

solution. They claimed that this would enhance disinfection by reducing the chance for silver to adsorb onto proteins and reduce the contact with bacterial cells. Hayes (1987) developed a copper and silver generating device to disinfect swimming pools and spas. The device utilized a 97% copper and 3% silver alloy for the cathode and anode. This allowed for the polarity to be switched to increase the life of the electrodes. The device relied upon the user to test the concentration of ions in the water to determine the amount of contact time required. The device was designed to operate within the recirculation loop of the pool. Another device developed by Dahlgren (1982) was designed to float on the surface of the pool, but again relied upon the user to determine adequate contact time.

To advance the potential of copper and silver disinfection treatment of potable water, better delivery devices need to be developed. The device should be able to produce the specified concentrations independent of water characteristics. Previous inventions were focused primarily on swimming pool treatment. They required the user to determine the contact time and measure the concentration using copper test kits. Inaccurate test results could result in unsafe levels of copper and silver in the water. It would also be desirable to allow implementation of feedback control for flow systems.

This work will focus on the design and testing of a simple ion generating device for batch treatment on a small scale. Possible applications include emergency potable water treatment, and portable water treatment for remote locations or in developing countries. Recommendations will be given to improve existing designs and the direction for future work.

Warnings regarding treatment of water and use of any designed devices will also be recommended. More research needs to be performed, addressing the long term effects of low level exposure to these ions before it can be regarded as an acceptable alternative disinfection method.

CHAPTER II

LITERATURE REVIEW

Obtaining water free from harmful bacteria, viruses, and protozoa microbes is essential to maintaining good health. Large-scale disinfection treatment helped to prevent epidemic proportions of disease and infection. Many bacteria and viruses are active in natural waters, and it is important to limit their contact with people. The objective of this chapter is to focus on current disinfection practices and their alternatives as presented in the literature.

Current Disinfection Methods

Chlorination

The most widely used disinfectant agent used today is chlorine. Chlorine can be added to water as elementary chlorine, or as chlorine-containing compounds. Some of these compounds include calcium hypochlorite, sodium hypochlorite, chlorine dioxide, and chloramines (Yahya et al., 1993). The chlorite (ClO^{-2}) and chlorate (ClO^{-3}) ions are believed to be the main contributors for the disinfecting action of chlorine dioxide. The other chlorine containing compounds and chlorine gas form both hypochlorous acid (HOCl) and hypochlorite (OCl^{-}) ion, which are believed to be the main contributors to disinfectant action for these compounds (Yahya et al., 1993).

Water treatment methods must be able to kill many different microbial species using a limited number of disinfectants if they are to produce safe water for human contact. Contact times must also be reasonably short for feasibility and convenience. Chlorination is widely used because it disinfects a wide variety of microbes (Pedahzur et al., 1995). The rapid kill rates of chlorine have also been a major reason for its use as a disinfectant (Cassells et al., 1995).

Although chlorination is effective in killing a variety of microbes, it does not come without some negatives. Organic material present in water has a large capacity for reacting with chlorine and chlorine containing compounds, and therefore limits their effectiveness as a disinfectant. Disinfection by-products (DBPs) are formed when the chlorine components react with the organic matter present in the water (Yahya et al., 1993). This results in a high concentration of chlorine being needed to effectively disinfect the water because most of the capacity goes towards oxidizing the organic material (Kuo et al., 1999). The residual effects of chlorination are also short term. Because of the low residual effects, injured bacteria that were not killed can regrow and cause high bacterial counts. This has been observed within distribution loops (Pedahzur et al., 1995). Tosa et al. (1997) showed that *Escherichia coli* (*E. coli*) exposed to chlorine was not able to be cultured using defined testing methods. They showed that disinfected bacteria can recover on non-selective medium, but showed no viable cultures on selective medium. Joret et al. (1997) came to the same conclusion using an epifluorescent technique versus the classic plating techniques. This leads to questions about current testing methods that may show no bacteria present, but in reality, there are viable cells that can regrow when given enough time.

In addition to low residual capacity, the DBPs formed from chlorine disinfection have been shown to be carcinogenic. Trihalomethanes are the most commonly formed DBPs (Yahya et al., 1995). Some of these specific carcinogenic compounds include chloroform and bromodichloromethane. Chloramines are illegal to use as a disinfectant in Germany and France because of the DBPs that can be formed from its use. Some of these compounds have been shown to cause problems in home dialysis units (Pedahzur et al., 1995). New rules have been mandated in relation to the Safe Drinking Water Act Amendments of 1996 (EPA, 1999). These rules regulate the number of microorganisms allowed and DBPs. This places increasing challenges on water utilities in the United States to increase residual capacity of disinfection systems while reducing the by-products that are formed (Kuo et al., 1999). The California Department of Health Services completed a study showing that there is a potential for increased miscarriages in pregnant women exposed to trihalomethanes (*Chemical Market Reporter*, 1998). The preliminary study showed that two percent of the population tested had an increased risk of miscarriage when they drank five glasses or more of water containing at least 75 μg of trihalomethanes (*Chemical Market Reporter*, 1998).

Landeen et al. (1989) showed that the levels of chlorine required to effectively kill *Legionella pneumophila* in cooling tower water was relatively high. It would be corrosive to plumbing systems in actual conditions. They also showed that the potential for decreased residual effect was greater at the elevated temperatures found in cooling towers.

Other potential problems using chlorination as a disinfectant is that it requires a continual supply of chemicals. In developing countries, road conditions and weather

may hinder the ability to supply needed chemicals. Chlorine and chlorine containing compounds cannot be stored for an extended period, which necessitates the need for dependable delivery service (Burch et al., 1998).

With increasing concern over DBPs, what can be done to improve chlorine disinfection performance? Kuo et al. (1999) suggested a possible way to improve the residual performance of chlorine disinfection while limiting DBPs. Using models to optimize the number of booster stations and their location would allow for lower concentrations of chlorine to be used while maintaining a higher residual capacity (Boccelli et al., 1998). Three models were developed by Uber et al. (1998) to perform similar optimizations.

Ultraviolet Light

Ultraviolet (UV) light is emerging as a possible disinfectant for small-scale systems. Ho et al. (1998) showed that a UV disinfection system had higher initial viral removal efficiency than a full-scale chlorination system located at the Southeast Water Pollution Control Plant in San Francisco, California. Tomowich (1998) tested an UV device under certain failure conditions. The device met disinfection requirements when a simulated failure of a portion of the lamps occurred and during treatment rates in excess of the designed maximum feed rate. UV disinfection produces very little DBPs and the kill rates are high.

The main problem with UV disinfection is that it requires a power source. Areas in developing countries may not have adequate infrastructure to support such a system. The residual effects of UV disinfection are short lived, which leads to concerns about regrowth (Burch et al., 1998). Another factor that can greatly affect UV disinfection

performance is the turbidity of the water. Higher turbidity will reduce the effectiveness of the UV light. Particles in the water will scatter the light and may direct it away from the microbes (Burch et al., 1998).

Physical and Biophysical Processes

These types of processes involve a broad category of disinfection methods. The majority of these processes involves some type of filtration. Filtration typically employs a coarse filter followed by a membrane filter. The coarse filter is used to remove major particles and reduce the turbidity of the water (Burch et al., 1998). The membrane filter can be synthetic or a naturally occurring biofilm. A typical biofilm filter is formed using a slow sand filter. The biofilm forms on the surface and, in larger scale filters, can remove 99% of all microbes present in the water (Burch et al., 1998). Slow sand filters would be feasible in developing countries because of the simplicity of construction.

Membrane filters are efficient at removing the majority of microbes present in water in a nanofiltration process, but there is the question of how to handle the reject waste that is generated. An acceptable plan to handle this concentrated reject has to be addressed before a system can be implemented. Other ultra filtration methods remove most microbes, but cannot achieve the required reduction percentages alone. Typical systems have a downstream disinfection device to complete the process (Kuo et al., 1999).

Slow sand filters require a large amount of labor. The flow rates need to be slow enough to allow the biofilm to form on the surface. The rates are approximately 2 m³/day for every square meter of surface area. The user must clean the biofilm every couple of weeks by raking the surface to remove major contaminant buildup. The top

layer of sand must also be replaced every couple of cleanings. The biofilm must be allowed to reform after sand replacements (Burch et al., 1998). It is possible during cleanings that the user could disturb the upper layer of sand, and unknowingly produce contaminated water.

An example of combining multiple technologies to achieve acceptable disinfection was shown by Abbaszadegan et al. (1997). They tested the performance of a pressed activated carbon block filter followed by UV light as a point-of-use disinfection system. They found that the disinfection met all of the US EPA guidelines for new water purification methods.

Another physical process to mention is simple pasteurization. Pasteurization would be appealing to developing areas because the process is simple. It is also very efficient at killing most microbes present in the water. Burch et al. (1998) investigated the possibility of using solar energy to pasteurize water on a scale large enough to benefit villages in developing countries. They found that the cost was more than other disinfection processes. They recommend using slow sand filters for these applications. Because of the large amount of fuel required, pasteurization using other forms of energy was not cost effective.

Ozonation

Ozonation is becoming a popular alternative to chlorination on large-scale systems. Ozone has a high disinfection performance and high kill rate for many microbes. It produces very little hazardous DBPs and does not produce a bad taste or odor.

One disadvantage of ozonation disinfection is its low residual capacity. Ozone behaves similar to chlorination when it contacts organic matter in the water. The organic matter has a high capacity for oxidation and most of the ozone will be consumed in oxidation. It is also more expensive to implement (Yahya et al., 1993). Ozone can also cause problems with corrosion in the distribution loops, and yields a number of low molecular weight ketones and aldehydes (Pedahzur et al., 1995).

Iodine Disinfection

Iodine disinfection was studied in depth in the 1940's. Iodine was shown to have bactericidal properties, is quite stable and is simple to apply. Iodine is not used as a large-scale disinfectant. It typically is used on a personal or small institutional basis. Many portable hiking and camping water disinfectant methods involve iodine (Brion and Silverstein, 1999). NASA uses iodine as a disinfectant on all their spacecraft (Willis and Schultz, 1987).

The most common method for introducing iodine into water is through an iodinated ion exchange resin or some type of ultra-filter embedded with iodine compounds. Other portable methods involve adding small amounts of triiodide solutions to the water (Gail and Silverstein, 1999).

Naranjo et al. (1997) tested a portable iodine disinfection device against several difference species. The device employed a two-stage disinfection system. It used microfiltration to remove protozoa and an iodinated exchange resin to introduce iodine into the water to inactivate bacterial and viral species. Their results showed that the device exceeded the US "*Guide Standard and Protocol for Testing Microbiological Water Purifiers*" (USEPA, 1987).

A negative associated with iodine disinfection is not all the ionic forms exhibit bactericidal activity. This could result in a higher concentration of iodine disinfectant required to maintain water quality (Silverstein and Hurst, 1993). Iodine can also exhibit a metallic taste at moderate levels (Willis and Schultz, 1987). This would be an undesirable effect for the consumer. Gailand et al.(1999) showed that the inactivation rates of iodine was significantly affected by the presence of dissolved organic substances, including detergents and proteins. Although iodine does not have the oxidation capacity that chlorine does, it does appear that organics can reduce the disinfection effectiveness of iodine.

The above disinfection methods comprise the majority of processes that are either currently being used or have been used. The methods that have been discussed perform well against bacteria inactivation, but there are some concerns over long term effects caused by these disinfectants. Residual concentrations appear to be a common problem with disinfectant methods that are used. Studies of possible alternatives have been completed. The next section will focus on one such alternative.

An Alternative Disinfection Method

Several metals have been shown to have bactericidal properties. Silver has been known for its ability to inactivate several different bacteria, and copper has been known to inhibit cellular activity above certain concentrations. This section presents findings related to copper and silver disinfection.

Disinfection by Copper and Silver Ions

Products containing silver are common. Hospitals and hotels use silver to control infectious agents in their distributions systems. Post-harvest cleaning of oysters involves the use of copper and silver to prevent bacterial growth. Chicken farms are also using copper and silver to control bacterial and fungal growth (Gupta et al., 1998). In Mexico, one can purchase colloidal silver in supermarkets to be used as a disinfectant for salads and drinking water. The bactericidal properties of silver and copper have been documented as far back as 1000 B.C. Silver is a health additive in traditional Chinese and Indian Ayurvedic medicine (Gupta et al., 1998). The Persians also stored water in silver and copper vessels because of the disinfection properties of these metals (Yahya et al., 1993). Silver salts used to be administered to newborn infant's eyes to prevent infection. Silver containing compounds are also used to treat burn wounds to prevent bacterial infections while the skin is healing (Gupta et al., 1998). Because of the apparent bactericidal properties of copper and silver, many studies have been conducted on the possibility of using these metals as water disinfectants. It has also prompted the design of several devices to introduce these metals into water.

How does copper and silver act as a biocide? Thurman and Gerba (1989) proposed some possible mechanisms by which copper and silver ions act as a disinfectant. For copper disinfection, they suggested that the oxidative power of copper is the main reason for its disinfection properties. They stated that copper ions bind with biological macromolecules and the resulting redox reactions form radicals near the binding site. Continued reactions form secondary radicals that form in the same

location. This increased concentration of radicals damages the microorganism inhibiting proper cell function.

Thurman and Gerba (1989) suggested a few possible mechanisms by which silver acts as a disinfectant. Silver interacts to form complexes at the cell surface, which interfere with the dehydrogenation process or electron transport. Studies have also shown that silver is able to bind phage DNA and inhibit processes within the cell. They suggested that it is possible for low concentrations of silver to penetrate a bacterial cell and cause structural damage to the cell membrane. After penetration of the cell membrane, silver may bind to the DNA and other proteins causing the normal function of the cell to cease. Chambers et al. (1962) showed that the germicidal action of silver ions is related to its concentration and not affected by the source of silver ion generation.

Due to the relatively low inactivation rates for copper and silver disinfection systems alone, most of the studies that have been reported are related to copper and silver in combination with low levels of free chlorine as a disinfectant. Landeen et al. (1989) showed that the kill rates for *E. coli* using 475 ppb copper combined with 40 ppb silver were 100 fold less than free chlorine alone or low levels of free chlorine combined with copper and silver. They also showed that the kill rates for *Legionella pneumophila* were a 1000 fold less for similar type systems. Cassells et al. (1995) showed that copper and silver concentrations of 800 ppb and 80 ppb, respectively, had no noticeable effect on *Naegleria fowleri* amoebas. This is not surprising since protozoa have shown resistance to high concentrations of chlorine (Cassells et al., 1995).

If the kill rates associated with copper and silver disinfection are small, why use it at all? When used in combination with low levels of another disinfectant, copper and

silver exhibit a synergistic effect. Yahya et al. (1993) developed a treatment method using potassium permanganate in combination with copper and silver ions. The method showed a ten-fold reduction in the time required for a 99.9% reduction in the number of Coliphage MS-2 versus copper and silver treatment alone. It also showed a 5 fold reduction versus potassium permanganate alone. This treatment method also exhibited a higher inactivation rate than current disinfection treatment methods. Cassells et al. (1995) showed that copper and silver combined with free chlorine exhibited a synergistic effect for inactivation of *Naegleria fowleri* amoebas. Their results showed a 99 percent reduction in amoebas using combined disinfectants versus only an 89 percent reduction for free chlorine alone. Landeen et al. (1989) showed that 400 ppb copper and 40 ppb silver in combination with 0.2 mg/L free chlorine exhibited enhanced kill rates for several bacterial species when compared to free chlorine alone. Some species showed more of an enhancement than others exhibited. They also performed a more detailed study using *Legionella pneumophila*, and found that silver and copper enhanced the inactivation rate versus free chlorine alone. Pedahzur et al. (1995) showed that 30 ppm of hydrogen peroxide in combination with 30 ppb silver nitrate exhibited a 99.9 percent reduction in *E. coli* exposed for 30 minutes. They showed that the combined effect was greater than the sum of the individual reductions. It was suggested that the combined toxic effect of silver and hydrogen peroxide may be related to damage caused to cellular proteins (Pedahzur et al., 1997). Yahya et al. (1990) performed comparison tests using only free chlorine at a concentration of 1 mg/L and a combined system of free chlorine, copper and silver. The combined system contained only 0.3 mg/L chlorine and 400 ppb copper and 40 ppb silver. The results showed that there

were no significant differences between the performance of the two systems. Lin et al. (1998) tested the inactivation potential of *Mycobacterium avium* by copper and silver ions. They found that it took 48 hours to achieve a 99.9% reduction in bacteria using a copper concentration of 800 ppb and a silver concentration of 80 ppb. These times were almost 100 times greater than what was observed for *Legionella pneumophila* (Lin et al., 1996). Liu et al. (1998) performed a case study on the distribution systems of three different hospital buildings. The systems were infected with *Legionella pneumophila*. Using copper and silver, they treated the distribution systems of two of the buildings. The first building was treated for 4 weeks before the detection of *Legionella pneumophila* was zero. The second building took 12 weeks before the count was zero. The residual effects of copper and silver were apparent when *Legionella pneumophila* remained undetected for 6-12 weeks after treatment was stopped.

