

Accuracy, Precision, Cost, and Acceptability of Silver Testing Methods in  
Ceramic Filter Manufacturing Facilities

A thesis submitted by

Rhiana Davida Meade

In Partial Fulfillment of the Requirements for the Degree

Master of Science

In

Civil and Environmental Engineering

Tufts University

February 2016

Adviser:

Dr. Daniele Lantagne



## Abstract

Ceramic water filters are one effective technology for household drinking water treatment. Silver nitrate or silver nanoparticles are applied during filter manufacturing to increase antimicrobial activity in the filter and effluent. There is currently no recommended method to test silver concentrations during manufacturing. Six commercially-available silver test strips, kits, and meters were evaluated by: 1) measuring in quintuplicate 6 samples from 0.0-1.0 mg/L and 6 samples from 100-1,000 mg/L of silver nanoparticles and silver nitrate to determine accuracy and precision; 2) conducting volunteer testing to assess ease-of-use; and, 3) comparing costs. No method was appropriate for testing silver nanoparticles. For silver nitrate, accuracy ranged from 0-100%, precision did not vary greatly, volunteers found test strip methods easiest but meters most reliable, costs ranged from 36-1,600 USD for 100 tests. Development of field test methods that accurately measure a larger range of concentrations and can test silver nanoparticles is needed.

### Keywords

ceramic water filter, drinking water, household water treatment, silver nanoparticles, silver nitrate



## Acknowledgements

First and foremost, thanks to Daniele Lantagne for giving me this opportunity and allowing me to take the time I needed. Many thanks to my thesis committee: David Gute, Justine Rayner, and Anna Murray. Thanks to Anjuliee Mittleman for her input on silver nanoparticles and to Jason Hnatko for assistance in running the ICP-OPES.



# Table of Contents

<b>Chapter 1 .....</b>	<b>1</b>
Part I: Background and Motivation .....	1
Scope of this chapter .....	3
Waterborne diseases and the need for household water treatment techniques .....	4
Ceramic filters for drinking water treatment .....	5
Silver as an antimicrobial agent .....	7
Part II: Methods for testing silver in water .....	13
Chapter Summary .....	17
<b>Chapter 2 .....</b>	<b>19</b>
Introduction to Chapter .....	19
Introduction .....	19
Methods .....	22
Testing Location .....	22
Test Method Selection .....	22
Test Solution Preparation .....	24
Laboratory Testing .....	25
Data Analysis .....	27
Cost .....	27
Volunteer Testing .....	28
Results .....	29
Accuracy .....	30
Precision .....	31
Cost .....	33
Usability – volunteer testing .....	33
Discussion .....	36
Conclusions .....	40
Chapter 3: Discussion .....	41
Decision Matrix .....	41

Final Conclusions.....	43
<b>Appendix A: Lab Protocol/Thesis Proposal .....</b>	<b>44</b>
<b>Appendix B: Volunteer Protocol .....</b>	<b>51</b>
<b>Appendix 3: R Code.....</b>	<b>56</b>
<b>References .....</b>	<b>57</b>



## List of Tables

<b>Table 1.</b> Comparison of six silver test methods used in study. ....	24
<b>Table 2.</b> Summary of volunteer testing questionnaire responses to several questions about test method usability (n=11, except where indicated). ....	35
<b>Table 3.</b> Summary of recommended silver test methods considering accuracy, usability, and cost. Each category is ranked as 0, 1, or 2, where low numbers are more favorable. ....	42

## List of Figures

Figure 1. Ceramic pot water filter.....	2
Figure 2. An illustration of the geometry of a ceramic water filter as used in this study. A ceramic, flowerpot-shaped filter is placed in a plastic bucket equipped with a spigot for dispensing. This bucket serves as the safe storage vessel for the water (UNICEF, 2008). .....	5
Figure 3. An illustration (not to scale) of a silver nanoparticle (A) and silver nitrate (B).....	7
Figure 4. Potential mechanisms of silver toxicity in microbial cells (Li et al, 2008) .....	9
Figure 5. Hach RapidSilver Visual Test kit with (L-R) filter box, forceps, 140 cc syringe and filter holder, 100 mL mixing bottle, and indicator reagent. ....	15
Figure 6. Interferences for Hanna Instruments photometer (Hanna, 2014). .....	16
Figure 7. Six commercially available silver tests evaluated in this study. ....	23
Figure 8. Average laboratory measurements for silver nitrate with 95% CI error bars.....	32

# Chapter 1

## Part I: Background and Motivation

Access to safe drinking water is a critical issue in many developing countries. More than 663 million people worldwide do not have access to an improved water source (WHO/UNICEF, 2014) and an estimated 1.2 billion more use drinking water at elevated risk of contamination at the source, or during collection, transport, or storage (Onda et al., 2012). Annually, 1.8 million people die from preventable and treatable diarrheal diseases (UNICEF, 2009). These diseases are caused by drinking water contaminated with bacteria, viruses, or protozoa. To combat this problem, a number of point-of-use water treatment technologies - such as chlorine tablets or household filters - have been developed and deployed around the world.

Ceramic filters are a readily available and widely used technology (Figure 1). They are locally manufactured in over 50 countries (The Ceramics Manufacturing Working Group, 2011). Their porous structure allows water to flow through, while trapping contaminants within its matrix. Painting, firing in, or dipping filters with silver nanoparticles (AgNP) or silver nitrate further enhances the antimicrobial properties of these filters and prevents growth within the filter itself. The addition of silver to the ceramic filter serves multiple functions, including prevention of a bacterial growth layer within the filter itself, increased reduction of bacteria in water being treated, and residual disinfection

due to the small (and acceptable) amount of silver that desorbs from the filter into the treated water.



Figure 1. Ceramic pot water filter

Silver discharge from filters over time is a major concern in terms of risk to human health and loss of antimicrobial properties. In general, silver has a minor effect on human health, but long-term exposure of levels above the United States Environmental Protection Agency (EPA) recommendations of 0.10 mg/L water or 0.01 mg/m<sup>3</sup> in air can discolor skin and damage tissues (ATSDR, 2011). Over time, the antimicrobial effects of silver applied to ceramic filters declines (Bielefeldt et al., 2009). It is unknown whether repeated applications of silver to the filter are necessary to retain its antimicrobial properties. Filters are generally only replaced when they break.

While methods to standardize the construction and application of silver to the filters have been developed and disseminated, there is little known about the accuracy of field methods to test the concentration of silver both in the silver mix and in the filtered water effluent (The Ceramics Manufacturing Working Group,

2011). This project aims to quantify the accuracy, precision, and usability, and to assess the acceptability of these methods for both silver nitrate and silver nanoparticle concentrations. A variety of methods are available for testing, from inexpensive test strips to more complicated meters and laboratory instrumentation. The question this thesis aims to answer is: what field test can we recommend to filter factories based on their accuracy, precision, cost, and usability?

In this thesis, I tested two different ranges of silver concentrations to mimic six addition and seven treated water silver concentrations. Each of these 13 samples will be tested with each of 6 potential test methods, using appropriate dilutions. Additionally, Tufts University volunteers participated in a focus group approved by Tufts Institutional Review Board to assess method usability. In the three chapters of the thesis I will present: 1) a literature review of silver, safe drinking water, and test methods; 2) the full manuscript for submission; and, 3) discussion.

## **Scope of this chapter**

In this chapter is the literature review portion of the thesis, and in it I will provide a review of several topics: provide an overview of the approaches to household water treatments, ceramic filters specifically, and the antimicrobial and health effects of silver use. I will look at silver as an antimicrobial agent in its historical and chemical contexts. Silver is in use today for its antimicrobial properties in applications as varied as athletic textiles, agriculture, and health care.

Its historical uses in health care date back to ancient times, and it were used for wound treatment during the 18<sup>th</sup> century (Chopra, 2007). I will detail the chemical explanation for silver's antimicrobial properties and also its human health effects for both acute and chronic exposure. A wide variety of literature is available about these topics, as well as the need for household water treatments in the prevention of diarrheal diseases, which is the topic I will start with below.

## **Waterborne diseases and the need for household water treatment techniques**

Diarrheal diseases cased by pathogens in drinking water are a leading cause of death for children under five years old worldwide (UNICEF, 2009). There are a number of low-cost solutions for household water treatment, from solar water disinfection, to chlorine treatment, to various filtration methods (Lantagne et al., 2006).

## *Ceramic filters for drinking water treatment*

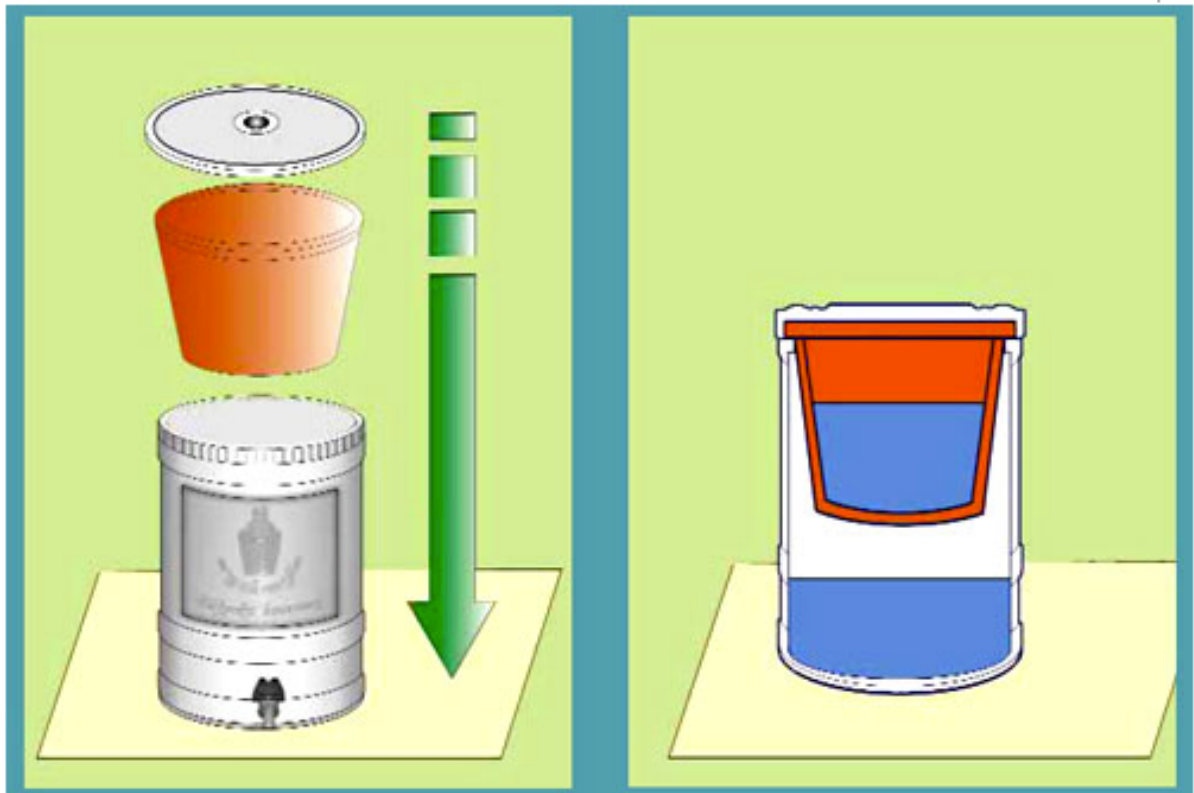


Figure 2. An illustration of the geometry of a ceramic water filter as used in this study. A ceramic, flowerpot-shaped filter is placed in a plastic bucket equipped with a spigot for dispensing. This bucket serves as the safe storage vessel for the water (UNICEF, 2008).