Copper and silver disinfection methods have some disadvantages as mentioned before. The kill rates using copper and silver ions alone are small. The contact time required to achieve a reasonable level of disinfection is not practical for most applications. Chronic exposure to higher concentrations of silver has also been shown to cause argyria, a blue-gray discoloration of the skin (Pedahzur et al., 1995). Copper is also a primary contaminant of the National Primary Drinking Water Regulations. It has a maximum contaminant level of 1300 ppb. Silver and copper are also listed as secondary contaminants. The EPA does not enforce these limits, but recommends that copper concentrations should not exceed 1000 ppb and silver should not exceed 100 ppb (EPA, 1999). Again, the National Primary Drinking Water Regulations are established to protect human health. The secondary regulations are set for cosmetic considerations

such as odor, taste, and skin discoloration. Other disadvantages related to copper and silver disinfection is the lack of performance against specific microbes. As mentioned earlier, amoeba inactivation by copper and silver was not noticeable. Abad et al. (1994) tested the disinfection performance of human viruses in water using copper and silver in combination with low levels of chlorine. The results showed that of the viruses tested (hepatitis A virus, human rotavirus, human adenovirus, and poliovirus), poliovirus was the only test system that exhibited a significant enhanced inactivation rate versus free chlorine alone. There is also a fear that silver resistant microbes could develop if its use as a disinfectant is increased (Gupta et al., 1998). Gupta et al. (1998) have cloned the silver resistance determinant from a isolate of *Salmonella*, and showed that the gene products are similar to proteins known for metal resistance. Ibarluzea et al. (1998) tested copper and silver disinfection against chlorine. They studied 12 indoor swimming pools. They found that copper and silver concentrations of 3.4 ppm and 0.34 ppm respectively resulted in only a 90 percent probability that the water was microbiologically acceptable. The risk for infection is substantially greater than pools using chlorination.

Health Effects

Information that is available about the health effects of exposure to copper and silver were related to high level exposure. Telisman et al. (2000) showed a link between various metals, including copper, to low semen quality in men. Okie (1997) reported on a study that showed a possible link to Parkinson's Disease and long term exposure to certain metals. The study showed that people who worked with copper for over 20 years

had double the risk of developing Parkinson's Disease. Other effects caused by copper have included acute gastrointestinal problems (Pizarro et al., 1999).

Health studies related to long term exposure to low levels of silver and copper could not be found. The current EPA regulations are based upon studies involving high concentrations of these metals.

CHAPTER III

PRODUCT DESIGN

Background

This chapter will focus on the theoretical basis for the design of a copper/silver ion generation device. A description of the prototype device, including a diagram, and summary of its operation is presented. The main design criteria were the accuracy of the delivery device and operational simplicity.

Faraday's Law

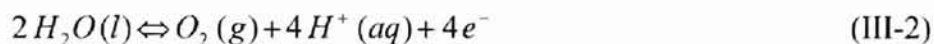
Electrochemical processes are most easily explained using Faraday's Law. Faraday's Law relates current flow through the circuit to oxidation and reduction rates at the anode and cathode (Equation III-1).

$$n_{eq} = \frac{\int I \cdot dt}{F} \quad \text{(III-1)}$$

In the above equation, n_{eq} is the number of equivalents of an ionic species that results from the flow of current I over a period of time t . It is also the number of moles of electrons available at the cathode or moles of electron required at the anode. F is Faraday's constant (96485.309 coulombs/mole electrons). This equation holds for reactions where the stoichiometric coefficient of the electrons is equal to the charge of the ionic species. This integral form is more general and accounts for fluctuations in

current over time. This will allow for internal monitoring of the total charge that has passed through the circuit without having to hold the current constant. This is important to the function of the device when being used to treat samples of water with a wide variety of conductivities. Monitoring the current also allows for correction due to temperature effects. Higher temperature increases the ionic conductivities of electrolyte solutions (Wendt and Kreysa, 1999).

This relation assumes that only one reaction occurs at the anode, the oxidation of the metal. This may not be an accurate assumption since there might be several reactions that are competing at the anode site. One such reaction is the oxidation of water.



Another reaction that might occur is the oxidation of chloride ions in the water.



This reaction competes with oxidation reactions of the metal electrode. Part of the current is used for secondary reactions and the rest of the current flowing through the circuit is used to oxidize the metal in the anode. When considering the oxidation of copper, other potential problems can be discussed. The goal is to produce Cu(II) ions, since this is the oxidation state of copper that has been studied in the literature. The standard electrode potentials show that the oxidation of copper metal to Cu(II) has a higher preference for oxidation than copper metal to Cu(I). However, if enough voltage is applied, it is possible that some of the current will be used for the competing reaction. In addition, the oxidation of Cu(I) to Cu(II) has a higher preference than either reaction. If any Cu(I) is near the anode, it will be oxidized to Cu(II), but the amount of charge

used to produce the combined total of Cu(II) ions is more than what would be required to generate Cu(II) by oxidation of the metal directly. This is caused by the total voltage required to cause the reaction to occur through the intermediate copper oxidized state is higher than the reaction from metal directly to Cu(II). This would result in a higher current flow through the system without an increase in copper ions being generated.

The amount of current that is applied toward a specific reaction is defined by the current efficiency. Overall, current efficiency can be calculated from the following equation.

$$\Phi_i^c = \frac{n_{eq} \cdot F}{\int I \cdot dt} \quad (\text{III-4})$$

This current efficiency can be determined experimentally by measuring the total charge that flowed through the circuit and measuring the amount of ions produced for the species of interest. This current efficiency may only apply to the water sample that was tested. If other chemical components are present that can compete for electron transfer at the anode, the current efficiency for the oxidation of the metallic anode will decrease. However, it is assumed that the major reaction that competes with the anode reactions is the oxidation of water. Most other reactions will be reduction at the cathode.

Another inherent problem in trying to design a delivery device is determining the amount of ions generated at the anode that will be reduced at the cathode. Table III-1 shows the major reduction reactions that might take place at the cathode site and their corresponding electrode potentials. E° is the standard half-cell electrode potential.

Table III-1. Cathode Reduction Reactions

Reaction	E° (V)
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.799
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.337
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83

The reason for including this table of reactions is to show that the potential for reduction of the metals might not be negligible. The more positive the standard electrode potential, the more likely the reaction is to occur as written. Some reactions may have exceptions to this rule because of higher activation energies required to start the reaction. This requires a higher applied voltage, referred to as overvoltage, to cause the reaction to occur. Although the reduction of nitrate has a higher standard electrode potential, the reaction is dependent upon the pH of the system. Since treatment conditions will be near neutral pH, the concentration of free hydrogen ions will be small which will reduce the chances of this reaction occurring. The same reasoning applies to the reduction of dissolved oxygen. This leaves the reduction of silver and copper as the next highest preferred reactions. Some of the ions being generated at the anode will be plated out onto the cathode. This will affect the generation efficiency of the device. The reduction reactions of silver and copper will be limited by the low concentrations that are being generated.

Mass Transfer Effects

In electrochemical processes, the reduction reaction rate at the cathode can be limited by the mass transfer effects of the system. As the voltage potential at the cathode becomes more negative, the cathodic current density increases. If the current

density increases above the mass transfer-limited current density, the rate of disappearance of the ions will be limited by the mass transfer rate of ions to the cathode surface (Wendt et al., 1999). In a stirred batch reactor, this rate is a first order differential function.

$$\frac{dc}{dt} = -k_m c a_e \quad (\text{III-5})$$

In Equation III-5, k_m is the mass transfer coefficient for the ionic species, c is the bulk concentration, and a_e is the electrode surface area divided by the volume in the tank (Wendt et al., 1999). As the concentration of ions increases in solution, the voltage potential at the cathode will become less negative. This will cause a decrease in the overvoltage at the cathode. The current density at the cathode will then decrease. If the current density at the cathode drops below the mass transfer-limited current density, then the rate of disappearance due to reduction at the cathode is derived from Faraday's law as shown in the following equation (Wendt et al., 1999).

$$\frac{dc_{eq}}{dt} = \frac{i a_e}{F} \quad (\text{III-6})$$

The current density, current divided by electrode area, is represented by i . C_{eq} is the equivalent concentration for the ionic species. If the current efficiencies for the anode and electrode are equal to one, then it is possible that the rate of generation will equal the rate of disappearance and the maximum concentration that is possible will be obtained.

Based upon standard electrode potentials, silver will have the higher preference for reduction relative to copper. This means that if significant ions are lost to reduction reactions at the cathode, silver will be impacted the most. However, a higher

concentration of copper will increase mass transfer resistance of silver to the cathode and inhibit the reduction of silver.

The final concentrations of interest are low enough that it is unlikely that the rate of reduction will obtain the levels defined by Equation III-6. The overvoltage at the cathode caused by low concentrations of metal ions will be great enough to cause competing reactions listed in Table III-1 to occur.

Based upon the information presented, there are two main factors to consider in the design of a ion generation device: 1) anode current efficiency less than one caused by competing reactions, and 2) reduction of metal ions at the cathode. It was assumed that the loss of ions due to reduction at the cathode would be minimal because of the low concentration ranges being generated.

Anode Design

Another parameter to consider when designing an ion generation device is the composition of the anode. Previous literature reported devices using copper and silver alloys with a composition of 97% copper and 3% silver by weight. Information regarding these composition determinations was not found.

The desired concentrations to be generated are 800 ppb copper and 80 ppb silver, a ratio of copper to silver of 10:1. If a copper and silver alloy anode will generate ions in concentrations directly proportional to the equivalent composition of the anode, it can be shown that the composition of the anode must be in a ratio of 10:1 copper to silver by weight. Please refer to the Appendix C for this calculation. This corresponds to 9.1% silver by weight.

Based upon standard electrode potentials, copper will have a higher preference for oxidation at the anode versus silver. Because the anode composition contains a higher amount of copper, the surface area for copper oxidation is higher also. This will further increase the current efficiency for copper. Typically, the metal with a more positive oxidation electrode potential will dissolve first at the surface, leaving behind a sponge or porous anode of the other metal. If the pores created by the oxidation of the first metal are too small, the other metal will begin to dissolve. It is possible, however, to generate solutions that have a composition equal to the composition of the anode. In several different solutions, brass alloys containing greater than 50% copper produced the same composition in solution as that of the alloy anode. If the copper content was less than 50%, the solution contained only zinc ions (Thompson, 1939). Generally, the way an alloy oxidizes is determined by its composition and also by the solution it is in. The effects of the electrolyte solution can be seen when brass of any composition functions as the anode of an electrolytic circuit in a sodium sulfate solution. The resulting corrosion or oxidation products have the same composition as that of the brass anode (Thompson, 1939).

It is possible to manufacture an electrode to generate the desired concentrations based upon the information presented. The difficulty is determining the effect of varying water compositions and their effect on the ion generation, and determining the correct composition of the anode.

Adsorption Losses

Another important factor to consider when designing an ion generation device is the loss of ions to vessel surfaces. Silver losses due to adsorption are of more concern

than copper because adsorption rates for silver are higher. Landeen et al. (1989) showed a 15.4% decrease in silver concentration for solutions stored in pyrex glass containers over 48 hours. They also showed that copper concentrations decreased 10.0% under the same test conditions. Polyethylene containers only exhibited an 11.6% decrease in silver concentration and a 2.5% decrease in copper concentration over a 48-hour period. They showed that most of the absorption took place during the first 24-hour period. Chambers et al. (1962) showed that the losses of silver due to adsorption caused a decrease in inactivation rates of *E. Coli*. It is also noted that the studies conducted the tests by waiting to inoculate the water samples over an extended period. Although the rate is decreased, bactericidal activity still exists. Thurman and Gerba (1989) reported a study performed by Muller et al. (1977) that showed water treated with 100 ppb silver and then stored in polypropylene containers for three years showed no bacterial growth, and that most of the silver had been adsorbed onto the container surface.

Devices tested for this work assumed that the adsorption effect would be minimal. This assumption is based upon ions being in contact with the microbes shortly following electrolytic ion generation.

Complex Ion Formation

Another potential interference to disinfection efficiency is the complexation of the disinfectants. Phosphates and chlorides are the two main ions of concern. Reactions with these ions form precipitates, which decrease disinfection potential (Thurman and Gerba, 1989). Hydroxides can also form colloidal suspensions and reduce the disinfection potential. This investigation is reserved for a later date and will not be addressed in this work.

Initial Prototype Designs

Device 1

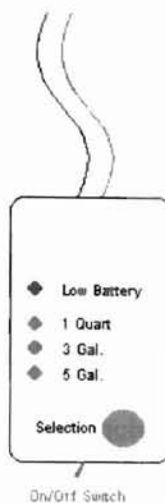


Figure III-1. Prototype Schematic

The first delivery device that was designed and tested in this work was for batch operation. Figure III-1 is a schematic of the initial prototype. It consisted of 4 LED lights that informed the user which cycle was selected and if the voltage potential of the batteries was too low for the device to operate. The device operated using 4 AA batteries, which produced a total voltage of 6 volts. The Selection Switch was used to choose which cycle to run and to start the cycle. The anode and cathode were attached to wires as shown. The device monitored the time and current, and shut off automatically based upon the total charge required to generate the needed concentrations. The total charge required was determined from simple Faraday's Law. The total charge required was supplied to Genesis Technologies Inc. in Tulsa, Oklahoma. The actual design of the timing circuit and the device was performed by Genesis Technologies Inc. The estimation of current efficiency would have to be

measured and adjustments made to future devices. A 10:1 ratio of copper to silver by weight was provided for the anode.

Device 2

Based upon test results shown in a latter chapter, recommendations for a second device design were given. The anode was changed from a single alloy anode to a dual anode of pure copper and pure silver. The device would pulse back and forth between the separate anodes and monitor the total charge for each. It would then shut off automatically based upon total charge calculations. From initial experimentation, the current efficiency was estimated and will be included in the controller. This should increase the actual ion generation performance to designed values.

CHAPTER IV

EXPERIMENTAL DESIGN

Device Testing Procedures

The main goal of this work was to test prototype devices and verify that they produced the concentrations required and in the correct composition range. Experiments were performed under controlled environments. Future work will focus on conditions related to real applications of the device.

Analytical Equipment

The main instrument used in testing the ion generation efficiency was ion-specific electrodes. In laboratory analysis the best choice for measuring concentrations of copper and silver would be to use an atomic absorption spectrophotometer. Unfortunately, one was not readily available. Other methods include photometric analysis, but they are cumbersome and introduce more experimental error.

Another consideration in using ion-specific electrodes is their possible use as an online monitoring system for feedback control in future designs. One of the final goals of the overall project is to develop a delivery system that will limit the risk of overexposure of copper and silver ions to the consumer. By implementing online control, it will aid in achieving this goal.

The electrode is composed of a specific membrane that generates an electrode potential when placed in contact with a solution containing the ion of interest. This potential is related to a standard reference potential, that is constant, and the activity of the specific ion in solution. This relation is described by the Nernst equation (Equation IV-1).

$$E = E^{\circ} - \frac{RT}{zF} \ln \prod a_i^{v_i} \quad (\text{IV-1})$$

E is the measured electrode potential, E° is the constant reference potential, z is the moles of electrons that are exchanged in the reaction, a_i is the activity of the ionic species in solution, v_i is the stoichiometric coefficient of the ion in the redox reaction, and R is the universal gas constant in J/mole-K. Activity is related to the ion concentration by the activity coefficient. The activity coefficient varies in relation to the total ionic strength of the solution. If the ionic strength is high and constant relative to the ion concentration being measured, then the activity coefficient is constant relative to the sensed ion concentration. This results in the activity of the ion being directly proportional to the concentration. By measuring the electrode potential, one can develop a calibration curve for known concentrations. If electrode potential is plotted against the logarithm of the standard concentration, a linear correlation should result. The high ionic strength is achieved by adding an inert electrolyte to increase the background ionic strength. In the case of silver and copper measurements, sodium nitrate is the best choice.

There are some disadvantages to using ion-specific electrodes to measure concentrations. The response time to changes in concentration at low levels is relatively long (1-5 minute range). This makes online monitoring of concentration during

generation difficult. The concentration readings versus time from the electrodes will lag behind the actual concentration versus time for the system. For a flow system, this would make online monitoring for control more difficult. For batch operations the electrodes would settle at the final concentration values following treatment. This will reduce the risk of overexposure to copper and silver.

Another problem is that ion selective electrodes only measure the free ion concentration in solution. If ions form complexes with other components present in the solution during generation, the concentration reading will be lower than what was actually generated. This stresses the importance of determining ion generation performance of the prototype device in a controlled environment.

Another problem with ion selective electrodes is interferences caused by other ionic species. For silver electrodes, mercury can interfere with the response of the electrode. Large amounts of protein can also inhibit the performance of the electrode. The performance of the electrode can be hindered by layers of silver metal and silver salts forming on the membrane surface, but they can be easily polished away to restore performance.

For the copper specific electrode, several different ionic species can cause interferences. Certain levels of chloride, bromide, and ferric ions can affect the measurement. However, the main ion interference of concern is silver. Experimental tests were performed to determine the effect of silver on the copper measurement. If the effect is additive and constant relative to the concentration of silver, using accurate data from the silver electrode, copper concentrations can be backed out of the data. If the effect is not constant, and no meaningful data can be collected for copper, other methods

will have to be used. For a dual anode design, copper and silver ions can be generated separately to collect initial data on device performance. Silver and copper data can then be compared to performance when both ions are being generated in the same system. Future experiments may be able to use atomic absorption spectroscopy to determine concentrations as equipment becomes available to use in the chemistry department.

Concentration Verification Procedure

Device 1

The controlled test system consisted of one quart of a solution of 0.05 M NaNO_3 or another electrolyte. The electrolyte was added to increase the conductivity of deionized water so the device could operate. In a real application the water should contain enough background electrolytes to allow the device to operate without the addition of other salts. Deionized water obtained from a Nanopure[®] system in the Biochemistry Department at Oklahoma State University was used to make up the test solutions. The electrolyte was added to the test systems to provide enough conductivity in the solution that a small current could be generated by the device. The device required a high enough conductivity to operate. If the current was so low that the ion concentration couldn't be achieved in an acceptable time limit, the device would not start the treatment cycle. After several experiments it was determined that sodium nitrate was the best choice for the electrolyte. Sodium nitrate was also used during electrode potential measurements to adjust the ionic strength of the sample. This work only focused on testing the performance for the one-quart cycle of the first prototype device.

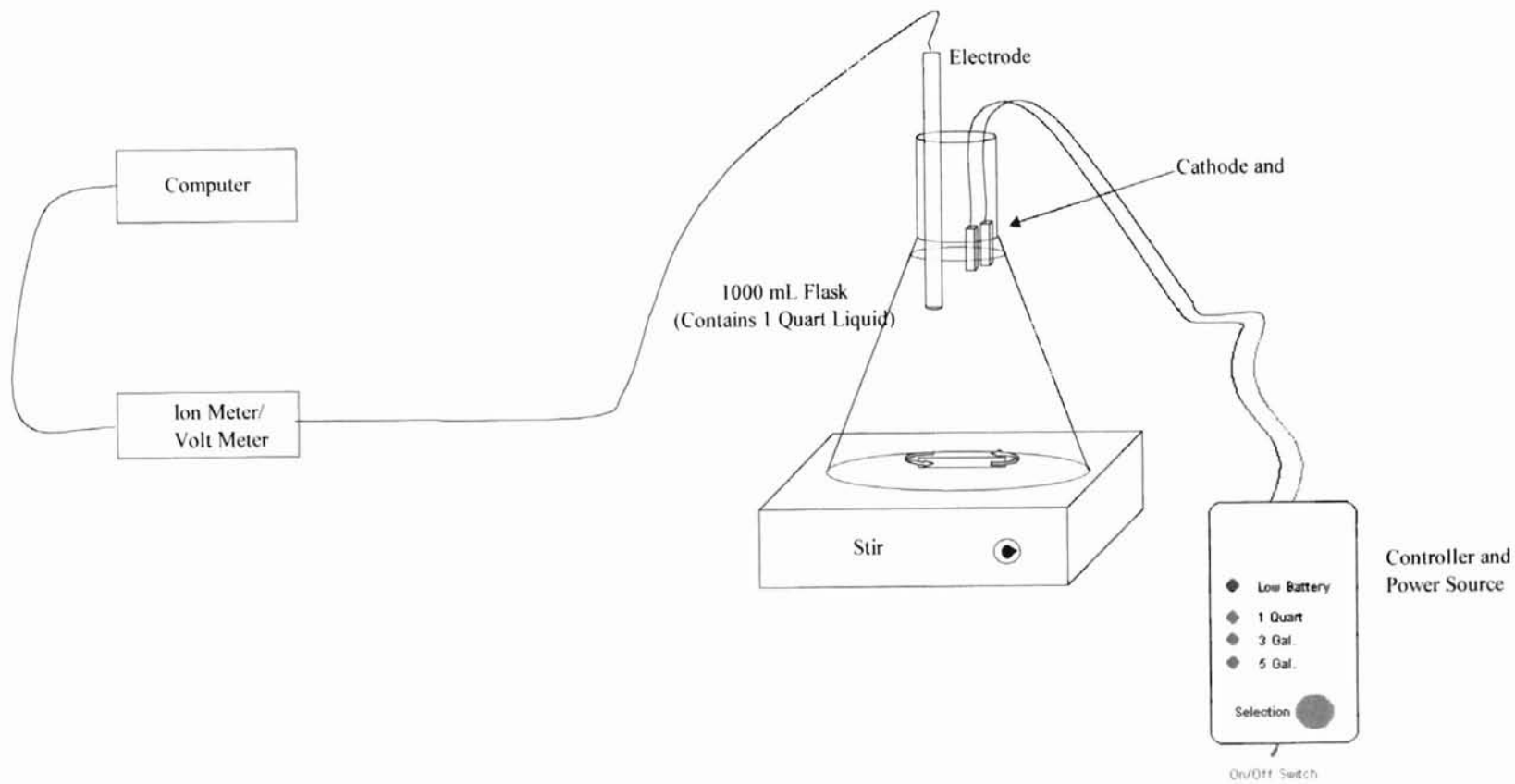


Figure IV-1. Generation Experimental Setup

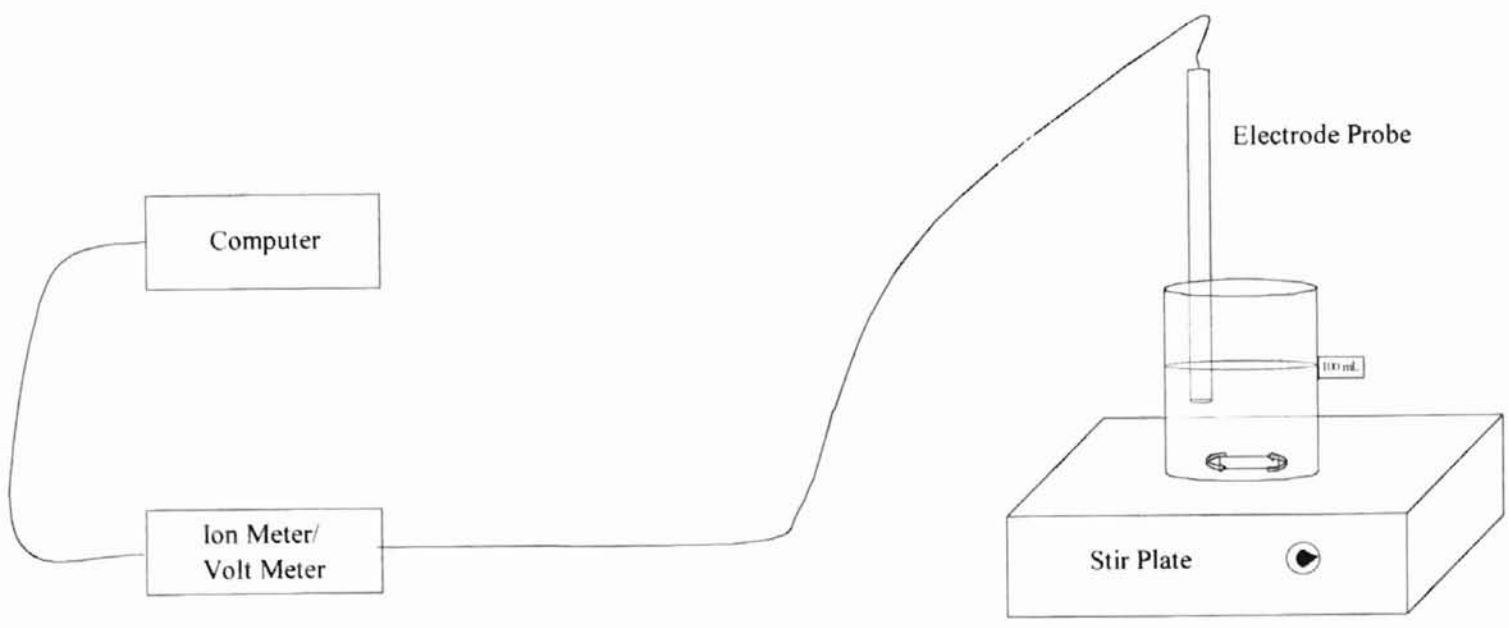


Figure IV-2. Final Concentration Measurement Setup

Figure IV-1 and Figure IV-2 show simple diagrams of the experimental setup that was used for treatment and final concentration measurements.

Treatment occurred in a 1 L Pyrex flask, as shown in Figure IV-1, with the anode and cathode spaced approximately 7.5 mm apart near the surface of the water. The system was stirred constantly to maintain a uniform concentration. The temperature was approximately 22 °C.

Final concentration measurements were obtained using the silver ion selective electrode to determine silver concentration. The volume that was measured was 100 mL in a 250 mL beaker. The concentration was calculated from calibration curves prepared each day of testing. Periodic checks of the calibration curve were done to ensure minimal amount of error in readings.

Please see Appendix A for a more detailed procedure and sample calibration curves.

Device 2

No actual tests were performed on the second prototype at the time this work was written. The device was in the manufacturing phase. However, detailed recommended procedures for completing concentration experiments are included in Appendix A. The following is a summary of proposed recommended procedures to test performance of the second prototype.

Similar tests will be performed for the second prototype device, but initial experiments will focus on determining ion generation efficiency in separate test systems. The pure copper and silver anodes will be placed in separate test systems during treatment cycles. This will allow more accurate measurements of the copper

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concentrations using the ion-specific electrode. Then copper and silver concentrations can be compared to treatment with both anodes in the same system. Estimates of copper concentrations can be made using the electrode, but should be verified using other analytical techniques. Testing of the second device should include all treatment cycles to verify generation performance.

Microbial Inactivation Performance

This work focused on device generation performance, but preliminary experimental techniques were developed to determine kill rates and microbial disinfection performance using the prototype devices. It is suggested that validation experimentation should follow guidelines set by the EPA in their "*Guide Standard and Protocol for Testing Microbiological Water Purifiers*" (USEPA, 1987). Preliminary procedures are presented in Appendix B.

CHAPTER V

RESULTS AND CONCLUSIONS

This chapter will focus on tests completed on the first batch deliver device. Tests were also performed to determine if the copper ion selective electrode could give accurate estimates of the copper concentrations generated. The online response of the ion selective electrodes was also estimated. The first section will present results from interference testing of the copper ion selective electrode. Results from Device 1 using the copper/silver alloy anode are then presented. The final section will focus on device performance using pure silver anodes. Current efficiencies, used to design future devices, were estimated using this configuration.

Copper Electrode Interference

Before testing the performance of the device, the interference of silver on the copper ion selective electrode needed to be investigated. An accurate measurement of both silver and copper are needed to verify ion generation efficiencies, so that improved designs can emerge. No quantitative information about the interference could be found, so it was determined experimentally.

Initially millivolt electrode potential readings were measured for two different copper concentrations in combination with several different silver concentrations. These tests determined if a trendable interference of silver ions on the copper selective

electrode exists. Their results are shown in Figure V-1. A third point for the pure copper solution was obtained to give a base calibration for copper. From the very few experimental points generated, it appears that there is a trend as the silver concentration increases. Unfortunately, with so few copper concentrations, the validity of the trends was undetermined due to suspected high experimental error. At such low concentrations, a small stock dilution error would have large error propagation. A new data set was generated to show better trend resolution, and remove some of the experimental bias. Initially, a calibration curve for pure copper was generated. These same copper concentrations were then measured at two different silver concentrations. The results are presented in Figure V-2. The data show that there indeed is a measurable trend for increasing silver concentrations. As the silver concentration increases, the electrode potential increases and the slope of the calibration curve decreases.

From these results, it appears that the copper selective electrode can be used to estimate the concentration of copper. This can be done by first measuring the silver concentration with the silver ion selective electrode, and then measuring the copper electrode potential and extrapolating the copper concentration from a plot similar to Figure V-2. Details of how to generate various calibration curves are presented in Appendix A. Semilog plots of the calibration curves are presented in Appendix A.

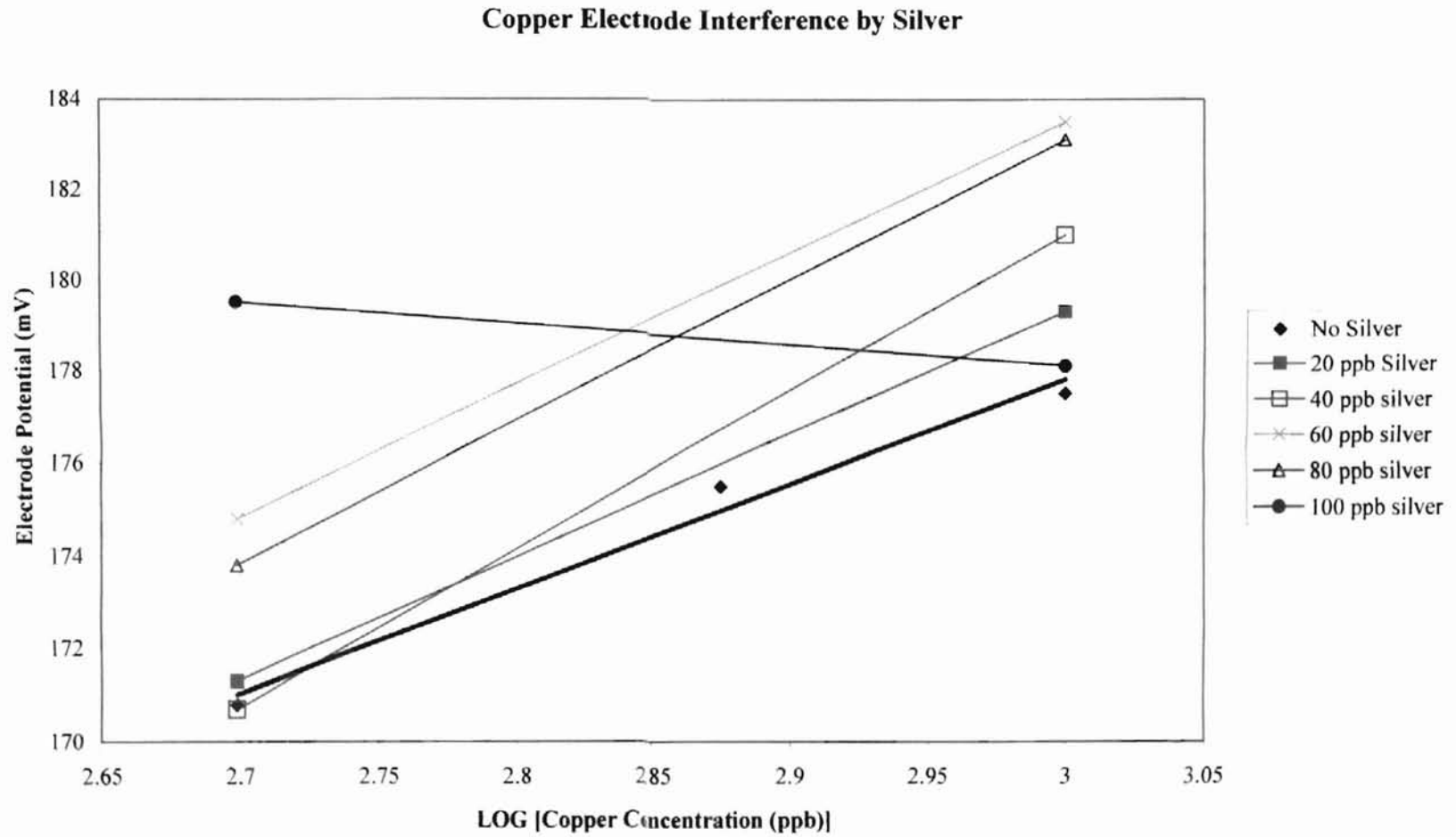


Figure V-1. Initial Plot Showing Silver Interference on Copper Ion Selective Electrode