Filtration has been put forward as one of the most effective low-cost household water treatment strategies (Sobsey et al., 2008). Ceramic filters are made from local clays and materials, and then placed in plastic buckets which also act as the safe storage vessel for the water after filtration (Figure 2) (Lantagne, 2001). The firing process creates a complex pore structure within the filter that removes pathogens. Ceramic filters have been shown to remove 99% of protozoan and 90-99% of bacterial organisms from drinking water (Lantagne

2001, Sobsey 2008, Brown et al., 2008). In addition, ceramic filters have been shown to be a more lasting solution than chlorine or solar disinfection strategies, likely due to their ease of use and ability to treat larger amounts of water at one time (Sobsey et al., 2008). In laboratory experiments with *Escherichia coli*-containing water, the bacteria disinfection efficiency was 3.8-4.5 log scale reductions of bacteria (Bielefeldt et al., 2009).

Several studies have been conducted to prove the efficacy of ceramic filter technology in reducing diarrheal disease. A randomized controlled trial in Cambodia found that those households which received a ceramic water filter experienced less diarrheal disease during the study compared to a control group (Brown et al., 2008). A second randomized controlled trial in rural South Africa and Zimbabwe for ceramic candle filters found both lower incidence of diarrhea and also found zero *E. coli* in drinking water in nearly 60% of the treated households (du Preez et al., 2008). In Colombia, filters were not found to have uniform microbiological performance and protection, though prevalence of diarrhea was 60% less in households with ceramic candle filters (Clasen et al., 2005). Silver nanoparticle impregnated filters in Guatemala were found to improve bacterial removal over ceramic filters with no silver over 23 months (Kallman et al., 2010).

In recent years, the Ceramics Manufacturing Working Group has completed a document to address differences in manufacturing processes in order to make ceramic filters more uniform across the 50+ countries that produce them



(CMWG, 2011). These recommendations include adding silver in the form of silver nanoparticles to filters to increase antimicrobial properties.

## Silver as an antimicrobial agent

Silver has been used for centuries in health care practices as a disinfecting agent. Commercial use of colloidal silver formations containing silver nanoparticles has increased dramatically over the past decade as their effectiveness as an antibacterial agent became well known and the strategies for producing nanoparticles became less costly (Tolaymat et al., 2010). Currently, silver nanoparticles are used in a number of applications as diverse as water disinfection and odor control in athletic fabrics. In this project, two types of silver are discussed – silver ions, in the form of silver nitrate ( $\text{AgNO}_3$ ), and silver nanoparticles (Figure 3).

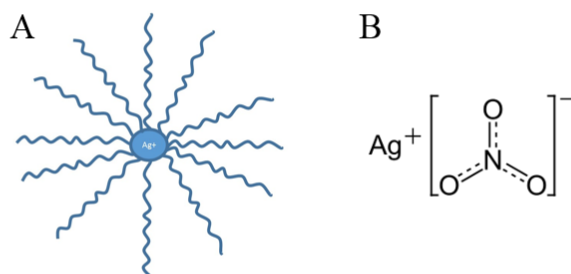


Figure 3. An illustration (not to scale) of a silver nanoparticle (A) and silver nitrate (B).

Silver occurs naturally in several oxidation states – most commonly as elemental silver or as monovalent (+1) ion. It is a generally inert metal, and the +1 state is the only available stable oxidation state (Housecroft and Sharpe, 2005).

Silver halides are light sensitive, and are used in all types of photography. Silver nitrate is the salt of ionic silver  $\text{Ag}^+$  and nitric acid  $\text{NO}_3^-$ . In an aqueous solution, these ions dissociate and free silver ions are generated. These are the ions that engage in mechanisms damaging to cells, described below. By contrast, silver nanoparticles are engineered structures with one dimension between 1 and 10 nanometers, with large surface areas and high reactivity, defined by one author as “nanoscale clusters of metallic silver atoms,  $\text{Ag}_0$ , engineered for some practical purpose” (Marambio-Jones and Hoek, 2010). In recent years, advances in technology has dramatically decreased the price of manufacturing nanoparticles, leading to their ubiquity. Common “capping agents” of silver nanoparticles are polysaccharides and polyphenols (Marambio-Jones and Hoek, 2010). Their synthesis and properties are the subject of much current study (Benn and Westerhoff, 2008; Chopra, 2007; Li et al., 2008; Pal et al., 2007; Song et al., 2012; Tolaymat et al., 2010, etc.).

There are a variety of proposed mechanisms for antibacterial action of silver (Figure 4). The active part of its bactericidal effects is the  $\text{Ag}^+$  ion (Housecroft and Sharpe, 2005). It is thought that silver ions attach to cell walls or enter cells and through their interactions with proteins and nucleic acids, are able to damage cell components. Silver nanoparticles are been shown to both damage cell membranes directly and also form reactive oxygen species (ROS) that go on to cause more damage (Ivask et al., 2014.) Reactive oxygen species include singlet oxygen, superoxide, and hydrogen peroxide, all molecules that are highly reactive and thus damaging to DNA, proteins, and other crucial cell elements.

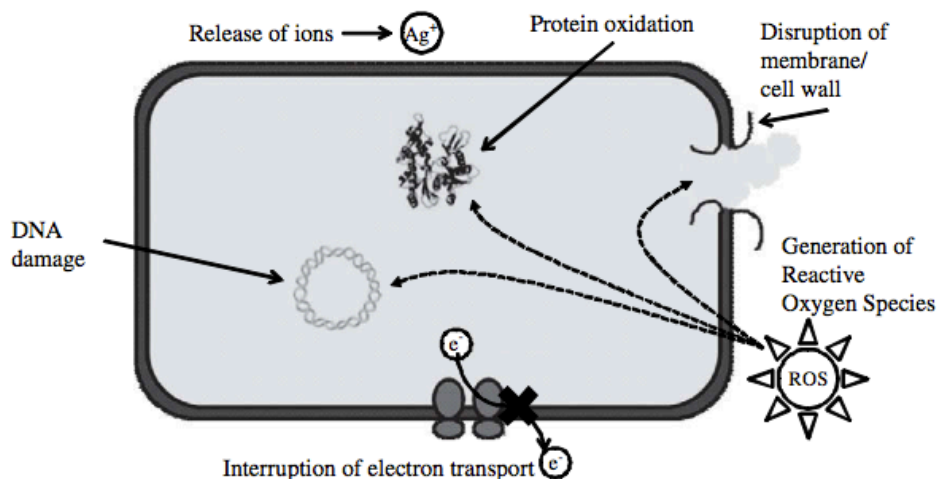


Figure 4. Potential mechanisms of silver toxicity in microbial cells (Li et al, 2008)

Silver nanoparticles have been shown to attach to cell walls of *E. coli*, accumulating on the cell membrane, forming “pits” visible from SEM and TEM (Sodi and Salopek-Sodi, 2004). *E. coli* grown in the presence of silver nanoparticles grew colonies according to an inverse linear relationship with the concentration of silver nanoparticles present – that is, with a lower concentration of AgNP, more colonies grew and vice versa (Sodi and Salopek-Sodi, 2004). The pits that form are likely the cause of greater permeability of the cells, which can lead to cell lysis and death (Sodi and Salopek-Sodi, 2004). As the ionic strength of solutions increases, the antimicrobial performance of silver nanoparticles decreases, likely because it causes the AgNP to aggregate, and larger particles are less harmful than small ones (Zhang and Oyandel-Craver, 2012).

While the prevailing theory of silver nanoparticle toxicity was that the active agent was the  $\text{Ag}^+$  ion, recent research suggests that it may be the

nanoparticle geometry itself, more than the silver, which exerts the toxic effects (Ivask et al., 2014). One study found that cell damage by silver nanoparticles was more similar to that of other nanoparticles rather than ionic silver (Ivask et al., 2014). This suggests that it is the nature of the nanoparticle, specifically size and properties, that causes cell death rather than the silver within them.

Many groups are experimenting with creating new silver-containing materials and testing their antibacterial properties. One group created paper impregnated with silver nanoparticles, and then passed a solution containing bacteria through the paper membrane (Dankovich and Gray, 2011). For both *E. coli* and *Enterococcus faecalis*, there were log reductions of 6 and 3, respectively, of colony forming units (CFU) (Dankovich and Gray, 2011). Another team created a silver nanoparticle-coated polyurethane foam to use as a water filter (Jain and Pradeep, 2004). When water containing  $10^5$  CFU was treated through this foam, zero bacterial colonies were found after treatment (Jain and Pradeep, 2004).

#### *Silver risk for human and environmental health*

There is concern about the presence of silver nanoparticles in the environment, and its eventual fate either in the greater environment or in wastewater treatment plants. Textiles treated with either silver nanoparticles or ionic silver have been found to produce silver in wash water (Mitrano et al., 2014). One study tracked the release of AgNP from clothing fibers and found that across different brands of AgNP-containing socks, from 3 to 1300 ppb silver was

released into wash water (Benn and Westerhoff, 2008). This released silver was then found to adsorb to biomass that would commonly be found in wastewater treatment plants, which could be problematic if that biomass was then used as agricultural fertilizer (Benn and Westerhoff, 2008). In another study of nanomaterial removal by wastewater treatment plants, there was highly variable removal into biosolids, from 30-99% (Reed et al., 2014).

Both aggregated and dispersed silver nanoparticles have been shown to accumulate in brine shrimp (*Artemia salina*) (Wang and Wang, 2014). In one experiment with brine shrimp consumed by marine medaka (*Oryzias melastigma*), a low trophic transfer of AgNP was found at less than 6% transferred, but this trend may not be true for all marine organisms or food chains (Wang and Wang, 2014).

Humans are exposed to silver in the environment and in occupational settings. Ingestion and inhalation are the routes of entry to the body, with ingestion primarily occurring in the workplace (Drake and Hazelwood, 2005). The greatest risk to human health, either from inhalation or ingestion, are argyria or argyrosis, which is the darkening of the skin or eyes, respectively, caused by absorption of metallic silver. Respiratory effects include both irritation and some staining, but are not extremely harmful to health (Drake and Hazelwood, 2005). The EPA recommends that silver in drinking water not exceed 0.10 mg/L (ATSDR, 2011). The Occupational Health and Safety Administration (OSHA) defines its permissible exposure to 0.01 mg/m<sup>3</sup> in air (OSHA, 2014). In one lifecycle study of nanomaterials found in drinks, nanomaterials were found to

have an effect on human intestinal microvilli (Reed et al., 2014). This could be of great concern if nanoparticles are used on filters, and then ingested by a population already experiencing environmental enteropathy, a condition which also affects the intestinal villi, and thus would be further unable to absorb nutrients from food effectively.

#### *Loss of silver effectiveness*

The major reason there is a need to test for silver in effluent from ceramic filters is the need to determine if the silver is still present on or in the filter, and thus able to perform its bactericidal duties. If after a few pore volumes of water are passed through, all the silver elutes off the filter, then either repeated applications or different methods of application are needed.

## **Part II: Methods for testing silver in water**

While methods to standardize the construction and application of silver to the filters have been produced, there is little known about the accuracy of field methods to test the concentration of silver both in the silver mix and the filter effluent (CMWG, 2011). This project aims to quantify the accuracy, precision, and usability of these methods for both silver nitrate and silver nanoparticle concentrations. A variety of methods are available for testing, from inexpensive test strips to more complicated meters and laboratory instrumentation.

Potential test methods were found by searching the catalogs of known manufacturers of environmental test methods (Hach, Hanna Instruments, etc.) for silver tests for the concentrations desired. A simple Google search yielded commercially available test strips designed for use by photographers for determining silver concentrations in their developing solutions. Kits were excluded if they were not readily available from reliable distributors or if a price quote could not be obtained.

Two sources of silver are regularly applied to ceramic filters: silver Collargol powder from Argenol Laboratories and commercial silver nitrate solutions. Two different ranges of concentrations were tested to mimic both potential influent and effluent silver concentrations. Influent concentrations were made up in six concentrations from 0.1 to 1 g/L at 0.1, 0.2, 0.5, 0.7, 0.8, and 1 g/L. Influent samples were diluted to the range of each testing method required. Effluent samples were made up in seven concentrations from 0.002 to 1 mg/L at

0.001, 0.005, 0.01, 0.05, 0.1, 0.5, and 1 mg/L. These concentrations were chosen based on regularly detected effluent levels as reported by the CMWG (CMWG, 2011).

Inductively coupled plasma-optical emission spectrometry (ICP-OES) and graphite furnace-atomic absorption spectroscopy (GF-AAS) were used as the laboratory standard for determining concentrations of the samples. These instruments were available at Tufts University and are standard methods for detecting low concentrations of metals in environmental samples.

Each of the methods tested is described below, beginning with test strips, then Hach kit, then photometer, and then electrode.

#### *Test strips*

Test strips are simple tools, cellulose-based solid pieces of paper that change color when exposed to the analyte of choice. The specific indicator chemicals are embedded within the cellulose matrix, and in the case of silver detection, these chemicals are trade secrets. They are likely some sort of organic compound which, when complexed with a silver ion, changes color. Test strips are available at both international technical and chemical suppliers and from photography suppliers, for varying concentration ranges. For this study, three different sets of test strips were purchased: one from Grainger Scientific for \$63.50/100 tests at 50-1000 ppb range, and two from CTL Scientific: one for \$18/100 tests for concentration less than 20 ppb (ug/L) and one for \$24.30/100 tests for 1-10 g/L. These were chosen due to their worldwide availability. Each



dilution as described above will be tested by placing several drops of solution on the test strip, allowing it to dry, and comparing it to the color charts provided.

### *Liquid Colorimeter*



Figure 5. Hach RapidSilver Visual Test kit with (L-R) filter box, forceps, 140 cc syringe and filter holder, 100 mL mixing bottle, and indicator reagent.

Liquid colorimetric technology works in much the same way as the test strips, with a color-change as the indicator of silver concentration. Again, the exact chemical indicator is a trade secret. The RapidSilver Visual Test Kit test was acquired from Hach Company for \$295.

This test uses a filter holder, 140 cc syringe, 100 mL mixing bottle, and solid reagents in single-use packets (Figure 5). First, open a filter holder, and then use tweezers to place a filter in the holder. Then reseal the filter holder, remove the plunger from the 140 cc syringe, and attach the filter holder to the syringe. Then pour 100 mL of the sample into the mixing bottle, and add one reagent packet to the bottle, cap and mix, pour the mixture in to the syringe, then

insert and depress the plunger, expelling the liquid in to a waste beaker.

Disassemble the syringe and filter holder and use tweezers to remove the filter and compare its color to the test chart.

### *Photometer*

Photometers work by measuring light that is able to penetrate a liquid sample, and comparing it against a blank sample, and calculate concentration of sample based on this difference. For silver detection, a photometer from Hanna Instruments equipped with a Tungsten lamp and a detector with a filter to detect at only 575 nm, which is presumably the wavelength at which silver, complexed with some chemical, absorbs. The photometer works by adding 1.0 mL of a trade secret indicator to 25 mL of both a blank sample (Millipore water) and the samples containing silver. Then 10 mL of the blank is added to a cuvette which is inserted into the photometer and read. According to the manufacturer, interferences can be caused by the ions listed in Figure 6 (Hanna, 2014).

#### **INTERFERENCES:**

Interference may be caused by:

$\text{Al}^{3+}$	above 30 mg/L	$\text{Fe}^{2+}$	above 1.5 mg/L
$\text{Ca}^{2+}$	above 1000 mg/L as $\text{CaCO}_3$	$\text{Fe}^{3+}$	above 10 mg/L
$\text{Cd}^{2+}$	above 20 mg/L	$\text{K}^+$	above 500 mg/L
$\text{Cl}^-$	above 8000 mg/L	$\text{Mn}^{2+}$	above 25 mg/L
$\text{CO}_3^{2-}$	above 1.5 mg/L	$\text{Mg}^{2+}$	above 1000 mg/L as $\text{CaCO}_3$
$\text{Cr}^{3+}$	above 20 mg/L	$\text{Na}^+$	above 5000 mg/L
$\text{Cr}^{6+}$	above 40 mg/L	$\text{Ni}^{2+}$	above 1.5 mg/L
$\text{Cu}^{2+}$	above 15 mg/L	$\text{Pb}^{2+}$	above 20 mg/L
$\text{F}^-$	above 20 mg/L	$\text{Zn}^{2+}$	above 30 mg/L

Figure 6. Interferences for Hanna Instruments photometer (Hanna, 2014).

### *Electrode*

Electrodes generally work by measuring the conductivity of the solution they are placed in. An ion sensitive electrode (ISE) can selectively detect certain ions, given different probes. A waterproof ISE was acquired from Hanna Instruments, that also contains a pH and temperature meter. This instrument is specifically designed for outdoor applications.. The interferences for the probe should be similar to that of the photometer (Figure 6).

## **Chapter Summary**

In this chapter, I discussed the background of silver as a antimicrobial agent in ceramic water filters, and the test methods available for testing silver in water. In the next chapter, I will present the manuscript of my thesis work as it will be submitted for publication.



# Chapter 2

## Introduction to Chapter

In this chapter of the thesis, I present the manuscript submitted for peer-review.

## Introduction

More than 663 million people worldwide do not have access to an improved water source (WHO/UNICEF 2014) and an estimated 1.2 billion more use drinking water at elevated risk of contamination at the source, or during collection, transport, or storage (Onda et al. 2012). Annually, 842,000 people die from preventable and treatable diarrheal diseases (UNICEF 2014). These diseases can be caused by drinking water contaminated with bacteria, viruses, and/or protozoa. Until such time as households are reached with piped, treated infrastructure water, a number of household water treatment (HWT) technologies, such as chlorine tablets and household filters, are being promoted to reduce this disease burden.

One promising HWT technology is the locally manufactured ceramic water filter (CWF) (Sobsey et al. 2008). CWFs are comprised of an approximately 10 liter (L) capacity filter that rests on its rim in a lidded receptacle. The receptacle serves as a safe storage container and is fitted with a tap for dispensing filtered water. Flow rate, generally recommended to be 1-3 liters per hour (L/hr), is the main quality control and manufacturing consistency indicator in the >50

filter factories worldwide (CMWG 2011). In the laboratory, filters effectively remove >99% of protozoan (Lantagne 2001) and 90-99.99% of bacterial organisms from drinking water (Lantagne 2001, Oyanedel-Craver and Smith 2008, Bielefeldt, Kowalski et al. 2010, Brown and Sobsey 2010, Lantagne, Klarman et al. 2010). In the field, CWF's have been shown to reduce diarrheal disease among users (Brown et al. 2008, Clasen and Haller 2008, Kallman et al. 2010).

Silver has been used for centuries as a disinfecting agent. Silver nitrate ( $\text{AgNO}_3$ ) dissolves in water to form silver ions ( $\text{Ag}^+$ ) which actively attack microbial proteins, DNA, and cell membranes (Li et al., 2008). Recently, commercial use of silver nanoparticles has increased dramatically over the past decade as its effectiveness as an antibacterial agent became documented and production of nanoparticles became less costly (Tolaymat et al. 2010). Silver nanoparticles are engineered structures with one dimension between 1 and 10 nanometers, large surface area, and high reactivity. Silver nanoparticles have been shown to: 1) damage cell membranes directly; 2) release  $\text{Ag}^+$ ; and, 3) form reactive oxygen species that also damage cells (Ivask et al., 2014.)