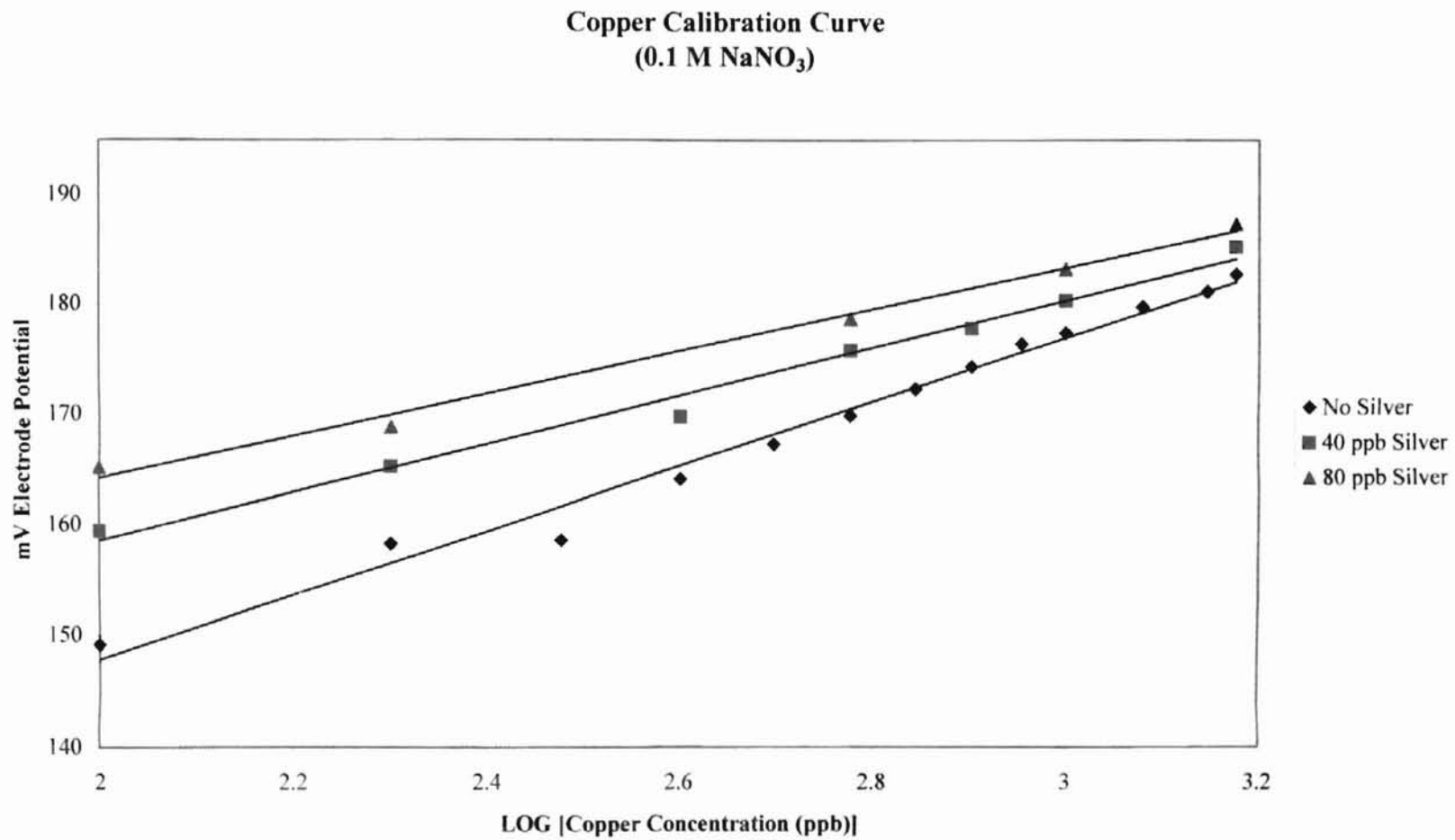


Figure V-2. Copper Calibration Curve With Low Levels of Silver Ions

Device 1 Performance

Initial testing of the first prototype delivery device focused on tests using a copper/silver alloy as described earlier in the design sections. The control device, cathode and anode were supplied by H2Ovation Oklahoma Inc. The cathode had the same composition as the anode to allow for polarity switching. Switching polarities will increase the life of the device by limiting excessive wear on a single anode and fouling of the cathode. Additional tests were run using a pure silver anode to determine device performance.

Copper/Silver Alloy Anode Results

The first experiments that were performed on the prototype delivery device were done using the copper and silver alloy as the anode and cathode. The mass ratio of copper to silver in the anode was 10 to 1. Please refer to Chapter III to see why this ratio was used. Initial tests addressed the amount of silver ions being generated by the device. Silver calibration curves were prepared each day of testing. All tests focused on testing performance for the 1.0 Quart cycle.

The first set of runs used a NaCl solution in deionized water. The salt concentration used to develop calibration curves and treatment systems was 250 ppm. Test volumes were all one quart. Table V-1 is a summary of the first set of tests that were performed on the device. Run 1 shows results for treatment of the test system using the 1 Quart setting on the device. No measurable silver was detected. Visual inspection of the water indicated no precipitate being formed. Observation also showed no silver being plated out onto the cathode.

Table V-1. Summary of Results Using NaCl as Background Electrolyte

Run Number	Silver Concentration	Observations
1	< 10 ppb	NA
2	< 10 ppb	NA
3	< 10 ppb	Water began to cloud and turn greenish blue color
4	<10 ppb	Further Clouding of water and color intensity increasing
5	< 10 ppb	NA
6	< 10 ppb	NA

Run 2 was a blank to verify the electrode potential measurement. An untreated test system was measured for silver concentration. The millivolt reading was higher than that measured for Run 1.

Run 3 shows the results of treating a one quart test system three times using the 1 Quart setting of the device. Again, the silver concentration was below the detection limit. The only difference between this test and the results of Run 1 was that the turbidity of the test water increased and the color began to turn a bluish green color. It was estimated that the cloudiness of the water was being caused by insoluble salts being formed by copper and chloride ions.

Run 4 was the result of treating the same test system in Run 3 with the 3 Gallon Setting of the device. The silver concentration reading remained below detection limits and the cloudiness of the water increased. The color also intensified.

Runs 5 and 6 were repeat tests of Run 1. Fresh tests systems were used in both of these runs. The results were the same as for Run 1.

Other experiments were performed using sodium sulfate to increase the conductivity of the test system. The concentration of sodium sulfate used was 300 ppm. Similar results were obtained. No silver was detected in the test systems that had been treated by the device. One test that was performed used a separate DC voltage power supply with the alloy anode and cathode. This test was to determine if the device controller was generating enough current to put ions into solution. The first run showed a concentration of 17.5 ppb silver. Upon verification of these results, all subsequent runs indicated that silver was below detection. Possible reasons why this may have occurred is because the first run may have contained residual ions on the glassware. Since the results of the first run could not be repeated, it was assumed that the concentration reading was a result of external contamination by residual ions.

The results of the previous two experiments showed that no silver was being generated by the alloy anode. It was possible that the chloride introduced in the first set of tests was interfering with measurements by precipitating out the silver that was being generated. There was a similar concern for the results of the second set of tests. Silver sulfate does not completely dissociate in solution, so silver may have been forming insoluble salts as it was being generated.

To verify previous results, additional experiments were performed. The electrolyte chosen to increase the conductivity in the test systems was sodium nitrate. The concentration used during generation experimentation and calibration curve generation was 0.05 moles/liter. An additional 1 ml of 5 M NaNO_3 was added to each 100 ml test sample before the electrode potential was obtained. This insured a high enough background ionic strength for proper operation of the ion selective electrode.

Results from two separate water treatments using the 1 Quart Setting showed that the silver concentration remained below the detection limit. No precipitates were observed. The possibility of insoluble salts being formed was negligible. Silver nitrate and copper nitrate are completely soluble at the concentrations of interest. There were no other ionic species present to form complexes.

The manufactured anode and cathode were determined to be the reason for the lack of silver generation. Visual inspection of the anode and cathode showed that silver metal was dispersed throughout the electrodes. The electrodes were not annealed, but were made by melting a ratio of 10 to 1 of copper and silver respectively, and allowing to cool.

Using the copper ion selective electrode, the copper concentration being generated was around 565 ppb. This is approximately 71 percent of the expected value. Possible reasons for the lack of silver generation include nonuniformity in the anode. If the silver is not uniform throughout the anode, but forms veins or channels within the copper matrix, then the copper will be oxidized into solution until mass transfer inhibits its oxidation. At this point, silver will begin to oxidize. The rate of oxidation of silver will increase as the rate of copper oxidation decreases.

If the composition of the anode was uniform, it is still possible that silver would not be oxidized. Figure V-3 shows the phase diagram for alloys of copper and silver. The phase diagram shows that a two-phase alloy exists at the composition of the anode used, a copper rich phase with dispersed silver phases. This would make it difficult to get a uniform dispersion of silver throughout the anode without significant annealing of

the metal. If a uniform dispersion of silver throughout the anode is obtained, as copper is oxidized away at the surface, individual silver ions would be released into solution.

If the alloy is not uniform, by increasing the current flow through the electrolytic cell, a high enough over-voltage may be induced to begin the oxidation of silver. Unfortunately, this defeats the purpose of designing a portable delivery system and is not feasible.

Based upon the results, it is recommended that a dual anode system be designed to achieve the desired concentrations of both ions. This will eliminate the problems associated with different oxidation potentials in a single alloy anode and also simplify anode manufacturing.

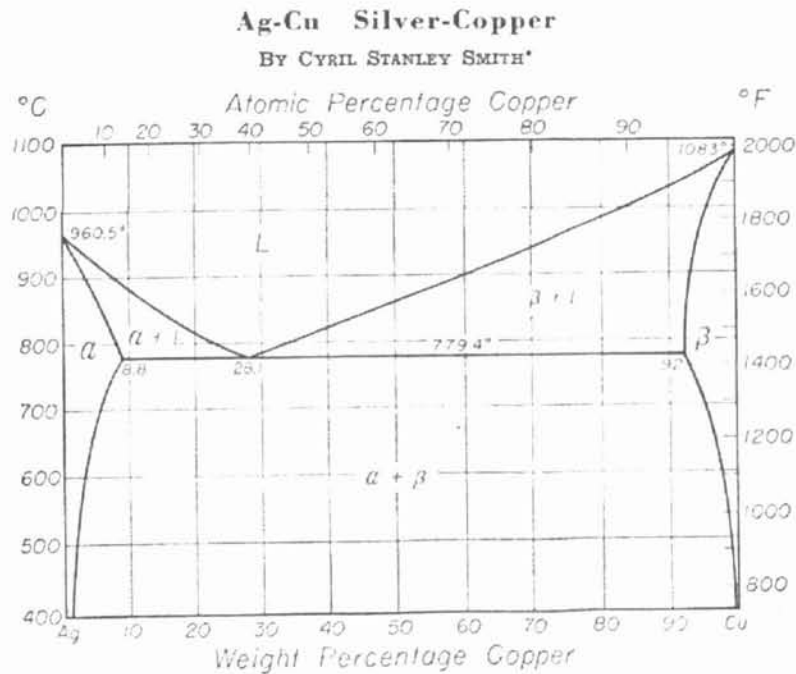


Figure V-3. Phase Diagram for Alloys of Silver and Copper (*ASM Handbook*, 1948).

Pure Silver Anode Results

Before design of a new device began, the current efficiency of the first device needed to be measured. It was also desirable to measure the concentration versus time during operation of the device and compare it to the theoretical generation rate. To accomplish these goals, tests were performed using a pure silver anode and cathode.

To determine the current efficiency of the device, several different treatment runs were performed. Table V-2 shows a brief description of each of the runs that were performed. A brief summary of the calibration procedures that were used for these tests is presented.

Table V-2. Silver Ion Generation Test Descriptions.

Run Number	Description
1	Test System: 0.05 M NaNO ₃ from DI Water Volume: 1 Quart Treatment: 1 Cycle of 1 Quart Setting Date of Run: January 17, 2000
2	Test System: 0.05 M NaNO ₃ from DI Water Volume: 1 Quart Treatment: 1 Cycle of 1 Quart Setting Date of Run: January 20, 2000
3	Test System: 0.05 M NaNO ₃ from DI Water Volume: 1 Quart Treatment: 1 Cycle of 1 Quart Setting Date of Run: January 20, 2000
4	Test System: 0.05 M NaNO ₃ from DI Water Volume: 1 Quart Treatment: 1 Cycle of 1 Quart Setting Date of Run: January 20, 2000
5	Test System: 0.05 M NaNO ₃ from DI Water Volume: 1 Quart Treatment: 1 Cycle of 1 Quart Setting Date of Run: January 20, 2000
6	Test System: 0.05 M NaNO ₃ from DI Water Volume: 1 Quart Treatment: 1 Cycle of 1 Quart Setting Date of Run: January 20, 2000
7	Test System: 0.1 M NaNO ₃ from DI Water Volume: 1 Quart Treatment: 1 Cycle of 1 Quart Setting Date of Run: January 20, 2000
8	Test System: 0.1 M NaNO ₃ from DI Water Volume: 1 Quart Treatment: 1 Cycle of 1 Quart Setting Date of Run: January 20, 2000
9	Test System: 0.1 M NaNO ₃ from DI Water Volume: 1 Quart Treatment: 1 Cycle of 1 Quart Setting Date of Run: January 20, 2000

The first run was performed on a separate day, so a different calibration curve was used to determine concentrations. The other runs were all performed on the same day. Two calibration curves were prepared for the runs on the second day. One

calibration curve took measurements from standard solutions with a background ISA concentration of 0.05 M NaNO₃. The millivolt reading was obtained before any additional ISA was added. After the reading was recorded, 1 ml of 5 M NaNO₃ was added to the sample and the reading repeated. This produced a final ISA concentration of approximately 0.1 M NaNO₃. For the treatment systems that contained 0.05 M NaNO₃, the millivolt potential reading was taken during or immediately following treatment. Then 1 ml of 5 M NaNO₃ was added to 100 ml of the treated sample and the millivolt reading was recorded again.

Adjusting the ionic strength by adding 1 ml to 100 ml of the sample produced a better calibration curve. All calibration results are shown in Appendix A. By generating the second calibration curve based upon the higher ionic strength, multiple data points for each run could be collected and compared. The second curve also allowed tests to be run at two different conductivity levels.

The final concentrations that were measured are shown in Figure V-4. The chart shows that there is some scatter in the data. The scatter is partially a result of experimental error. The calibration curve is dependent upon accuracy in dilutions when making up the standards. The 5 percent line shows the experimental error that was determined for the experiments. The error is a result of both user error in generating calibration standards and error in the linear regression correlation that was obtained. Please see Appendix A for a detailed error analysis. In Figure V-4 all the data are within 3 percent of the plotted average. The points are well within experimental error of the measured average.

The average value plotted is 2107 ppb silver ions. The theoretical value calculated using Faraday's Law is 2796 ppb silver ions. See Appendix C for details on how this value was obtained. Using these values, an overall current efficiency for silver generation of 75 percent is calculated. Although the current efficiency for copper alone was not tested, a similar efficiency should be observed. Since copper has a higher oxidation potential compared to silver, the efficiency for copper generation may be slightly higher. The standard potential difference between the oxidation of copper and other competing reactions is greater, which decreases the potential for the competing reactions to occur. At the cathode, copper has a lower potential for reduction. The amount of copper lost due to reduction should be lower than silver.

As discussed earlier, this efficiency is most likely the result of competing reactions at the anode. The electrolyte added to increase the background conductivity for the last three runs, increased the current flow through the device, but the overall efficiency remained the same. The amount of silver being reduced at the cathode is assumed negligible. If reduction of silver ions at the cathode was significant, an increase in efficiency would have been expected at higher concentrations of NaNO_3 . The higher concentration of background electrolytes would increase the preference for reduction of those species. There would be more competition for reduction sites at the cathode; thus limiting the amount of silver that could be reduced. Since this was not observed, the assumption seems reasonable.

Based upon the results of the efficiency experimentation, dividing the total charge that was used to determine treatment times for the first device by a value of 75 percent should increase the final concentrations to the desired levels. The copper and

silver concentrations can then be measured in separate test systems to determine if the efficiencies are accurate.