Painting, firing in, or dipping CWF with silver nanoparticles or silver nitrate has been shown to prevent microbiological growth within the filter media, increase bacterial inactivation, and maintain an acceptable level of silver residual in treated water (Oyanedel-Craver and Smith 2008). At the factory, it is necessary to balance the amount of silver applied to ensure prevention of microbiological growth and bacterial inactivation without exceeding the United States

Environmental Protection Agency's and World Health Organization's health-based recommended in drinking water silver maximum concentration of 0.1 mg/L (ATSDR 2011; WHO 2011).

The Ceramic Manufacturing Working Group (CMWG) currently recommends silver nanoparticles be used in ceramic manufacturing as nanoparticles have been shown to: 1) have a higher relative increase in bacterial reduction in filters than nitrate (2.5 log increase in *E. coli* reduction over filters without silver compared to 0.3 log increase) (Rayner 2013b); and, 2) more reliably maintain effluent waters safe for human consumption (Rayner et al. 2013a, Mittelman, 2013). However, some factories use silver nitrate because it is less expensive and locally available. In a survey of 18 factories, 15 factories reported using silver nanoparticles, and 3 reported using silver nitrate (CMWG 2011, Rayner et al. 2013a). Further, the CMWG recommends that 302 mg of 211 mg/L silver nanoparticle solution be applied to filters that have already passed flow rate and microbiological indicator quality control tests (CMWG 2011). Fully half of factories surveyed were using incorrect equations for mixing their silver applications (Rayner 2013a). Lastly, it was found that factories do not test: 1) the concentration of silver they apply; or, 2) the residual silver concentration from their filters. The CMWG does not currently recommend a test to confirm these application and residual silver concentrations.

There is a need to test application and residual concentrations of silver at the ceramic filter factories to ensure there is sufficient silver to prevent bacterial growth and increase microbiological inactivation, but not too much that effluent

water exceeds international guidelines for silver consumption. In this research, we investigated the accuracy, precision, ease-of-use, and cost of commercially available methods to test field relevant application and residual concentrations, using both silver nanoparticles and silver nitrate. The project aim was to develop silver quality control testing recommendation for ceramic filter factories.

## **Methods**

### **Testing Location**

The testing was conducted in the Environmental Sustainability Laboratory in the Civil and Environmental Engineering Department at Tufts University in Medford, Massachusetts.

### **Test Method Selection**

Potential test methods were identified by searching catalogs of known environmental testing equipment manufacturers and by Google search. Methods were excluded if a price quote could not be obtained or they could not be ordered. Test methods available include test strips, field test kits, ion-selective electrodes, and element-specific photometers from four suppliers: Hach Company (Loveland, CO, USA), Hanna Instruments (Woonsocket, RI, USA), Industrial Test Systems, Inc. (Rock Hill, SC, USA), and Machery-Nagel (Bethlehem, PA, USA). These six test methods included three test strips (Waterworks Silver Check II HR (“Waterworks”); Machery-Nagel Quantofix Silver (“Quantofix”); Machery-Nagel Silver Test Paper (“Machery-Nagel”)); one field test kit (Hach RapidSilver Visual



Test Kit (“Hach”)); one electrode (Hanna HI 98185 pH/ORP/ISE Waterproof Portable Meter (“electrode”)); and, one photometer (Hanna HI 96737 Silver Portable Photometer (“photometer”)) (Figure 7). Each of the identified test methods had a recommended range of silver they could test, which encompassed a large range from 0 mg/L-10 g/L (Table 1).



Figure 7. Six commercially available silver tests evaluated in this study.

a) Hach RapidSilver™ Silver Test Kit; b) Waterworks Silver Check II HR; c) Machery-Nagel Quantofix Silver Test Strips; d) Machery-Nagel Silver Test Paper; e) Hanna HI 98185 pH/ORP/ISE Waterproof Portable Meter; f) Hanna HI 96737 Silver Portable Photometer.

**Table 1.** Comparison of six silver test methods used in study.

	Short name	Measurement range (mg/L)	Measurement increment	Test method	Equipment Cost, Initial	Incremental Test Cost	TOTAL COST (100 tests)	TOTAL COST (1000 tests)
Waterworks Silver Check II HR	Waterworks	0.0-1.0	0, 0.005, 0.010, 0.025, 0.50, 1.0	Test strips	0	\$0.64	\$64	\$640
Machery-Nagel Quantofix Silver	Quantofix	1000-10000	0, 1000, 2000, 3000, 5000, 7000, 10000 mg/L	Test strips	0	\$0.97	\$97	\$971
Machery-Nagel Silver Test Paper	Machery-Nagel	20 limit	Presence/absence	Test strips	0	\$0.36	\$36	\$360.00
Hach RapidSilver™ Visual Test Kit	Hach	0-0.05	0, 0.005, 0.01, 0.025, 0.05	Test kit	\$285.00	\$2.68	\$285	\$2,965
Hanna HI 98185 pH/ORP/ISE Waterproof Portable Meter	Electrode	1.00 E <sup>-7</sup> - 9.99 E <sup>10</sup>	0.001 mV	Ion selective electrode	\$1,600.00	\$0.50	\$1,600	\$2,100
Hanna HI 96737 Silver Portable Photometer	Meter	0.00-1.00	0.001 mg/L	Photometer	\$882.00	\$3.02	\$882	\$3,902

\*The Hach, electrode, and photometer come with enough materials for 100, 500, or 150 tests respectively, after which additional supplies must be purchased.

## Test Solution Preparation

Solutions were prepared from two sources of silver: silver nanoparticle ‘Collargol’ Powder (Argenol Laboratories, Zaragosta, Spain), and silver nitrate (AlfaAesar, Ward Hill, MA). These sources were chosen because they are most commonly used by existing factories (CMWG 2011, Rayner 2013a). Silver nanoparticle solutions were confirmed to be nanoparticles by filtering solutions through 5 kDa centrifugal filters (Amicon 3k, Millipore, Billerica, MA) to separate silver nanoparticles from ionic silver in solution, and subsequently tested by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (7300 DV, Perkin Elmer, Waltham, MA).

The silver stocks were diluted in MilliQ (MQ) water (Millipore, Darmstadt, Germany) in two concentration ranges: 1) application concentrations from 100-1000 mg/L at 100, 200, 500, 700, 800, and 1000 mg/L silver; and, 2)

residual concentrations from 0.005-1.0 mg/L silver at 0.005, 0.01, 0.05, 0.1, 0.5 and 1.0 mg/L. Solutions were mixed in opaque plastic containers to reduce metal leeching from glass, and made daily to reduce the effects of nanoparticle aggregation.

## Laboratory Testing

Graphic furnace-atomic absorption spectroscopy (GF-AAS) (ThermoScientific, Waltham, MA) and ICP-OES in axial view mode were used to verify total silver (that is, the silver in nanoparticle form and in free ionic  $\text{Ag}^+$  form) concentration in the application (ICP-OES) and residual (GF-AAS) concentration ranges. Samples outside the instruments' ranges were diluted with MQ water but were otherwise unmodified. ICP-OES samples were introduced through a cross-flow nebulizer at 0.5 mL/min and silver concentrations were determined at 328.068 nm.

All identified test methods was used according to manufacturer's instructions, in quintuplicate at all silver concentrations and types, even if silver concentrations were outside manufacturer recommended ranges. To ensure consistency of stock silver solutions, testing was completed in one day for each silver type and concentration range.

Waterworks test strips (0.0-1.0 mg/L) were dipped in 250 mL of sample in beakers for 5 seconds, removed, and shaken once to remove excess water. After 10 seconds the color was compared to the chart on the bottle, from yellow (0 mg/L) to orange (1 mg/L).

A droplet of solution was applied to the Machery-Nagel test strip (lower limit 20 mg/L), which was allowed to dry. If the paper turned red or developed a ring around the drop location, silver was recorded as present.

Quantofix test strips (range 0.0-10,000 mg/L) were dipped in 10 mL samples for 1 second, shaken to remove excess liquid, then after 15 seconds were compared to a chart on the bottle ranging from yellow (0 g/L) to dark brown (10 g/L).

In the Hach test kit (range 0.0-0.05 mg/L), 100 mL of sample was mixed with a reagent package, added to a syringe, and pushed through a filter. The filter was removed from the syringe, and color change compared to the included chart from no color (white) (0.0 mg/L) to pink (0.005 mg/L) to blue (0.050 mg/L).

The electrode (range  $1.00 \times 10^{-7}$  -  $9.99 \times 10^{10}$ ) was calibrated before each test using fresh calibration standards for a five-point calibration at 0.1, 1, 10, 100, and 1000 mg/L. All samples tested with the electrode had 1 mL of ionic strength adjusting solution added per 50 mL of sample before testing, as per the instructions, to increase total ionic strength of the sample and thus remove background noise. The electrode was submerged in 50 mL of sample solution and gently swirled in the liquid; results were recorded from the digital readout in mg/L (ppm).

The photometer (range 0.0-1.0 mg/L) uses four proprietary solutions mixed with two 50 mL samples of solutions to create a “blank” and “sample”. Thus, the meter is not calibrated with a standard curve, but instead the comparison between the two solutions is used to calculate solution concentration. After setting

the blank solution, the “sample” is read and results from the digital screen are reported in mg/L (ppm).

## **Data Analysis**

Data were analyzed in Microsoft Excel 2010 with the Analysis ToolPak (Microsoft Corporation, Redmond, WA, USA) and R (R Foundation for Statistical Computing, Vienna, Austria). Accuracy was assessed by comparing the mean silver measurements across all concentrations for each test method to the GF-AAS or ICP-OES results using: 1) percent measurement error; and, 2) the Spearman rank correlation to determine if results differed at a 0.05 significance level and Spearman's  $\rho$  to rank closeness of fit (this is a nonparametric test of statistical dependence between ranked variables). Error was defined as low (<10% measurement error), medium (10-25% error), or high (>25% error) in analysis. Precision was assessed by calculating the standard error for readings at each concentration, and a composite mean percent measurement error was calculated for each test kit across all concentrations.

## **Cost**

Costs for test equipment were calculated by adding fixed equipment and reagent costs from the manufacturers' websites and purchase receipts, as of January 2015. Costs were calculated for 100 tests and 1,000 tests. Reported costs do not include shipping or handling.

## Volunteer Testing

Volunteers recruited at Tufts University conducted tests with each of the six test methods, recorded their results, and self-administered a survey about the experience in a testing period lasting 3.5 hours. Twelve water samples, six of silver nitrate and six of silver nanoparticle, at 0.2, 0.5, 1.0, 200, 500, and 1000 mg/L were prepared as described above and placed in opaque HPDE plastic bottles. To ensure sample concentrations were random and unknown to the participants and researcher, a random number generator was used to select 24 numbers. These numbers were assigned to samples; the key was stored electronically.

Six stations were set up containing: one test method; all necessary supplies; written instructions; three random samples of silver nitrate solutions; and, three random samples of silver nanoparticle solutions. Eleven volunteer participants conducted testing using all six test kits (with six samples per station), in duplicate, for a total of 72 tests conducted per volunteer.

Following the water testing, participants completed a questionnaire including both Likert-scale and open-ended questions about: 1) prior laboratory and water testing experience; 2) relative difficulty of test procedures; 3) confidence in the results; and, 4) which test kit they would recommend for a variety of contexts. Average measurement error and standard error were calculated as described above for these volunteer test results. Free and informed consent of the participants was obtained and approved by the Social, Behavioral,

and Educational Research Institutional Review Board at Tufts University (Protocol #1501043, July 2, 2015).

## Results

Silver nitrate solutions, made by weight, all were found to contain 20% less silver than intended. In silver nanoparticle solutions, it was found that 97-99% of all silver was contained within the nanoparticle matrix, and thus not free ions in solution. The three test strips and one test kit method evaluated all advertised they tested for “silver”, and did not distinguish between silver nanoparticles and silver nitrate. Both the electrode and the photometer advertised as testing for silver ions in solution.

In actual testing, all six test methods were inaccurate for silver nanoparticles, as evidenced by unreadable color changes. Waterworks test strips turned purple rather than orange or red; the Quantofix test strips turned orange rather than the expected brown; the Machery-Nagel test strips were deep purple rather than red; and, the Hach test kit turned black rather than pink or blue. Readable results were also not obtained from the electrode and photometer as solutions were all near zero in the electrode and were darker than the photometer’s maximum detection limit. Thus, all nanoparticle data is excluded from further analysis.

## Accuracy

All test methods were used to test all silver concentrations, regardless of manufacturer recommended testing range. We found all test kits had unusable data outside manufacturer recommended ranges. For the Waterworks test strip, application concentrations were all at the top of the range; Quantofix test strips at residual concentrations all read 0; Machery-Nagel test strips read 0 for residual concentrations; Hach test kit was unusable outside the manufacturer range of 0.05 mg/L; and the photometer was at its maximum or showed no data because solutions were too dark. Thus, only data within manufacturer recommended ranges is presented herein.

Each test kit had different ranges advertised by the manufacturer (Table 1), which did not overlap with the application or residual ranges required by ceramic filter manufacturers. Here we present the remaining data, including results from two methods at application concentrations and four methods at residual concentrations (Figure 8).

For application concentrations, the electrode had a composite measurement error of 13% (range 3-39%) with Spearman's  $\rho=0.898$  ( $p<0.001$ ). The presence/absence Machery-Nagel test strips, with a lower detection limit of 20 mg/L silver, had no sample in the application range (0-1000 mg/L) produced a detectable result.

For residual concentrations, the Waterworks test strip had composite measurement error of 93% (range 50-100%) with Spearman's  $\rho=0.764$  ( $p=0.027$ ); the Hach test kit had composite measurement error of 66% (range 5-100% for 0-



0.05 mg/L solutions) with Spearman's  $\rho=0.932$  ( $p<0.001$ ); the electrode had composite measurement error of 84% (range 15-100%) with Spearman's  $\rho=0.873$  ( $p<0.001$ ); and, the photometer had composite measurement error of 75% (range 8-89%) with Spearman's  $\rho=0.939$  ( $p<0.001$ ). The presense/absence Machery-Nagel test strips showed silver in every concentration in this range. Based on these results, the photometer was the most accurate test for residual concentrations.

## **Precision**

Precision varied somewhat among the test methods (Figure 8). For application concentrations, standard error ranged from 0.4-11.4 mg/L (for concentrations from 0-1000 mg/L). For residual concentrations, standard error was below 0.01 mg/L for all concentrations and all methods except Waterworks, which had a standard error of 96.7 mg/L at the 500 mg/L concentration only.

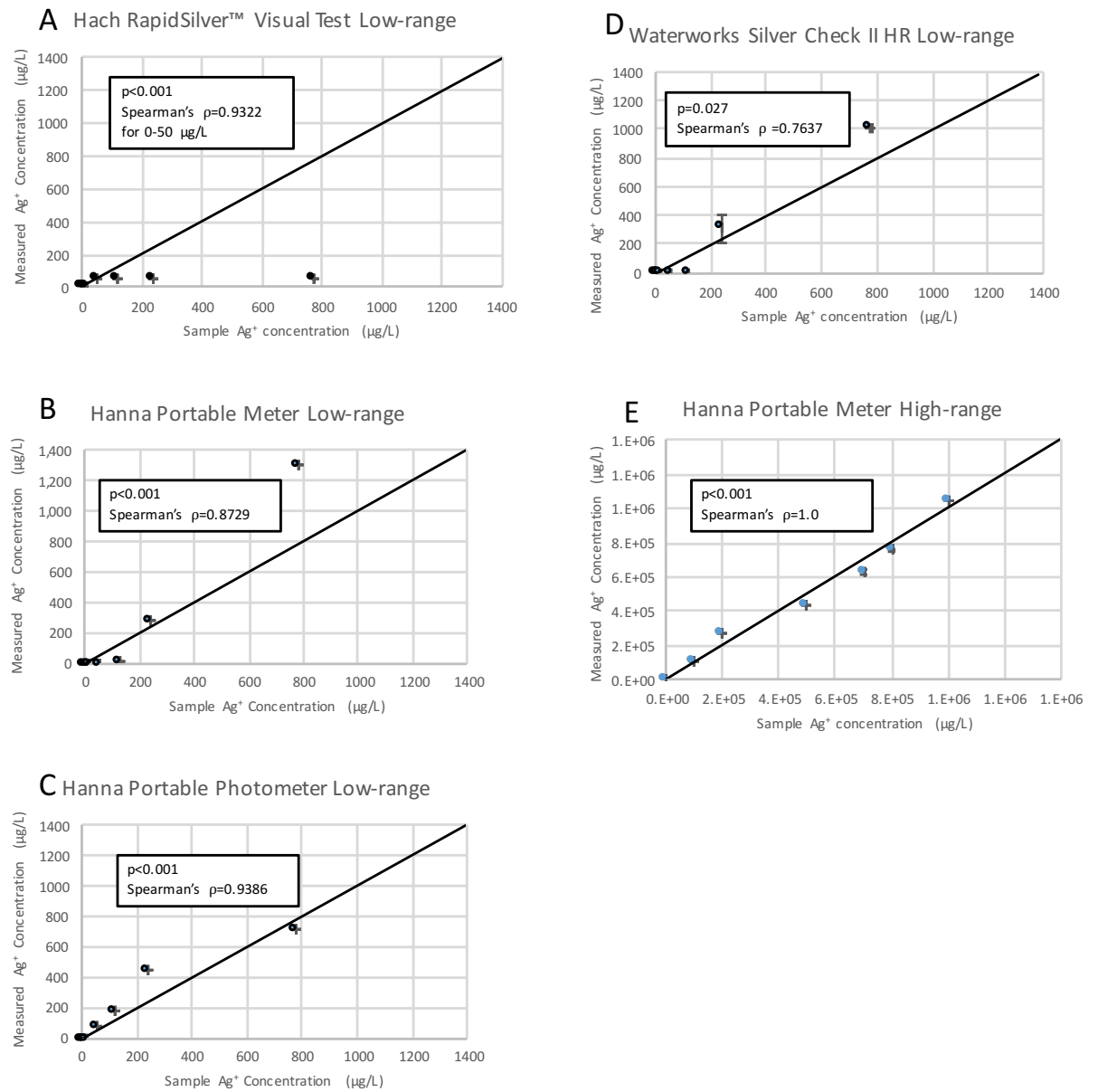


Figure 8. Average laboratory measurements for silver nitrate with 95% CI error bars.

For residual range: A: Hach, B: electrode, C: photometer, D: waterworks. For application range: E: electrode.

## **Cost**

Three tests have fixed equipment costs: Hach, photometer, and electrode, and each is initially supplied with enough reagents for 100, 150, or 500 tests, respectively (Table 1). The three test strip methods contain only consumables. For 100 tests, costs ranged from 36-1600 USD: 36 USD for Machery-Nagel, 64 USD for Waterworks, 97 USD for Quantofix, 285 USD for Hach, 882 USD for photometer, and 1600 USD for the electrode. For 1000 tests, costs ranged from 640-3902 USD: 360 USD for Machery-Nagel, 640 USD for Waterworks, 970 USD for Quantofix, 2965 USD for Hach, 2100 USD for photometer, and 2902 USD for the electrode.

## **Usability – volunteer testing**

Eleven Tufts University undergraduate and graduate students participated in volunteer testing (Table 2). Eighty-two percent of participants (9/11) reported some general lab experience, and 36% (4/11) reported prior lab experience testing for water quality parameters. Of those who had water testing experience, 50% (2/4) self-reported a beginner level, 25% (1/4) an intermediate level, and 25% (1/4) an expert level of experience.

Participants found the Quantofix test strips easiest to use and the Hach test kit most difficult (Table 2). All participants reported that test strips using color-change charts (Waterworks and Quantofix) were “simple,” “quick,” and/or “easy.” The Machery-Nagel Silver Test Paper was described as “confusing” (7/11), and participants did not think the presence/absence results provided

sufficient information. The Hach test kit was described as the most difficult because of the physical difficulty of pushing the liquid in the syringe through the filter membrane. The electrode was ranked as having low difficulty and participants were confident in the results; however, 73% (8/11) of participants reported it was difficult to know the exact number to report due to readout drift. Participants reported the photometer was “easy to mess up” (5/11) and “took a long time” (5/11). Participants were confused by false-color silver nanoparticle readings on paper test strips.