Final Silver Concentrations

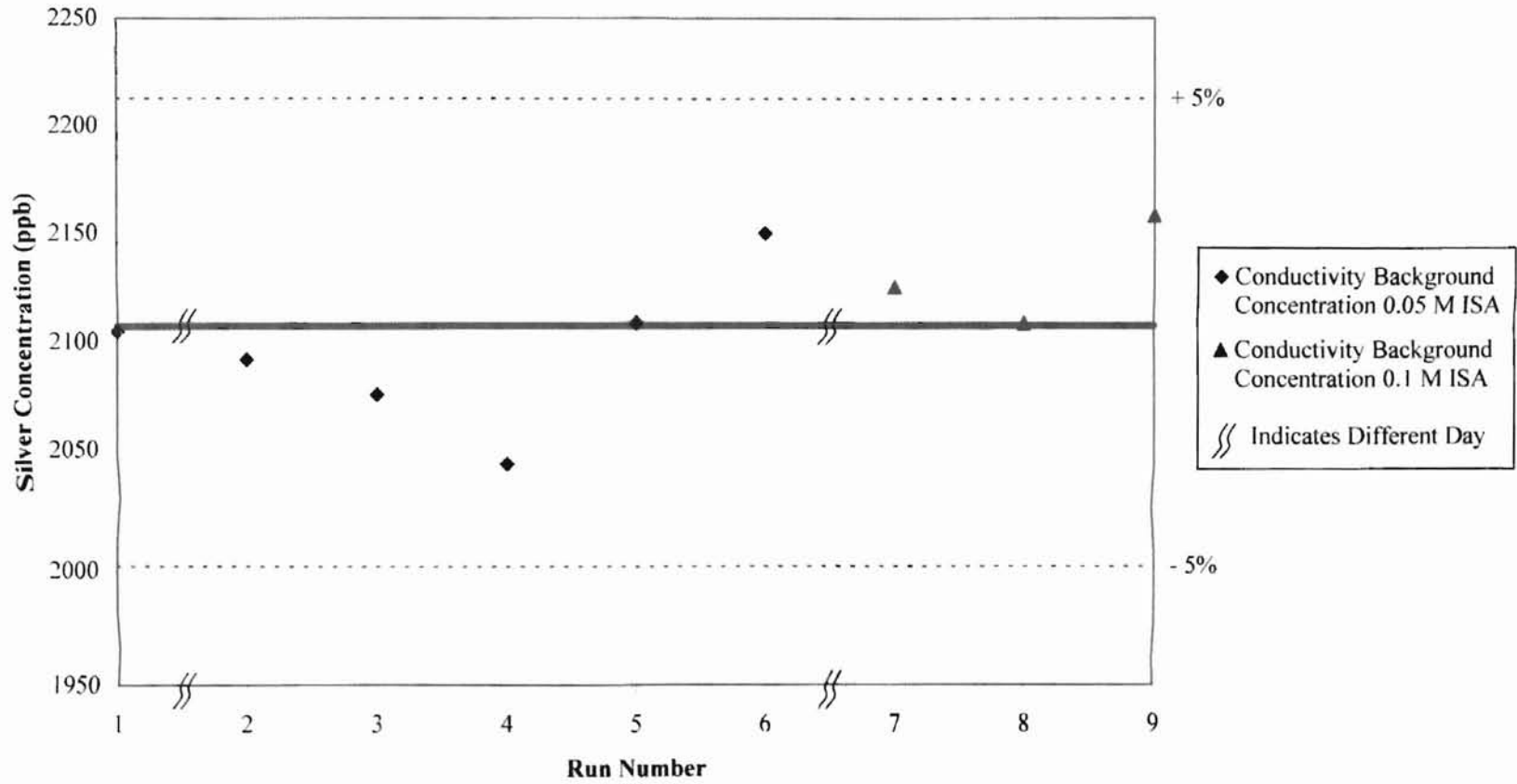


Figure V-4. Final Silver Concentrations

When comparing the results among runs, there is no significant difference between the final concentrations for the systems with low background conductivity levels and higher background conductivity levels. It appears that the device is operating as designed and can compensate for the treatment time based upon the conductivity levels.

The last set of tests that were performed on the device was to measure the generation rate using the ion selective electrode to determine the electrode response and compare the results against Faraday's Law. The concentration reading of the silver ion selective electrode is expected to lag behind the theoretical values because of settling time for the probe. Figures V-5 and V-6 show the electrode potential measurements obtained during a 1.0 Quart treatment cycle. Figure V-5 shows the millivolt response during Run 1. The data indicate that the millivolt potential rises suddenly when the device begins to operate. This is due to the ion-specific electrode. Initially, no silver is present in solution, so the electrode potential being measured should only be the potential of the reference electrode. As silver begins to enter solution, the electrode potential increases suddenly because of the added potential across the sensor being caused by the low silver levels. After the initial rise in potential, the millivolt reading increases at a lower rate that is representative of the electrode behavior during calibration. Figure V-6 shows a similar plot for a second treatment run. The data in this plot show similar behavior as in the previous figure, but there appears to be an overshoot just before the cycle ends. The time between samples in the second run was approximately 10 seconds versus 5 seconds for the first run. The overshoot is a result of the placement of the electrode during treatment. It is probably being affected by a local

concentration near the anode. From these results, the importance of placement of the ion selective electrode during online sampling is crucial. If the placement is poor, the readings could cause excess or low concentrations to be generated in a feedback control scenario.

Figure V-7 shows that the concentration reading lags behind the theoretical value, but the rate at which the concentration increases is about the same as the predicted rate using Faraday's Law. So why does the concentration not reach the theoretical value? The measuring electrode may be indicating a local concentration during generation caused by incomplete mixing. This is the case for the data shown in Figure V-8. The measured concentrations exceed that of the theoretical values, but when the device is shut off and the concentration in solution becomes uniform, the concentration returns to a level similar to the results shown in Run 1. The reason that a local concentration effect is suspected is because of the close proximity of the ion-selective electrode to the anode of the device.

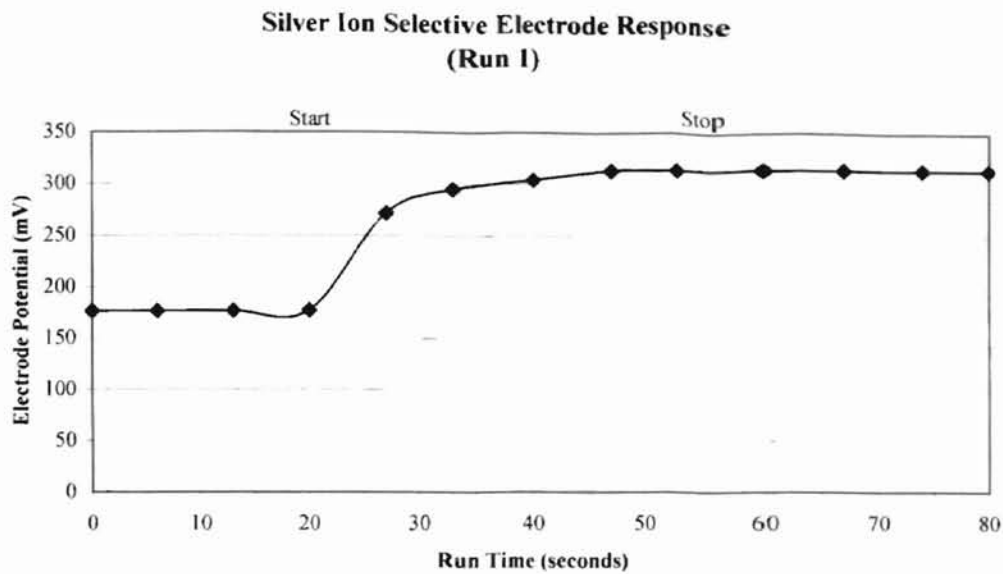


Figure V-5. Electrode Potential Versus Time for Run 1

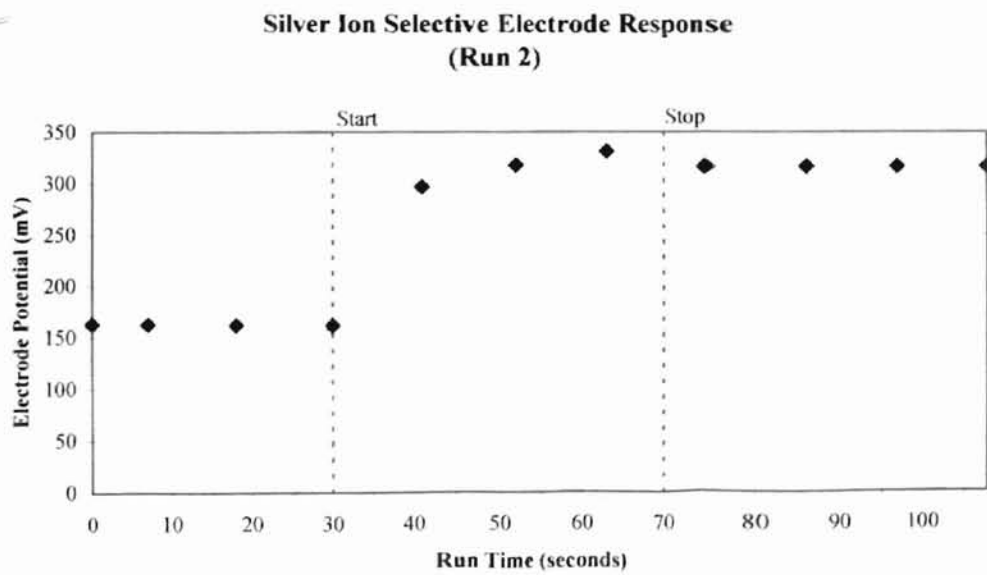


Figure V-6. Electrode Potential Versus Time for Run 2

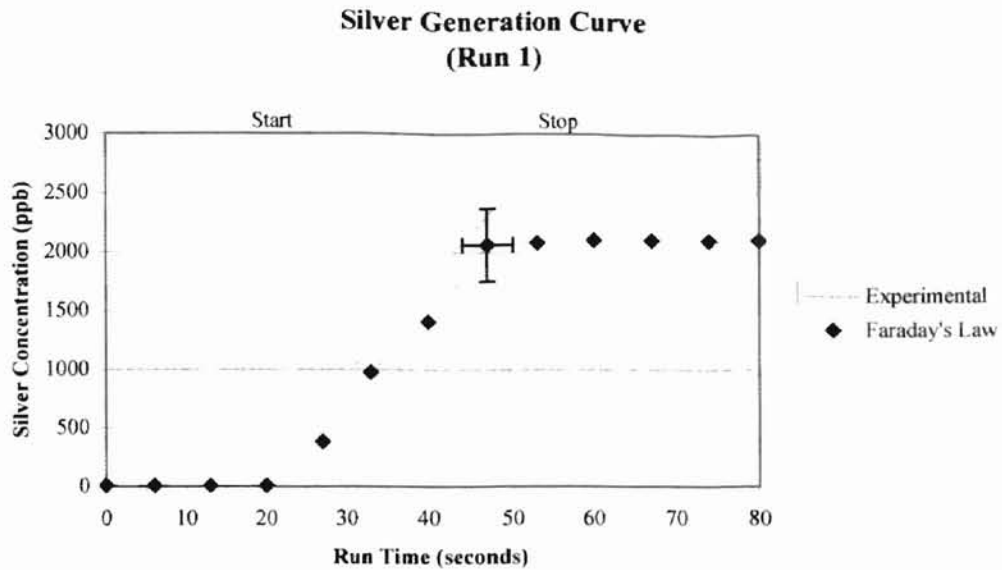


Figure V-7. Concentration Versus Time For Run 1

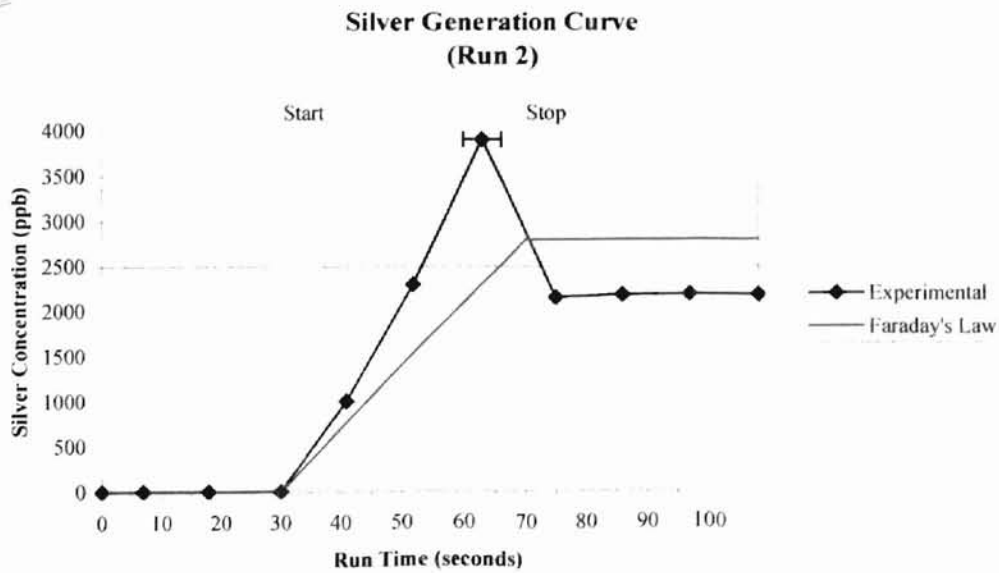


Figure V-8. Concentration Versus Time for Run2

The generation rate is expected to be lower than the rate predicted by Faraday's Law because of a current efficiency less than one. Possible reasons why this was not observed can be explained as follows. The exact run time may be off by a few seconds. This could account for some error in the theoretical generation rate being the same in Figure V-7. Another source of error is the current measurement used to generate the correlation. The current was estimated using a multimeter. The current was observed to fluctuate constantly during the run. Since the current versus time relation was not determined, an average value was used to generate the Faraday Law curves, which introduces error in the theoretical curve. Another reason expected trends were not observed may be a result of the characteristics of the ion selective electrode. The settling time of the electrode can be on the order of minutes at low concentrations. The readings may be over predicting the concentrations and then settle as the device ends the treatment cycle. There is also substantial error associated with the measured concentrations. This is shown by the error bars for one point on the graph.

The data in these figures show that it might be possible to use the ion selective electrodes as an online monitoring device. The reading would only give general trends, because of large error in measured concentrations, but it would be possible to observe deviations from the steady state values. For accurate readings, calibration must be performed at least once every day. The placement of the electrode during online measurements is crucial. If positioned too close to the generating anode, a local concentration profile will be generated, which will not be representative of the total concentration in the system.

Conclusions

Design and testing of an initial ion generation device has been completed. The device was designed to operate in a batch operational mode. The device had three treatment settings: 1.0 Quart, 3.0 Gallons, and 5.0 Gallons. All performance testing focused on the 1.0 Quart treatment setting. Testing of the ion selective electrodes was also completed. Based upon the data presented, the following conclusions have been made.

- A copper ion selective electrode can be used to estimate copper concentration in the presence of silver.
- The copper/silver alloy anode provided with the first prototype generated no silver concentration because of non-uniformity.
- Using a pure silver anode and cathode, the generation efficiency of the device was determined to be 75 percent. This efficiency has a maximum error of 5 percent.
- Concentration versus time measurements showed that the generation rate was similar to that predicted by Faraday's law. The amount of error in the theoretical generation curve is significant.

CHAPTER VI

RECOMMENDATIONS

Based upon the results and conclusions of this work, recommendations for future work and applications for potable water treatment by metal ions is presented in this section. Although the initial prototype did not operate as designed, information useful for future designs was obtained. The following recommendations are made regarding future designs.

- Dual anodes of pure copper and pure silver are recommended
- The control times need to be adjusted to account for a current efficiency of 75 percent at the anode.
- Precipitation and complexation issues need to be investigated further.
- Initial testing of ion generation performance for the second device should be performed in separate systems for copper and silver, and then verified in a combined treatment system.
- Biological verification should address performance guidelines set by the EPA's "*Guide Standard and Protocol for Testing Microbiological Water Purifiers*" (USEPA, 1987).
- Generation performance of future designs should be verified at all treatment settings.

- Online concentration monitoring using ion selective electrodes should be tested using a flow system to verify feasibility.
- It is recommended that applications of an electrolytic device in combination with other technology be used. Some examples may include microfiltration technology in combination with electrolytically generated copper and silver to purify water. Use of low levels of iodine and copper and silver ions to disinfect may be another application
- Consumers should be warned of health effects associated with overexposure to copper and silver ions.
- Portable emergency treatment systems using electrolytically generated copper and silver ions should have a method of reducing metal concentrations before consumption.
- More information on the health effects associated with long term exposure of low levels of metal ions should be investigated.

Potable water treatment using copper and silver ions in combination with other disinfectants appears to be a plausible disinfection method in the future. If DBP's cannot be reduced by making operational changes to current chlorination methods, copper and silver combined with lower levels of chlorine disinfectants may be a feasible solution. For portable and emergency applications, ultra-filtration in combination with copper and silver could be a feasible alternative to iodine.

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APPENDICES

APPENDIX A

GENERATION PERFORMANCE TESTING PROCEDURES

A detailed procedure for measuring ion concentrations to determine the efficiency of the generation device is presented in this section. Procedures for generating a calibration curve for the ion selective electrodes is presented. An error analysis was performed to determine the validity of the data and is presented here.

Equipment Required

Table A-1 presents a detailed list of the equipment that was used.