Participants reported the most confidence in the results from the electrode (6/11), and recommended the photometer (6/11), electrode (3/11), or Quantofix (2/11) tests for trained users. For untrained users, participants recommended Quantofix test strips (5/11), electrode (3/11), Waterworks test strips (2/11), and the photometer (1/11).

Accuracy varied for volunteer testers: 21-100% for Waterworks, 50-100% for Quantofix, 30-100% for Hach, 7-70% for the electrode, and 18-100% for the photometer. We did not identify a correlation between difficulty and accuracy ( $R^2=0.047$ ).

**Table 2.** Summary of volunteer testing questionnaire responses to several questions about test method usability (n=11, except where indicated).

	Difficulty of Test Procedure <sup>1</sup>		Confidence in Test Results <sup>2</sup>		Easiest <sup>3,7</sup> (Frequency)	Most Confident <sup>4</sup> (Frequency)	Choice for use by trained testers <sup>5</sup> (Frequency)	Choice for use by untrained testers <sup>6</sup> (Frequency)
	Ave (Min, Max, SD)	Max	Ave (Min, Max, SD)	Max				
Waterworks Silver Check II HR	1.9 (1, 3, 0.8)	3	2.7 (1, 5, 1.1)	5	2	0	0	2
Machery-Nagel Quantofix Silver	1.1 (1, 2, 0.3)	2	3.5 (2, 5, 1.1)	5	9	2	2	5
Machery-Nagel Silver Test Paper	2.3 (1, 4, 1.0)	4	2.0 (1, 4, 1.0)	4	0	1	0	0
Hach RapidSilver™ Visual Test Kit	4.6 (4, 5, 0.5)	5	2.3 (1, 3, 0.8)	3	0	0	0	0
Hanna HI 98185								
pH/ORP/ISE Waterproof Portable Meter	2.8 (1, 4, 1.0)	4	4.0 (1, 5, 1.3)	5	0	6	3	3
Hanna HI 96737 Silver Portable Photometer <sup>8</sup>	3.8 (3, 5, 0.8)	5	4.1 (2, 5, 0.9)	5	0	2	6	1

Notes:

1. "Indicate the difficulty of each test procedure on a scale of 1-5, where 1 is the simplest and 5 is the most difficult."
2. "Indicate your confidence level in each test's results on a scale of 1-5, where 1 is least confident and 5 is the most confident."
3. "Which test did you find to be the easiest to perform today?"
4. "Which of the test results are you most confident in?"
5. "If you were to receive silver test results from a laboratory in the United States, which test would you be most confident receiving results from?"
6. "If you were to train local people in a developing country to take silver measurements and report them to you, which test would you be most confident receiving results from?"
7. n=6
8. n=9

## Discussion

We compared six commercially available silver test methods, including three test strips, a test kit, a portable electrode, and a portable photometer, in terms of accuracy, precision, ease-of-use, and cost. No method provided readable results to test for silver nanoparticle concentrations, and only the Hanna electrode was appropriate for both application and residual concentrations necessary for testing in ceramic filter factories. Accuracy in the laboratory varied between 4-100%, with the electrode as most accurate across both concentration ranges. Four of six test methods, including the electrode, were found to be precise. Volunteer users had concerns with all test methods and were confused by the silver nanoparticle results; however, they reported that test strips were easiest to perform, and were most confident in results from the photometer and electrode. Costs ranged from 18-1600 USD for 100 tests, with the electrode the highest cost. Thus, the only method that was found to be accurate and precise across all application and residual concentrations (for silver nitrate only, not considering silver nanoparticles) was the electrode, which was also difficult to use and extremely high cost. As such, we found that there is not a clear recommendation for testing silver.

Given the current available options, developing application and residual concentration silver quality control testing recommendations for ceramic filter factories is difficult. Only the electrode worked for both ranges of silver nitrate unmodified, but it is expensive and difficult to use, requiring personnel with some laboratory training and access to clean, silver-free water. This is outside the

capacity of most ceramic filter factories. The photometer and Hach test kit could be appropriate for both concentrations ranges of silver nitrate; by diluting high range samples to a measurable concentration. However, this requires users to accurately dilute samples with clean, silver-free water, raising ease-of-use concerns, in addition to other cost concerns. If factories would like to test immediately, interim recommendations for residual concentrations of silver nitrate only, to ensure filter effluent water is safe to drink, include: 1) the Hach test kit to determine silver concentrations up to 0.05 mg/L (or with dilution higher), or 2) the less accurate but much less expensive Waterworks test strip. For application silver nitrate concentrations, a test method could not be recommended.

More importantly, our research findings indicate the need for additional development of appropriate test methods, particularly for testing silver nanoparticle concentrations. A severe limitation of the results is no test method produced readable results with silver nanoparticles, the most widely used form of silver in ceramic manufacturing. In the laboratory, specialized instruments such as particle counters or single-particle inductively coupled plasma-mass spectroscopy (ICP-MS) are used to directly measure nanoparticles. Total silver (nanoparticles and ion together) can be tested in the laboratory by digesting the silver nanoparticles to silver ion using concentrated acid, high heat, and increased pressure, followed by using particle counters or ICP-MS. In resource-limited contexts such as ceramic filter factories, these methods are not feasible. Despite several test methods that we evaluated having steps where solutions were mixed with proprietary digestion solutions or indicators (such as the Hach test kit and

Hanna photometer) it appeared no test method was able to dissociate the nanoparticles from the matrix to test silver in solution. We thus recommend further research and development in three areas with potential.

First, we recommend working with the existing test strips and kit manufacturers to determine if: 1) color charts could be accurately developed for the color changes seen with silver nanoparticles; and, 2) a new method could be developed that is an inexpensive presence/absence test strip to ensure residual silver concentrations in filter effluent is  $<0.1$  mg/L, the EPA and WHO recommended limit.

Secondly, we recommend development of a colorimetric field test kit or strip specific to application concentrations of the predominantly-used silver nanoparticle manufacturer, Argenol (Zaragosta, Spain), in existing ceramic filter factories, or developing procedures for digesting Argenol in the field to encourage silver nanoparticle dissolution into silver nitrate. Development of this field tests could be applicable more broadly as well, as the increased nanoparticle use in manufacturing and industry is leading to environmental releases and the subsequent need for environmental testing (Tolaymat et al. 2010).

Thirdly, despite these test methods not being appropriate for silver nanoparticles, they may still be usable for ceramic filter manufacturers. Previous research has documented that effluent from test silver nanoparticle-treated ceramic disks is 90% silver ions, which is able to be detected by the methods appropriate for silver nitrate studied herein (Mittelman, 2013). However, in Mittelman et al's work, only six filter recipes using only one clay source were



tested. It is unclear that the 90% silver ion effluent concentration would be consistent across various the raw materials used in the >50 factories worldwide, and all the various filter recipes used therein. Additional research comparing effluent concentration nanoparticles to ions ratios in multiple filter types is necessary to assess the possibility of using only silver nitrate test kits for residual concentrations of silver.

This study had various limitations including: 1) potential bias in laboratory measurements due to reliance on subjective visual color matching and solution concentration being unblinded to the researcher; 2) volunteer testing results should be cautiously interpreted, since all participants, were relatively well-educated university students many of whom had previous laboratory experience; and, 3) all solutions were made using MQ water at a neutral pH and low ionic strength and not with real waters. In many places these test methods may be used, water will have varied pH or high ionic strength and these factors will likely change the chemistry of many of the test methods (Mittelman 2013). While the data needs to be understood in light of the limitations, the data and recommendations remain valid, as several silver test kits were evaluated over a wide range of concentrations, accuracy was evaluated by several different measures, and volunteer test participants provided valuable data on measurement accuracy and quantitative information on ease-of-use for users new to water quality testing.

## Conclusions

Overall, while we were unable to achieve our project aim of developing application and residual silver quality control testing recommendations for ceramic filter factories, we did complete research that identified critical needs in silver testing method research and development. We provided interim recommendations for ceramic filter factories interested in beginning to test silver concentrations, although these results were limited by the lack of any simple-to-use, inexpensive test methods that are able to test both application and residual concentrations. As increased commercial use of silver nanoparticles is causing environmental releases, the lack of commercially-available test methods to accurately test silver nanoparticle concentrations is critical to address. We recommend new tests be developed to address both a targeted range of silver nanoparticle and silver nitrate concentrations applicable to both ceramic water filter manufacturers and the broader nanoparticle community.

## Chapter 3: Discussion

### Decision Matrix

Originally, a decision matrix was developed as a tool for determining which silver test method was appropriate for testing silver in water in CWF manufacturing facilities. However, this matrix was not straightforward and usable, so it is not included in the submitted paper manuscript, though it is included here.

Each test method was rated 0, 1, or 2 (where a lower number is more favorable) in each of five categories: 1) accuracy; 2) precision, 3) usability – difficulty; 4) usability – confidence; and, 5) cost. Accuracy was ranked using the laboratory data, by deviation from the laboratory tested standard. Precision was ranked by the mean composite measurement error across all doses, considering laboratory and volunteer test results. Method difficulty and confidence in results were ranked according to the mean reported values from volunteer testing questionnaires. Cost was ranked on the total equipment and reagent cost for performing 1,000 tests. Values were summed, and the tests were ranked according to the total score, with a lower score more favorable (Table 3).

**Table 3.** Summary of recommended silver test methods considering accuracy, usability, and cost. Each category is ranked as 0, 1, or 2, where low numbers are more favorable.

	Accuracy, lab	Accuracy, volunteer	Difficulty, volunteer	Confidence, volunteer	Cost	Total	Rank
Hach RapidSilver™ Visual Test Kit	0	0	2	1	1	4	4
Waterworks Silver Check II HR	1	1	0	1	0	3	1
Machery-Nagel Silver Test Paper	2	1	1	1	0	5	5
Hanna HI 98185 pH/ORP/ISE Waterproof Portable Meter	1	2	0	0	0	3	1
Hanna HI 96737 Silver Portable Photometer	0	0	1	0	2	3	1
	0	1	2	0	2	5	5

Based on the available data, [presented above in Table 3, we](#) found that the Hach kit may be appropriate for testing low concentrations of silver nanoparticles for ceramic filter factories, since it uses packets of solid reagents rather than liquids, does not rely on complicated procedures to perform, and comes packaged in a field-safe toolbox-style kit. For settings with more resources, the portable photometer or electrode may be appropriate for all concentrations of silver nitrate, if there was availability of resupply for liquids and trained operators. However, both the photometer and electrode require clean, silver-free water (such as bottled water) to make standards or blank solutions, which may not be available. It should be noted that each category is weighted equally in the decision matrix, and we recommend decision makers adapt category weights to their specific context: 1) whether the kits are actually appropriate for their silver source; 2) accuracy and precision required; 3) who will be performing the tests and how they will be trained; 4) how many readings will be made; 5) the available budget; and 6)

project location in terms of equipment portability and availability of replacement parts and liquid or powder reagents.

## **Final Conclusions**

While the results of this project were not as straightforward as I may have expected or wished, useful information was obtained nonetheless. A silver nanoparticle field test is critical to develop both for ceramic filter factories and for use in waterways near industrial areas where nanoparticles are used in manufacturing.

# Appendix A: Lab Protocol/Thesis Proposal

## Comparison of Silver Tests Accuracy and Precision

Rhiana Meade

---

### Objective

The objective of this study is to compare field test methods used to test silver concentration in potable water after application to ceramic filters to recommend an appropriate test for use by ceramic filter manufacturers and purchasers in developing countries.

### Background

Access to safe drinking water is a critical issue in many developing countries. Annually, 1.8 million people die from preventable and treatable diarrhea diseases (UNICEF, 2009), and it is estimated that nearly one billion people worldwide do not have access to clean water. These diseases are caused by drinking water contaminated with bacteria, viruses, or protozoa. To combat this problem, a number of point-of-use water treatment technologies - such as chlorine tablets or household filters - have been developed and deployed around the world.

Ceramic filters are one readily available and widely used technology. They are locally manufactured in over 30 countries (The Ceramics Manufacturing Working Group, 2011). Their porous structure allows water to flow through, while trapping contaminants within its matrix. Painting, firing in, or dipping filters with

silver nanoparticles or silver nitrate further enhances the antimicrobial properties of these filters and prevents growth within the filter itself. Silver discharge from filters over time is a major concern in terms of risk to human health and loss of antimicrobial properties. In general, silver has a minor effect on human health, but long-term exposure can discolor skin and damage tissues (ATSDR, 2011). Over time, the antimicrobial effects of silver applied to ceramic filters declines (Bielefeldt et al., 2009).

While methods to standardize the construction and application of silver to the filters have been produced, there is little known about the accuracy of field methods to test the concentration of silver both in the silver mix and the filter effluent (The Ceramics Manufacturing Working Group, 2011). This project aims to quantify the accuracy, precision, and usability of these methods for both silver nitrate and silver nanoparticle concentrations. A variety of methods are available for testing, from inexpensive test strips to more complicated meters and laboratory instrumentation (Table 1, Table 2).

Potential test methods were found by searching the catalogs of known manufacturers of environmental test methods (Hach, Hanna Instruments, etc.) for silver tests for the concentrations desired. Tests for both high-range and low-range concentration are needed for two purposes: first to assess the concentration of silver that is painted on, dipped, or fired in, and second, to assess the silver concentration in silver effluent. A simple Google search yielded commercially available test strips designed for use by photographers for determining silver concentrations in their developing solutions. Kits were excluded if they were not readily available from reliable distributors or if a price quote could not be obtained. Total cost to purchase these kits and supplies is \$2814.

Table 1. Potential silver test methods to be studied.

<b>Manufacturer</b>	<b>Type of test</b>	<b>Range</b>	<b>Cost \$/100 tests</b>	<b>Reference</b>
Hach	Liquid colorimetric	5-50 ppb	258	<a href="http://www.hach.com/rapidsilver-visual-test-kit/product?id=7640218480">http://www.hach.com/rapidsilver-visual-test-kit/product?id=7640218480</a>
Grainger	Test strips	50-1000 ppb	63.5	<a href="http://www.grainger.com/product/INDUSTRIAL-TEST-SYSTEMS-Test-Strips-3UCW8">http://www.grainger.com/product/INDUSTRIAL-TEST-SYSTEMS-Test-Strips-3UCW8</a>
CTL Scientific/ Machery-Nagel	Test strips	Limit 20 ppm	18	<a href="http://www.ctlscientific.com/cgi/display.cgi?item_num=90732">http://www.ctlscientific.com/cgi/display.cgi?item_num=90732</a> <a href="http://www.mn-net.com/tabid/10457/default.aspx">http://www.mn-net.com/tabid/10457/default.aspx</a>
Hanna Instruments	Electrode		\$1926	<a href="http://www.hannainst.com/usa/prods2.cfm?id=028002&amp;ProdCode=HI%2098185">http://www.hannainst.com/usa/prods2.cfm?id=028002&amp;ProdCode=HI%2098185</a>
Hanna Instruments	Photometer	0-1000 ppm	\$518	<a href="http://www.hannainst.com/usa/prods2.cfm?id=009001&amp;ProdCode=HI%2096737">http://www.hannainst.com/usa/prods2.cfm?id=009001&amp;ProdCode=HI%2096737</a>

Table 2. Test kits for high-concentration samples.

<b>Manufacturer</b>	<b>Type of test</b>	<b>Range</b>	<b>Cost \$/100 tests</b>	<b>Reference</b>
Machery-Nagel	Test strip	0-10g/L	30.20	<a href="http://www.mn-net.com/Testpapers/QUANTOFIXteststrips/QUANTOFIXSilber/tabid/12047/language/en-US/Default.aspx">http://www.mn-net.com/Testpapers/QUANTOFIXteststrips/QUANTOFIXSilber/tabid/12047/language/en-US/Default.aspx</a>



**Testing location**

The testing will be conducted in the Environmental Sustainability laboratory, classroom, and exterior locations at Tufts University in Medford, Massachusetts.

**Testing Procedure**

Two sources of silver are regularly used by ceramic filter manufacturers: silver Collargol powder from Argenol Laboratories (imported from Spain) and locally-manufactured silver nitrate solutions. Two different ranges of concentrations will be tested to mimic both potential influent and effluent silver concentrations. Influent concentrations will be made up in six concentrations from 0.1 to 1 g/L at 0.1, 0.2, 0.5, 0.7, 0.8, and 1 g/L. These concentrations mimic the range of silver that are painted, dipped, or fired into ceramic filters (CMWG, 2011). Influent samples will be diluted to the range of each testing method required. Effluent samples will be made up in seven concentrations from 0.002 to 1 mg/L at 0.001, 0.005, 0.01, 0.05, 0.1, 0.5, and 1 mg/L. These concentrations mimic the maximum silver concentrations found eluted from ceramic filters (CMWG, 2011). With 13 concentrations tested in quintuplicate with 10% duplicated, 72 tests are required of each method, except for the high-range test strips which will only be used at 6 concentrations. At least 100 tests from each method will be purchased to allow for testing by volunteers.

**Procedure I: Collargol solution preparation**

A stock Collargol solution at 1 g/L will be prepared from solid powder and Millipore water. The remaining concentrations will be made from serial dilutions of this stock fresh before each testing period.

**Equipment required:**

- Silver Collargol powder from Argenol Laboratories

- Pipette
- Pipette tips
- Millipore Water
- Plastic containers

#### **Procedure II: Silver nitrate solution preparation**

A stock silver nitrate solution at 1 g/L will be prepared from solid nitric acid silver salt (Sigma-Aldrich) and Millipore water. The remaining concentrations will be made from serial dilutions of this stock fresh before each testing period.

#### **Equipment Required:**

- Laboratory-grade silver nitrate powder
- Pipette
- Pipette tips
- Millipore Water
- Plastic containers

#### **Procedure II: ICP-OES Silver analysis**

Silver will be analyzed via inductively-coupled plasma-optical emission spectroscopy (ICP-OES) (7300 DV, Perkin Elmer) run in axial view mode. Silver will be detected at a wavelength of 328.068. The detection limit reported by users is 0.01 mg/L. Samples will be introduced without modification from the state they will be used for the field tests.

**Procedure V: Test strip analysis (Machery-Nagel (2 kinds) and Grainger)**

Silver will be analyzed via the three test strips per manufacturer's instructions (to come).

**Procedure IV: Hach Colorimeter Analysis****Procedure V: Hanna Electrode Analysis****Procedure VI: Hanna Photometer Analysis****Volunteer Test Subject Focus Group**

Volunteer Tufts University undergraduates will be given written instructions on how to perform each silver test, and will test water samples with each kit. Three sample concentrations of silver nitrate and three sample concentrations of silver nanoparticles will be provided. Each water concentration sample will be tested in duplicate with each test method. Following the testing, the volunteers will take a survey to answer questions about the testing procedures. The exact test method and concentrations of silver will be determined prior to the volunteer testing. Testing will take place in the Environmental Sustainability Unit Operations room, and all volunteers will wear personal protective equipment (goggles, gloves, and lab coats). Institutional Review Board approval for working with human subjects will be obtained.

**Waste Disposal Procedure**

Silver waste will be disposed in labeled containers in designated waste areas compliant with Tufts Environmental Health and Safety and Clean Harbors. Material Safety Data Sheets will be filed in the laboratory.

**Analysis Procedure**

Data will be entered into Excel and analyzed in Excel and Stata. To address accuracy, the percent measurement error will be calculated for mean readings at each dose, and a composite mean percent measurement error will be calculated for each test method across all doses. Error will be defined as low (< 10% measurement error), medium (10-25% error), or high (> 25% error). To address precision, the set of mean silver measurements across all doses for each test method will be compared to that of a to-be-determined reference method using a nonparametric test for equality of medians in a paired sample, the Wilcoxon signed rank test, to determine if the results differ at a

0.05 significance level. Usability will be addressed from results from the focus group; cost will be analyzed based on purchase price. Using all four criteria, a decision matrix to determine which test method is most appropriate to be used by ceramic filter manufacturing facilities and purchasers of ceramic filters will be developed.