Table A-1. Equipment List for Ion Concentration Testing

Equipment Description	Vendor and Part No.
Silver/Sulfide Combination Glass Body Electrode	Cole Parmer [®] , Cat. No. 27502-41
Copper Combination Glass Body Electrode	Cole Parmer [®] , Cat. No. 27502-15
pH/mV/Ion Benchtop Meter	Cole Parmer [®] , Cat. No. 59003-30
Multiple Beakers—250 mL	
Erlenmeyer Flask—1 L	
Pipettes—5 and 10 mL	
Micropipette—1 mL	
Volumetric Flasks	
100 mL	
1000 mL	
Stir Plate and Stir Bars	
Stock Solutions	
1000 ppm Silver	Cole Parmer [®] , Cat. No. 27503-32
1000 ppm Copper	Cole Parmer [®] , Cat. No. 27503-11

It was shown that the micropipette readings were incorrect. A calibration curve was generated and is presented in Appendix B (Figure B-1). Please refer to this section for correct pipette settings to use.

The stock solutions can be prepared from standard chemicals. Silver solutions need to be stored in a brown plastic bottle to avoid degradation of the concentration. The conditioning of the electrodes was completed according to the manufacturer's operating instructions. The use of a combination electrode eliminated the need for an external reference electrode. This simplified measurements.

Preparation

1. Electrode Preparation. The electrodes were conditioned according to the manufacturer's operating instructions that came with the electrodes.
2. Ion Meter Setup. The ion meter was operated according to the manufacturer's operating instructions. The meter was operated only in the millivolt mode. This allowed the electrodes to be switched without having to worry about updating the calibration curve stored in the meter. The meter was mainly operated using a computer interface and data acquisition software provided by the manufacturer. Please read the operating manual for detailed operation.
3. Calibration Curve Generation. The calibration curve was generated using known concentrations and collecting electrode millivolt readings. The known standards were prepared from the 1000 ppm standard by serial dilutions. To improve the accuracy of the results, the standards should have an overall background concentration similar to the samples that are to be measured. This was accomplished by diluting a stock solution of the electrolyte that was used to raise the conductivity

of the test system. The electrolyte that was recommended is sodium nitrate. Other electrolytes were initially used but discontinued because of potential interferences with the measurements.

An example of how to prepare one calibration standard is given below.

- a. Dilute 1 mL of the 1000 ppm Ag^+ stock solution to 1 L. Concentration is 1 ppm.
- b. In a 100 mL volumetric flask, place 1 mL of the previous dilution and 1 mL of 5 M NaNO_3 . Dilute to 100 mL to obtain 10 ppb silver and 0.05 M NaNO_3

Larger volumes of the 1 ppm silver standard can be used to generate other silver calibration standards. Similar dilutions can be performed to prepare various copper standards.

Once the standards were prepared, the 100 mL samples were placed in a 250 mL beaker, one at a time, with a stir bar. The beaker had been rinsed with deionized water and dried. The sample was placed on a stir plate and stirred at a constant rate. The ion selective electrode was rinsed with deionized water and blotted dry using Kimwipes[®]. It was then lowered into the sample so the tip of the electrode was approximately $\frac{1}{2}$ inch below the surface of the solution. The mV reading on the meter was monitored until the value stabilized (approximately 2-3 minutes for low concentrations, 1 minute or less for higher concentrations). The reading was then recorded. With the electrode still in the sample, 1 mL of 5 M NaNO_3 was added to the sample to give a background concentration of 0.1 M NaNO_3 . The reading was allowed to stabilize and then recorded. This process was repeated for every

calibration standard measured. The purpose of taking readings for both background concentrations was to compare the calibration curves and choose the curve that gave the best fit. It also allowed for generation tests to be performed at two different conductivity levels.

Once all the points were collected, a plot of mV reading versus the logarithm of the standard concentration was prepared. This was done because the operation of the electrode should follow the Nernst Equation. The data was fit to a straight line. Initially, calibrations for silver based upon procedures given by manufacture were tested, but the curve was not linear. Using the methods described above, the calibration curves were more linear. Please see figures at the end of this appendix for various calibration curves that were created.

4. Ion Generation Tests. The test systems were one-quart volume solutions of 0.05 M NaNO_3 and 0.1 M NaNO_3 . As mentioned in the Chapter V of this work, other electrolytes were initially tested, but based upon concerns with interferences, their use was discontinued. The rest of these procedures will focus on sodium nitrate as the background ionic strength adjuster.

The solutions were prepared by diluting 10 mL of a 5 M NaNO_3 stock solution to 1 L to create a final concentration of 0.05 M NaNO_3 . A volume of 20 mL of 5 M NaNO_3 was used to prepare a test system with a concentration of 0.1 M NaNO_3 . Then 53.6 mL was removed to obtain a final volume of 1 quart.

The test solutions were placed in a 1 L flask and stirred at a constant rate on a stir plate. The anode and cathode were placed so that approximately $\frac{1}{2}$ inch was submerged in the solution. The anode and cathode were separated by 7.5 mm. To

measure the generation rate as a function of time, the ion selective electrode was placed in the solution also. The device was operated according to the manufacturer's instructions to treat one quart of water. The start time and stop time were recorded. Data was acquired by a computer interface with the ion meter to sample mV readings every 5 seconds, which was the smallest time interval available.

After the treatment cycle ended, the mV reading of the electrode was allowed to settle and then recorded. The electrode was then removed from the sample, rinsed with deionized water, and blotted dry. 100 mL of the treated sample was placed in a 250 mL beaker. The background ionic strength was then adjusted to 0.1 M NaNO₃ by adding 1 mL of 5 M NaNO₃. The electrode was then dipped into the sample and the mV reading was allowed to settle before being recorded.

The concentrations were then calculated using the fit for the calibration curve, and compared to determine if the device was operating as designed.

It is recommended that similar type experiments be performed for the second prototype delivery device. Set up two test systems initially so that copper and silver can be generated separate from each other. These values can be used to determine initial efficiencies and performance. Then perform tests in a single system and prepare a calibration curve similar to Figure A-6 to estimate the copper concentration. The silver concentration should be able to be directly measured using the silver electrode. This should show if there are any changes in generation efficiencies when both anodes are generating in the same system.

Error Analysis

There are several sources of error involved with this experiment. The main source of error is a result of human variance. When generating the calibration curves, the volume measurements used to prepare the standards may not be exact. Through repeated measurements using deionized water and a mass balance, the variance in measured volumes using pipettes was determined. The micropipette showed a maximum variance of 2 μL . The 5 mL and 10 mL disposable pipettes showed a variance of 0.05 mL. The variance in measured volumes of the 100 mL and 1 L volumetric flasks was 0.1 mL and 0.5 mL respectively. In performing dilutions, the worst case would be if the pipetted volume was low and the diluted volume in the flask was high. For concentration calibrations less than 100 ppb, the maximum error in concentrations of the prepared standards was 2.8 percent, and for concentrations greater than 100 ppb, the maximum error was 2.9 percent. The measured concentration values will have a maximum error possible of 2.9 percent as a result of accuracy in calibration standard preparation. The next error to calculate is the propagation error due to a variance of 0.1 mV in the meter reading. The maximum error in ion concentration is calculated by the following equation (Bethea and Rhinehart, 1991).

$$|\delta_y| = \sum \left| \frac{\delta f}{\delta x_i} \right| |\delta x_i| \quad (\text{A-1})$$

The function f will have the form of the Nernst equation.

$$x = a + b \text{Log}(y) \quad (\text{A-2})$$

The variable x is the mV reading that is related to concentration y . Solve the equation for y and take the derivative with respect to x . Then substitute the values into

Equation A-1 to calculate the maximum propagated error. This was done for several different calibration curves, and the maximum propagated error caused by variance in the mV reading is 0.4 percent.

The next error that was determined is caused by errors in the linear regression fit of the calibration curve. The average error associated with variance of the correlated values from the calibration standards was 2.0 percent. Summing the various errors gives a total error in concentration measurements of 5 percent. At this level of error, the generated concentrations should still be below the EPA limits if the measured concentration is not greater than the designed operating conditions.

The following figures are various calibration curves that were used during experiments. Figure A-1 shows that the calibration curve prepared for the low silver concentration range was not linear. This particular curve was prepared according to the manufacturer's instructions, which used a diluted ISA concentration. The nonlinear behavior of the curve is caused by the low concentration of ISA. It is recommended that the ISA not be diluted to ensure a linear calibration.

Figures A-2 through A-5 show the calibration curves that were used during electrode response measurements, current efficiency and ion generation performance measurements. The R^2 values for the linear correlation show that the curves for standards with a background ISA concentration of 0.1 M NaNO_3 provide a better linear fit to the data. Again this could be caused by a lower ISA concentration in the measured sample. A ISA concentration that is low enough for the activity coefficient to no longer be constant would cause the curve to be nonlinear, as shown in Figure A-1.

Figure A-6 shows the linear regression correlations that were fit to each of the copper calibration curves. It may be possible to plot each of the slopes and intercepts of the correlations versus silver concentration to find an equation that relates copper mV response to copper concentration and silver concentration. Values could then be calculated from a regression correlation instead of interpolating on a graph.

This analysis was attempted, but the results showed that the amount of error in the calculated mV reading would be at least 3 mV. This results in a 26% error in predicted concentrations. The data in the figure also show that there was significant scatter in the no silver curve. During data collection it was noticed that the mV reading did not stabilize well. This may have been a result of contamination of the electrode membrane. Soaking the electrode in copper standard should correct this problem. This may explain why the data became more stable for the other silver points that were collected.

Figures A-7 and A-8 show variations of calibrations plots for copper. Figure A-7 shows the calibration data plotted in cartesian coordinates fitted with a logarithmic trend line. Figure A-8 shows the same data on a semi-log plot. Both of these plots allow the direct correlation of electrode potential to concentration.

Low Level Silver Calibration
Silver Electrode

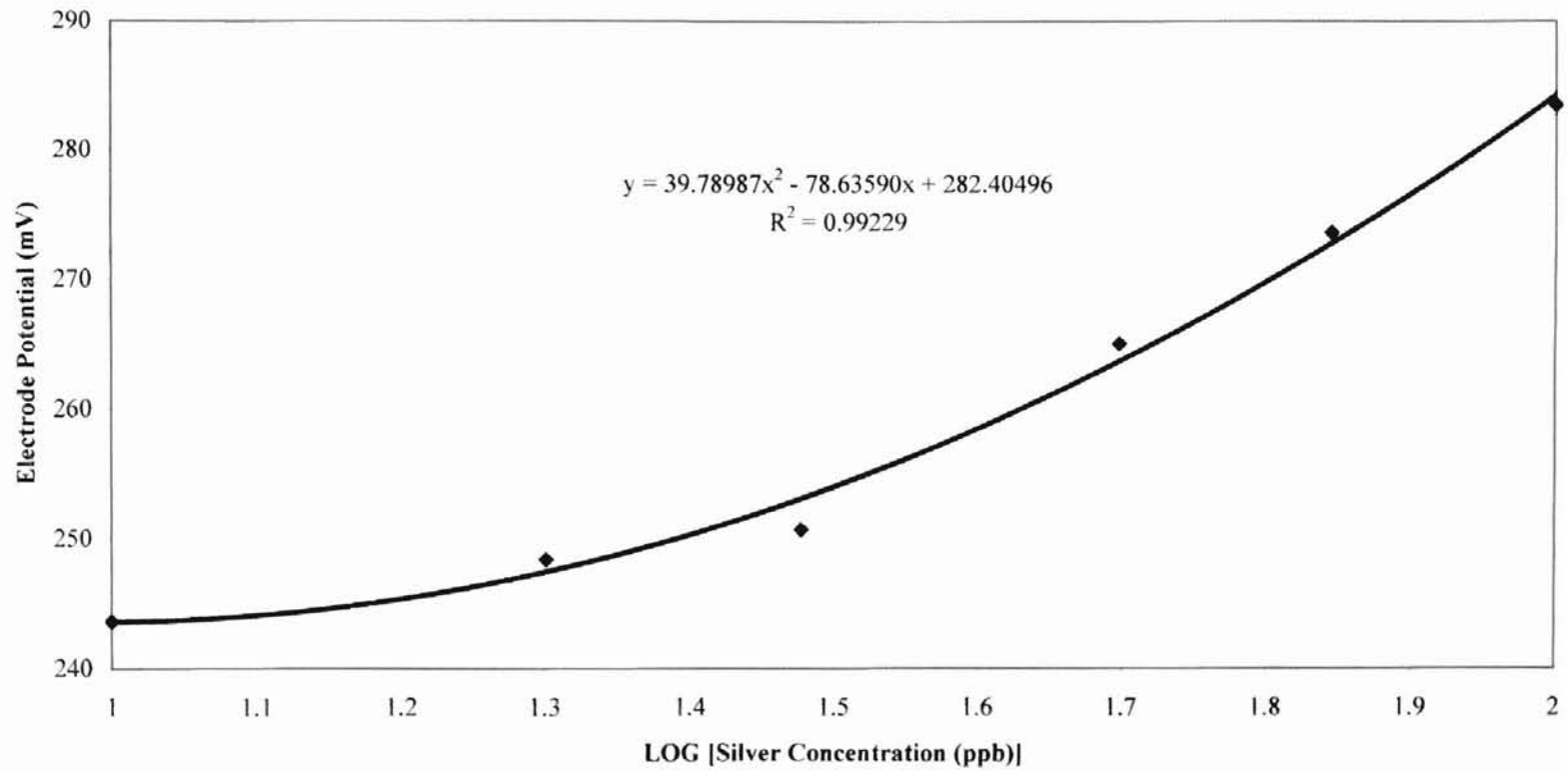


Figure A-1. Low Level Silver Calibration of Silver Electrode

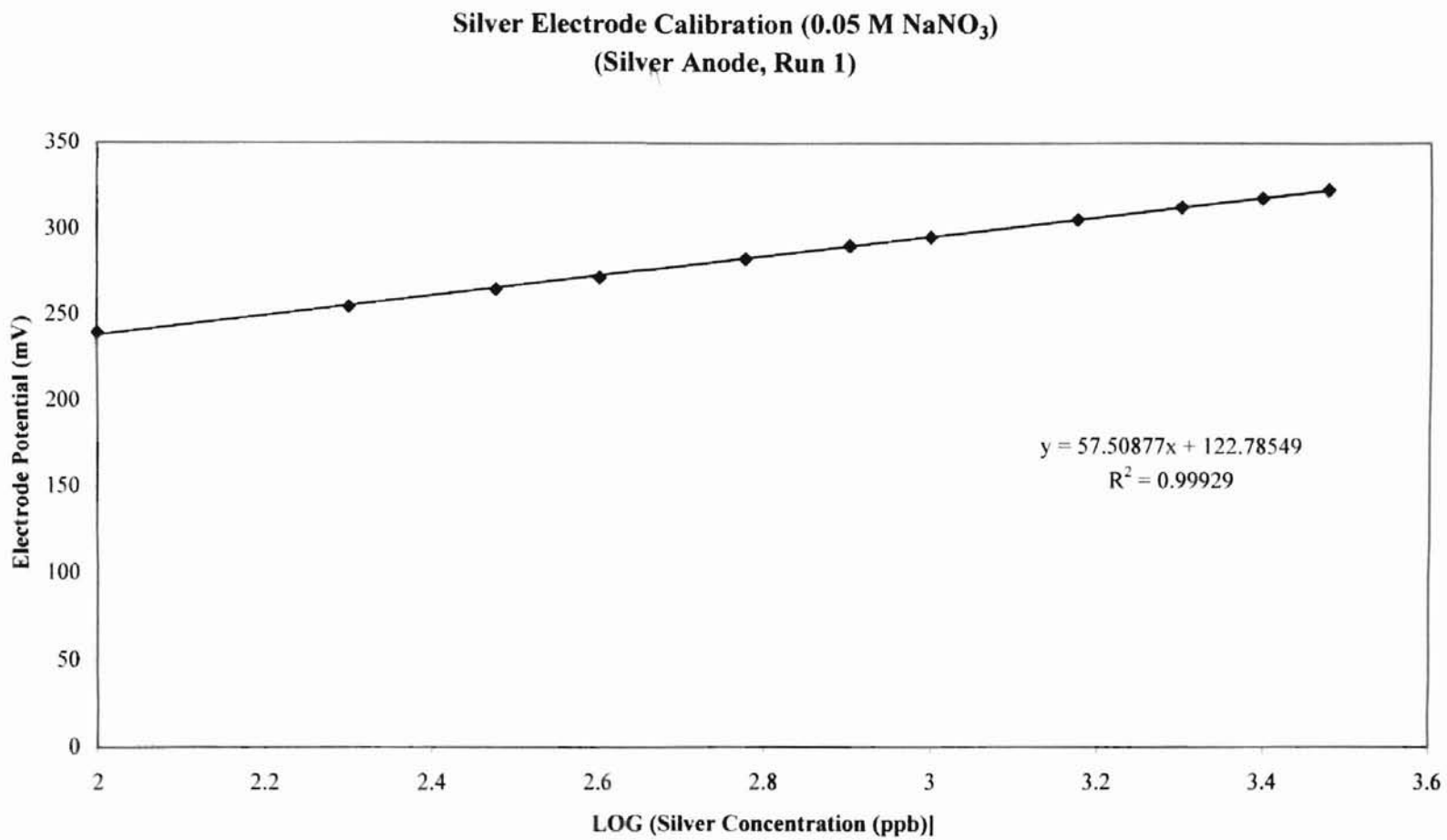


Figure A-2. Silver Calibration Curve for Run 1, 0.05 M NaNO₃

Silver Electrode Calibration (0.1 M NaNO₃)
(Silver Anode, Runs 1)

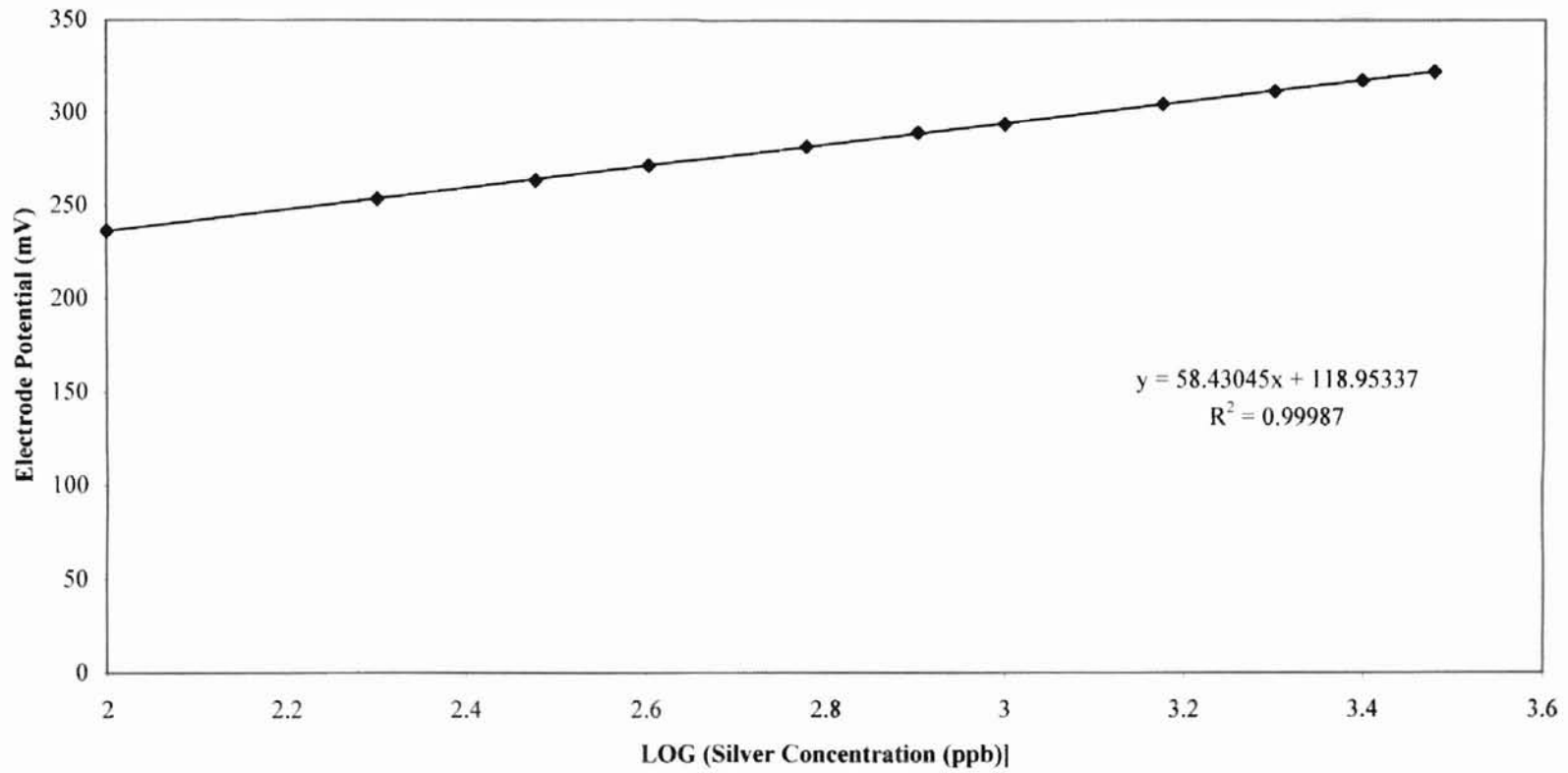


Figure A-3. Silver Calibration Curve for Run 1, 0.1 M NaNO₃

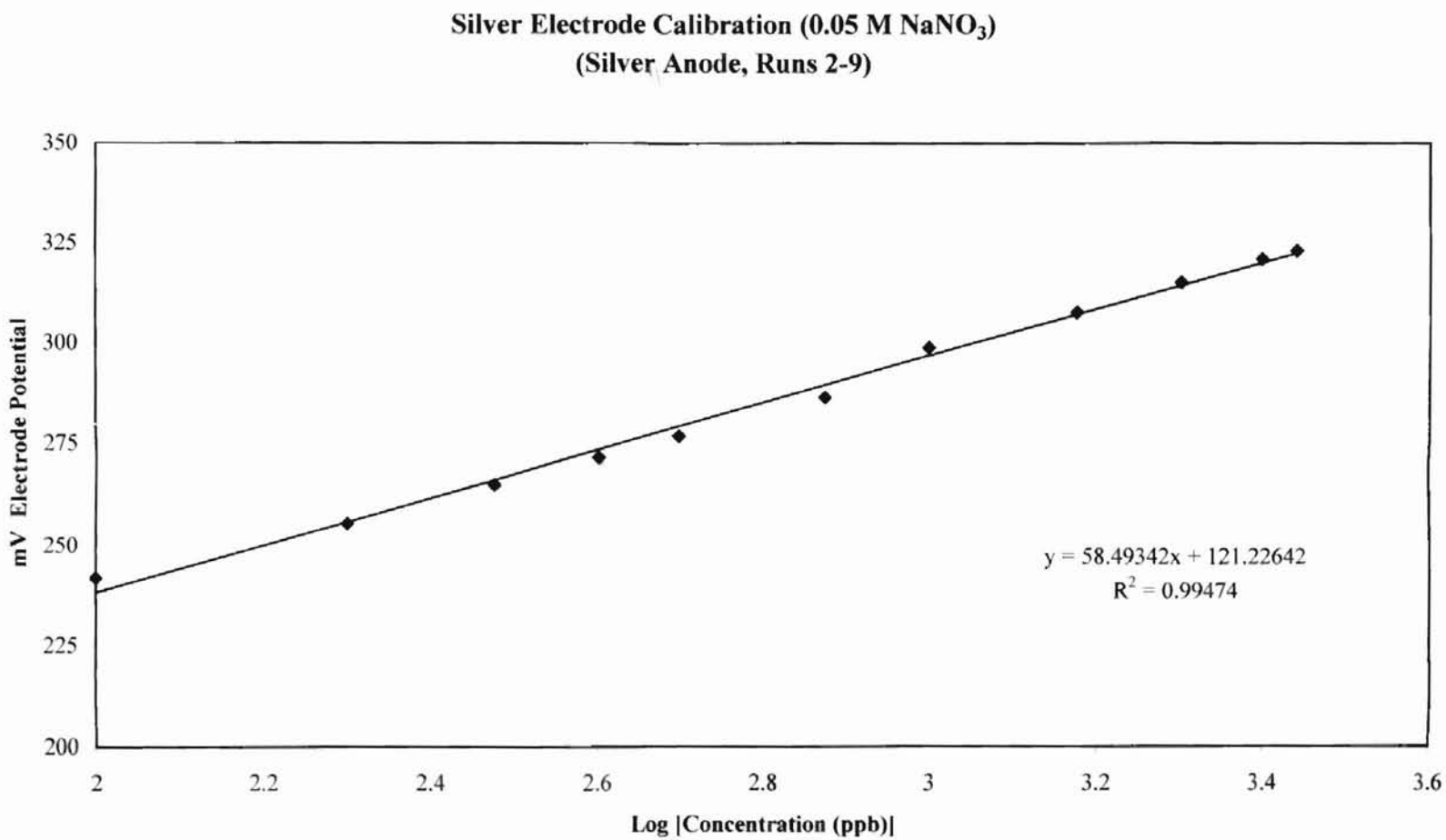


Figure A-4. Silver Calibration Curve for Runs 2-9, 0.05 M NaNO₃

Silver Electrode Calibration (0.1 M NaNO₃)
(Silver Anode, Runs 2-9)

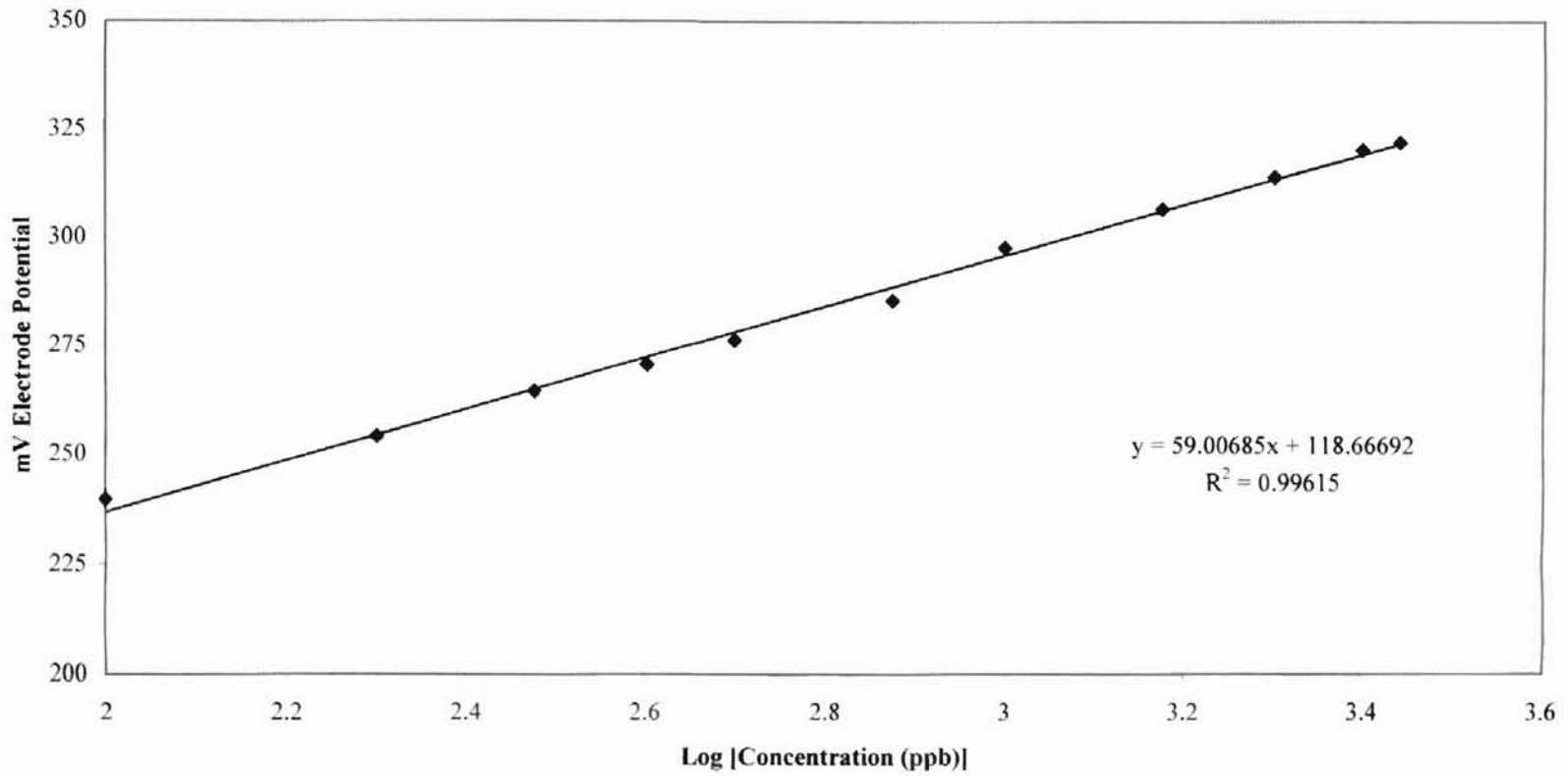
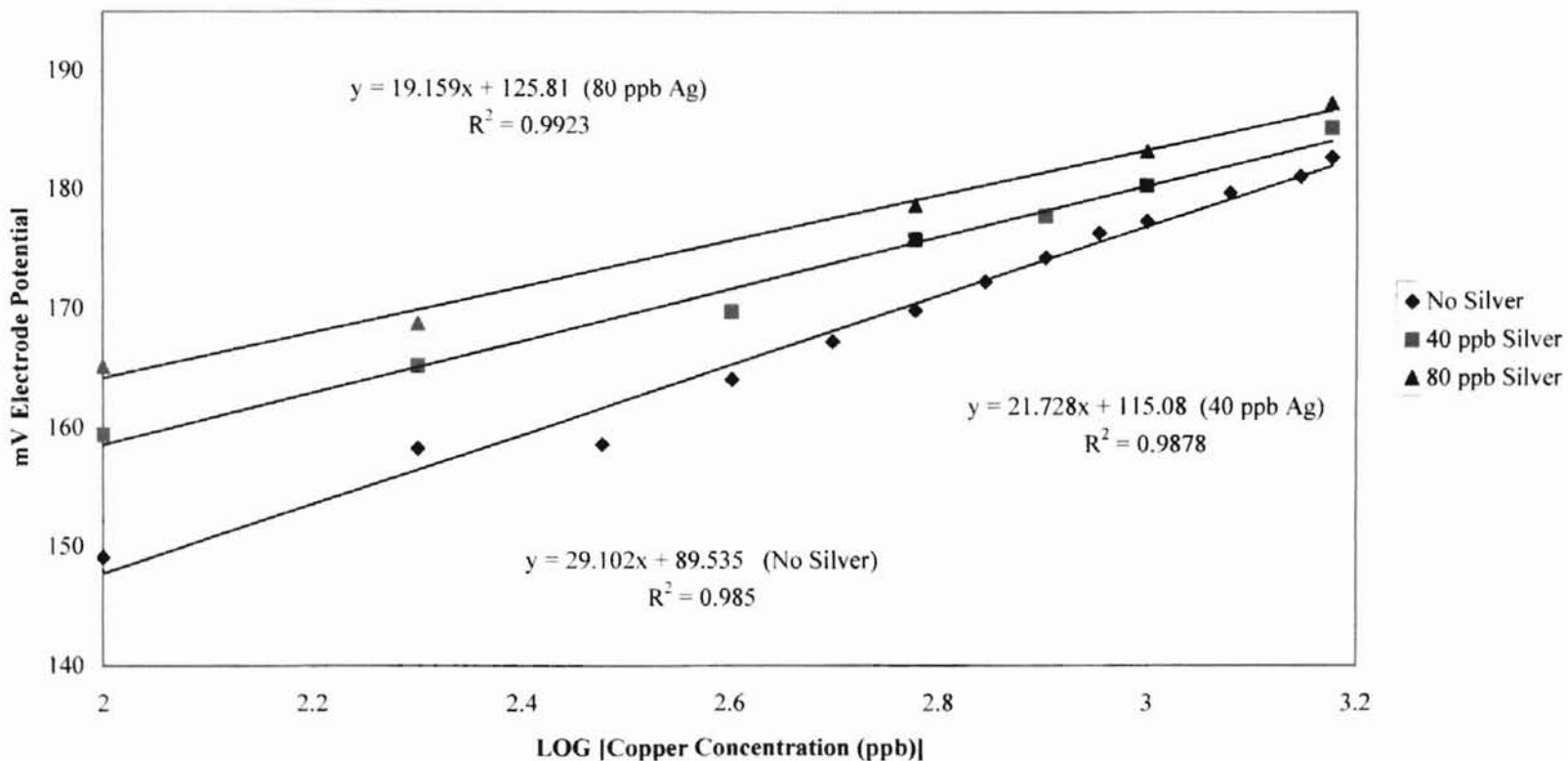


Figure A-5. Silver Calibration Curve for Runs 2-9, 0.1 M NaNO₃

Copper Calibration Curve (0.05 M NaNO₃)



08

Figure A-6. Copper Calibration Curve With Low Levels of Silver

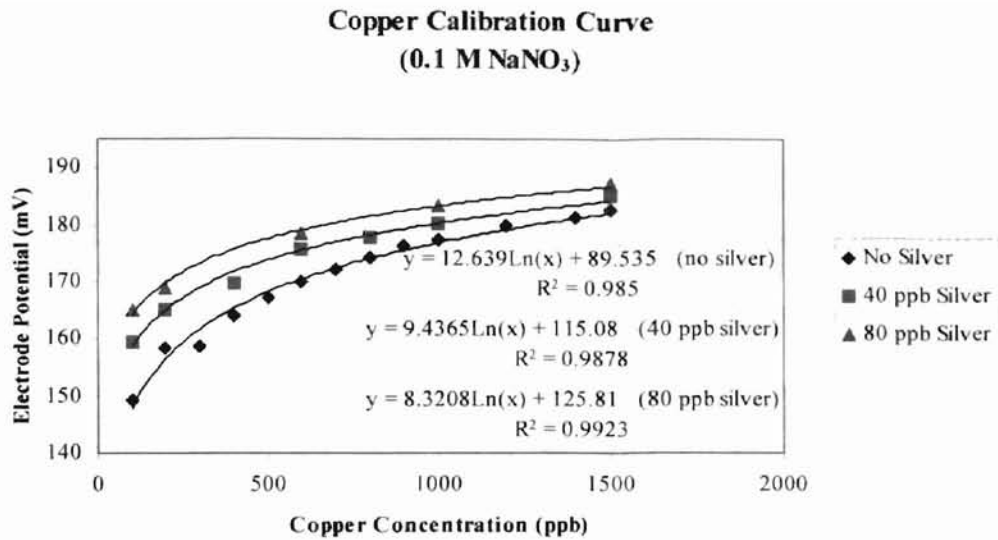


Figure A-7. Plot in Cartesian Coordinates showing Logarithmic Trend Lines

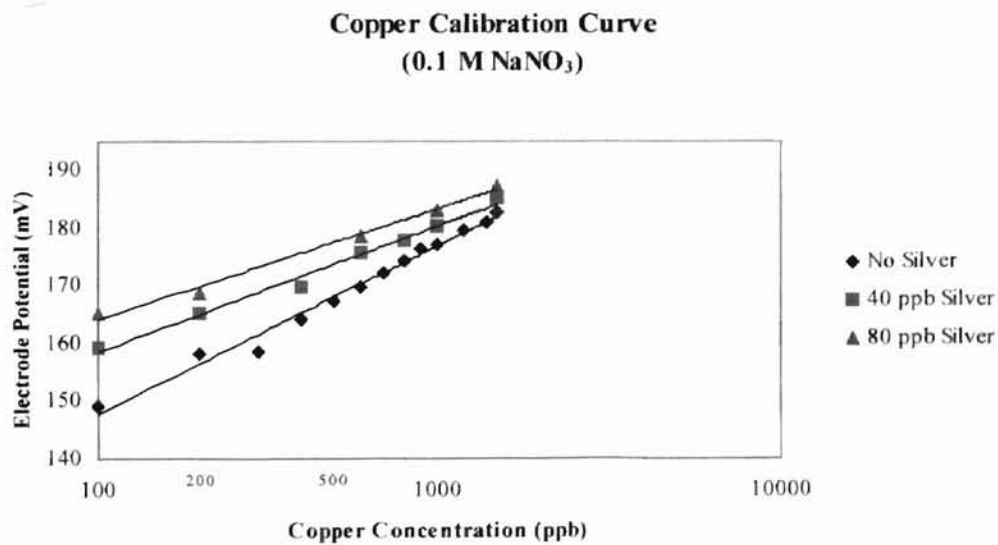


Figure A-8. Semi-log Plot Calibration

APPENDIX B

PROPOSED BIOLOGICAL TESTING PROCEDURES

This section presents a proposed experimental procedure for the determination of inactivation rates of bacterial species using copper and silver ions as the disinfectant. It is important to establish the biological performance of a disinfection method so that the viability of certain applications can be verified. The EPA developed a “*Guide Standard and Protocol for Testing Microbiological Water Purifiers*” to ensure that point-of-use disinfection units maintain a safe level of performance (EPA, 1987). This procedure is specific for *E. coli*. *E. coli* was chosen as the first test organism because of the amount of data available in the literature for comparison of results. The strain of *E. coli* is safe to work with in a lab, and easy to culture and collect data.

Experimental Procedure

The procedure that is presented here is adapted from work presented by Landeen et al. (1989) and other references as given. The author recommends the researcher read *Handling Laboratory Microorganisms* by Charles Penn to gain a basic understanding of techniques involved in microbiological work.

Equipment Required

A list of the equipment needed to perform the proposed procedure is listed in Table B-1.

Table B-1. Experimental Equipment and Supplies Needed

3 to 4 Straight Neck Erlenmeyer Flasks—500 mL
2 Straight Neck Erlenmeyer Flasks—1000 mL
Nutrient Agar
Nutrient Broth
Neutralizer Solution 14.6% Sodium Thiosulfate and 10% Sodium Thioglycolate in Deionized Water
3 to 4 Polyethylene or Polypropylene Bottles—1 L
Sterile Petri Dishes: 100 x 15 mm
Lyophilized <i>Escherichia coli</i> specimen Cole Parmer Cat. No. LF-14016-16
Sterilized Dilution Bottles—at least 20 mL volume (Number determined by number of samples to be plated)
Stir plate
Bunsen burner
Concentrated Nitric Acid
0.1% Peptone in Deionized Water—need about 500 mL
Pipets—5 mL and 10 mL (sterile, disposable)
Copper and Silver ion source, either chemical or electrolytic
Micropipettor—100-1000 μ L range, and 2-20 μ L range (Need to Purchase the 2-20 μ L) Use with disposable tips

A 100-1000 μ L pipette is available in the lab (Eppendorf, model no. 4710). The calibration of the pipette was checked using deionized water and a mass balance. The calibration showed that the pipette readings were not correct. Figure B-1 shows the results of the calibration. The data fit a linear correlation well. This is shown by the R^2 term being equal to 1. The curve shows that the pipette readings need to be adjusted up by 15 μ L to obtain the desired concentration. For example, to pipette a volume of 1000 μ L (1 mL) the user needs to set the pipette volume reading to 1015 μ L. Repeated

measurements at a setting of 1015 μL showed that the variance in volume measured is 2 μL .

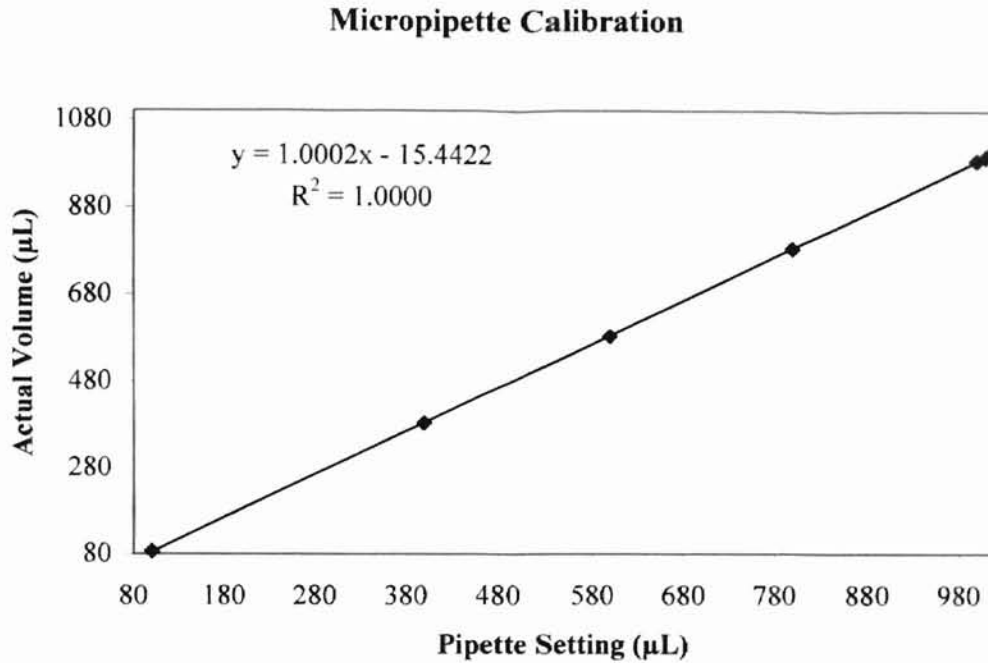


Figure B-1. Micropipette Calibration Curve

Experimental Procedure

1. Glass Preparation. All glassware that will be used in the experimentation should be soaked overnight in a 10-15% nitric acid bath. This should remove any copper and silver metal contaminants on the glass. Any contaminants could give false inactivation results. Rinse with deionized water and autoclave. For the dilution bottles, cover with aluminum foil before autoclaving. The foil will protect the bottles from contamination after sterilization has been performed.
2. Medium Preparation. Prepare Nutrient Agar according to manufacturers instructions, except only make up 500 mL at a time using a 1 L flask. A 1 L volume of agar will boil over during preparation and autoclaving. After the agar has been

dissolved in a flask, partially cover using plastic cap, but ensure that adequate airflow is achieved. Autoclave at 121 °C for 15-20 minutes. Allow to cool for approximately ½ hour, and then pour out into sterile petri dishes filling the dish about half way. After cooling sufficiently, place dishes upside down in the bag that they were shipped in until ready to use. It would be beneficial to let agar plates sit over night to determine if any plates were contaminated.

3. Broth Preparation. Prepare Nutrient Broth according to manufacturers instructions, except only make 500 mL in a 1 L flask. Again, if a 1L volume is used, it will boil over. The 500 mL volume allows for a higher initial concentration of bacteria so that high enough counts can be generated on a the spread plates. Partially cover using plastic cap and autoclave at 121 °C for 15-20 minutes.
4. Peptone Solution Preparation. The 0.1% peptone solution will be used for dilutions before the samples are spread plated onto the agar. Phosphate buffer solution is not used because of the complexation that can occur between phosphate and the disinfectant ions. Dissolve 1 gram of peptone powder into 1 L of water. Sterilize by autoclaving at 121 °C for 15-20 minutes.
5. Neutralizer Preparation. This solution should be prepared the morning that inactivation rate experiments will be done. The chemicals use degrade quickly, so the solution cannot be stored overnight. In a 20 mL dilution bottle, dissolve 968.2 mg of sodium thiosulfate and 663.1 mg of sodium thioglycolate into 5 mL of deionized water. Filter through a 0.2 µm-pore-size filter, cover with foil and autoclave at 121 °C for 15-20 minutes. This should produce a 14.6% sodium thiosulfate and 10% sodium thioglycolate solution.

6. Disinfectant Test Systems. Prepare two to three test systems by mixing up a 200 mL solution of 800 ppb copper and 80 ppb silver for each test system in 500 mL flasks. The source of ions can be electrolytic or chemical compounds. If using standard chemicals, choose strong electrolyte salts that will dissociate completely. Use deionized water to make the solutions. You will also need 200 mL of deionized water as a blank control system to give you the initial concentration of bacteria. Autoclave at 121 °C for 15-20 minutes. Other experiments may want to use polypropylene containers to minimize adsorption losses to the wall of the container. Make sure that the container is autoclavable.
7. *E. coli* Specimen Preparation. Dissolve one lyophilized pellet in the broth that was prepared in Step 3 according to the instructions of the manufacturer. Incubate at 37 °C overnight.
8. Inactivation Rate Determination. Place 10 µL of the neutralizer in several sterilized dilution bottles. Place the test systems on a stir plate and stir at a continuous rate. Inoculate each test system with 1 mL of the broth from Step 7. At predetermined time intervals, remove 1 mL of the test sample and place in a dilution bottle that contains neutralizer. Dilute with 4 mL of 0.1% peptone solution. Mix thoroughly and spread plate a 0.1 mL sample onto the prepared agar plates. Spread plate using a stainless steel spreader or glass spreader. Dip in 50% ethanol solution and flame sterilize using the bunsen burner. Invert the plate and incubate at 37 °C for 24 hours. Follow the same procedure for the control to determine the original concentration in the test systems. Several different plates may be spread for each sample to reduce the amount of error in the total counts.

9. Enumeration and Rate Determination. Remove plates from the incubator and count the number of colonies on each plate. Count the number of colonies on the control plates. The inactivation rate is usually calculated from the following equation (Hoff, 1986).

$$K = -\frac{\log_{10}\left(\frac{N}{N_0}\right)}{t} \quad (\text{B-1})$$

The variable N is the number of colonies at time t and N₀ is the initial number of viable colonies. Time, t, is usually taken in minutes. In essence, K is the log₁₀ reduction per unit time.

The reader is referred to several standard methods to aid in the techniques used during experimentation and analysis. ASTM Standard Methods D5465-93 and D3870-91 give standard practices used in spread plating techniques. The American Public Health Association also provides standard practices in determining bacteria counts through spread plating techniques (APHA, 1992)

Waste Disposal

All biologically contaminated waste (pipettes, petri dishes, etc.) need to be placed in a plastic bag that can be autoclaved. The bag must be able to be identified as being autoclaved or not. Once waste has been autoclaved, check with the safety manager to determine proper disposal.

APPENDIX C

ALLOY ANODE COMPOSITION DESIGN

This Appendix presents the calculations that were used to determine the composition of the alloy required to generate a solution of copper and silver ions in a concentration of 800 ppb Cu^{2+} and 80 ppb Ag^+ .

Theory and Methodology

The goal is to produce copper and silver in a mass ratio of 10 to 1. The relation between the total number of equivalents that is generated at the anode is derived from Faraday's Law (Equation C-1).

$$n_{eq} = \frac{It}{F} \quad (\text{C-1})$$

Assuming that in a binary alloy the generation of each ion is proportional to the equivalent composition of the anode, one can determine the composition of the anode that is required to produce a desired concentration in solution. This can be written as Equation C-2.

$$n_{eq,i} = \frac{It}{F} \frac{n_{a,i}}{\sum n_{a,i}} \quad (\text{C-2})$$

The variable $n_{eq,i}$ is the number of equivalents of species i that is generated. The variable $n_{a,i}$ is the number of equivalents of species i present in the anode. The other variables are the same as those defined in previous chapters.

For a binary alloy, one can write the following two equations for the number of equivalents generated for each species

$$n_{eq,1} = \frac{It}{F} \left(\frac{n_{a,1}}{n_{a,1} + n_{a,2}} \right) \quad (C-3)$$

$$n_{eq,2} = \frac{It}{F} \left(\frac{n_{a,2}}{n_{a,1} + n_{a,2}} \right) \quad (C-4)$$

The variables $n_{eq,1}$ and $n_{eq,2}$ are the number of equivalents that are generated, $n_{a,1}$ and $n_{a,2}$ are the number of equivalents of each specie present in the anode.

It would be beneficial to introduce the composition of the anode as a mass ratio of copper to silver. This can be done by substitution of the following definitions.

$$n_{a,2} = \frac{m_{a,2}}{w_{eq,2}} \quad n_{a,1} = \frac{m_{a,1}}{w_{eq,1}}$$

The variables $m_{a,1}$ and $m_{a,2}$ are the mass of each metal present in the anode, $w_{eq,1}$ and $w_{eq,2}$ is the equivalent weight of each metal. The equivalent weight is typically just the molecular weight of the metal divided by the valence of the ion that is generated. After making the substitutions and rearranging Equations C-3 and C-4 are the result.

$$n_{eq,2} = \frac{It}{F} \left(\frac{1}{1 + \frac{m_{a,1} w_{eq,2}}{m_{a,2} w_{eq,1}}} \right) \quad (C-5)$$

$$n_{eq,1} = \frac{It}{F} \left(\frac{1}{1 + \frac{m_{a,2} w_{eq,1}}{m_{a,1} w_{eq,2}}} \right) \quad (C-6)$$

Dividing Equation C-5 by Equation C-6 and rearranging, the following equation is obtained.

$$\frac{n_{eq,2}}{n_{eq,1}} = \frac{m_{a,2} w_{eq,1}}{m_{a,1} w_{eq,2}} \quad (C-7)$$

Making use of the relation between mass and equivalents and substituting into the previous equation, the following equation results.

$$\frac{m_{g,2} w_{eq,1}}{m_{g,1} w_{eq,2}} = \frac{m_{a,2} w_{eq,1}}{m_{a,1} w_{eq,2}} \quad (C-8)$$

The variables m_g are the mass of each species being generated. If the desired ratio of copper to silver in solution is designed to be 10 to 1, then by equation C-8 the mass ratio of the anode must be the same.

Solving Equation C-5 or C-6 for time will allow the user to determine the total time required to generate the desired concentrations based upon a specified current. Using the time that was obtained through this method and the associated current, one can insert these values into Equation C-1 to determine the total number of equivalents that will be produced. Since the device was designed for a binary alloy anode, if a pure anode is used, the total number of equivalents of the pure species that will be generated is the number of equivalents obtained from Equation C-1.

VITA

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