## References

- Bielefeldt, A.R., Kowalski, K., Summers, R.S. (2009). Bacterial treatment effectiveness of point-of-use ceramic water filters. *Water Res.* 43 (14) 3559-65.
- Cheng, W., Stuart, E.J.E., Tschulik, K., Cullen, J.T., and R.G. Compton. (2013). A disposable sticky electrode for the detection of commercial silver NPs in seawater. *Nanotechnology* 24 505501.
- Oyanedel-Craver, V.A. and J.A. Smith. (2008). Sustainable colloidal-silver-impregnated ceramic filter for point-of-use water treatment. *Environ. Sci. Technol.* 42 927-933.
- Sobsey, M.D., Stauber, C.E., Casanova, L.M., Brown, J.M., and Elliott, M.A. (2008). Point of use household drinking water filtration: a practical, effective solution for providing sustained access to safe drinking water in the developing world. *Environ. Sci. Technol.* 42 4261-4267.
- The Ceramics Manufacturing Working Group (2011). Best Practice Recommendations for Local Manufacturing of Ceramic Pot Filters for Household Water Treatment, Ed. 1. Atlanta, GA, USA: CDC.
- Tschulik, K., Palgrave, R.G., Batchelor-McAuley, C., and R.G. Compton. (2013). 'Sticky electrodes' for the detection of silver nanoparticles. *Nanotechnology* 24 295502.
- UNICEF/WHO. Diarrhoea: Why Children Are Still Dying and What Can Be Done; Jensen, L., Ed.; The United Nations Children's Fund (UNICEF)/World Health Organization (WHO), 2009.  
Available  
at [http://whqlibdoc.who.int/publications/2009/9789241598415\\_eng.pdf](http://whqlibdoc.who.int/publications/2009/9789241598415_eng.pdf)
- Zhou, Y-G., Rees, N.V., and R.G. Compton. (2011). The electrochemical detection and characterization of silver nanoparticles in aqueous solution. *Angew. Chem. Int. Ed.* 50 4219-4221.

# **Appendix B: Volunteer Protocol**

## **Comparison of Silver Concentration Tests**

### **Focus Group Protocol**

**Rhiana D. Meade**

Tufts University Department of Civil and Environmental Engineering

---

#### **OBJECTIVE**

The purpose of the volunteer focus group testing portion of the study is two-fold:

1. To determine how silver concentration test results for a variety of test types may be influenced by the individual performing the test, and
2. To determine the relative ease-of-use of each of five types of silver concentration testing.

This evaluation will measure the accuracy and repeatability of test results (readings of silver concentration) by different volunteer test subjects. After performing the tests, the volunteer subjects will also indicate the relative simplicity or difficulty of each test procedure, and their confidence in the test results.

Ten volunteer test subjects, who may be either experienced or inexperienced in water testing and laboratory work, will perform the testing procedures in a “focus group” setting.

#### **BACKGROUND**

Silver is commonly painted on ceramic filters used to treat drinking water in developing countries. It is applied either as silver nanoparticles or as silver nitrate solutions.

Following the application of silver to the filters, there is a concern about silver discharge from filters over time. This is a major concern in terms of risk to human health and loss of antimicrobial properties. In general, silver has a minor effect on human health, but long term exposure can discolor skin and damage tissues (ATSDR, 2011). Over time, the antimicrobial effects of silver applied to ceramic filters declines (Bielefeldt et al., 2009). While methods to standardize the construction and application of silver to the filters have been produced, there is little known about the accuracy of field methods to test the concentration of silver both in the silver mix and the filter effluent (The Ceramics Manufacturing Working Group, 2011).

A variety of methods are available for testing, from inexpensive test strips to more complicated meters and laboratory instrumentation. This focus group will test four different types of tests: a liquid colorimetric test, two kinds of test strips, an electrode, and a photometer. These methods vary in cost from the inexpensive (Machery-Nagel test strips at \$18/100 tests) to the expensive (Hanna Electrode, \$1926 total cost). Most of these tests, excepting the electrode, depend on a color change to indicate silver concentration.

This protocol is one piece of a study, which also includes laboratory work that is not human subjects research. The goal of the entire study is to recommend which of these silver field tests is most appropriate for testing drinking water in developing countries. The study aims to quantify accuracy, precision, and usability of these methods.

The purpose of this focus group portion of the study is to determine the relative ease of performing the different tests, and also to measure the effect of different users on the accuracy and precision of test results. The volunteers, who may not have experience with water testing, will provide written feedback on the tests and their preference for which they would prefer to use. The following five test types will be compared in this study for solutions of both silver nitrate and silver nanoparticles:

- Liquid Colorimetric (Hach)
- Test strips (Grainger)
- Test strips (Machery-Nagel)
- Electrode (Hanna)
- Photometer (Hanna)

## **TESTING LOCATION AND PARTICIPANT RECRUITMENT**

Volunteers will be solicited through an email sent to Tufts University graduate and undergraduate students, and a flier posted on the campus (see attachment). As this study is targeted towards Tufts students, it is not anticipated that non-English speakers will respond. Study participants will receive a \$50 gift card as compensation for their participation.

The focus group testing session will last approximately three hours and will be held in the Environmental Sustainability Lab Operations room which acts as a laboratory classroom in Anderson Hall on the Tufts University Medford Campus. No hazardous chemicals will be used in this test, and the procedure poses no health or safety risks to participants. Participants will wear personal protective equipment in the form of nitrile gloves, safety glasses, and lab coats as is procedure in this laboratory.

### *TESTING PROCEDURE*

The volunteer testing session will proceed in a “focus group” format, where all volunteers are present at the same time. The procedure will be as follows:

1. The participants will be presented with and asked to sign an Informed Consent to Participate in Research Form, including a photo and video release (see attachment).
2. The participants will be briefed with an oral explanation of water disinfection using silver-painted ceramic filters; and discussion of why silver testing in drinking water is important. They will also be presented with a brief introduction to the six test types.
3. The room will be set up with 5 stations (one per test type), labeled “A” through “E”.

Each station will have the following items:

- Six sets of one type of silver test method
- Three copies of test instructions for that method, as provided by the test manufacturer (see attachment)
- Six containers of sample water, labeled “Sample 1,” “Sample 2,” “Sample 3,” “Sample 4,” “Sample 5,” and “Sample 6.”

Each container will contain 1 Liter of sample water with silver nitrate concentrations verified in the laboratory prior to the testing session. Concentrations will be as follows:

- Sample 1: 0.001 mg/L silver nitrate
  - Sample 2: 0.05 mg/L silver nitrate
  - Sample 3: 1 mg/L silver nitrate
  - Sample 4: 0.001 mg/L silver nanoparticles (as Collargol powder)
  - Sample 5: 0.05 mg/L silver nanoparticles (as Collargol powder)
  - Sample 6: 1 mg/L silver nanoparticles (as Collargol powder)
  - One 5-gallon plastic bucket for collecting waste water
  - One roll of paper towels
4. Participants will each be given a test results collection sheet for recording their results (see attachment).



5. Participants will be asked to go to one of the five stations throughout the room.
6. Using the written test protocol instructions provided, participants will individually perform the test for silver concentration on the three doses of sample water.
  - a. All tests shall be done in duplicate.
  - b. Participants will dispose of the tested water in the plastic buckets provided on each table.
  - c. Participants will record the silver test results on their own sheet of paper (attached)
7. Upon completing the tests at one station, participants will move to another station, in no particular order, until all tests have been completed (for a total of 30 measurements).
8. Photo and video may be taken of the participants as they perform the water testing procedures.
9. Upon completion of the full testing regime, participants will fill in a survey about the relative ease of each testing procedure and confidence in the results (see attachment).
10. Test results and survey forms will be collected together.
11. Participants will be given a \$50 gift card as compensation for their participation.

### *Supplies Needed*

- 10 Informed consent forms (per test subject)
- 10 Test results recording sheets (per test subject)
- 10 Post-testing survey forms (per test subject)
- Silver residual test methods (3 of each)
- 3 copies of instructions for performing each test
- 36, 1-liter containers of samples of water to be tested (6 of each sample)
- Five 5-gallon plastic buckets for waste water (one per table)
- 10 Pens
- 6 rolls of paper towels

## Appendix 3: R Code

Sample: residual range statistics:

```
> statslow1<-read.csv(file.choose())
>attach(statslow1)
  >statslow1.hach<-subset(statslow1,testkit1==2)
> statslow1.waterworksnitrate<-subset(statslow1,testkit1==3)
> statslow1.quantofixnitrate<-subset(statslow1,testkit1==4)
> statslow1.electrodenitrate<-subset(statslow1,testkit1==5)
> statslow1.photometernitrate<-subset(statslow1,testkit1==6)
> statslow1.waterworksnano<-subset(statslow1,testkit1==7)
> statslow1.electrodenano<-subset(statslow1,testkit1==8)
> statslow1.photometernano<-subset(statslow1,testkit1==9)
  >

cor.test(statslow1.electrodenitrate$meanlabAg1,statslow1.electrodenitrate$Aas1,method='spearman')
```

# References

- Agency for Toxic Substances and Disease Registry (ATSDR) (2011).  
Toxicological Profile for Silver.  
<http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=539&tid=97>
- Bielefeldt, A.R., Kowalski, K., Summers, R.S. (2009). Bacterial treatment effectiveness of point-of-use ceramic water filters. *Water Res.* 43 (14) 3559-65.
- Brown, J., Sobsey, M.D. and Loomis, D. (2008) Local Drinking Water Filters Reduce Diarrheal Disease in Cambodia: A Randomized, Controlled Trial of the Ceramic Water Purifier. *Am. J. Trop. Med. Hyg.* 79(3): 394-400.
- Brown J, Sobsey M. (2010) Microbiological effectiveness of locally produced ceramic filters for drinking water treatment in Cambodia. *Journal of Water and Health.* 8:1–10
- Clasen, T.F. and Haller, L. (2008). Water Quality Interventions to Prevent Diarrhoea: Cost and Cost Effectiveness. Geneva. Retrieved from [http://www.who.int/water\\_sanitation\\_health/economic/prevent\\_diarrhoea.pdf?ua=1](http://www.who.int/water_sanitation_health/economic/prevent_diarrhoea.pdf?ua=1)
- Clasen, T., Parra, G.G., Boisson, S., and Collin, S. (2005) Water filters for the prevention of diarrhea: a randomized, controlled trial of a pilot program in Colombia. *Am. J. Trop. Med. Hyg.* 73(4) 790-795.
- du Preez, M., Conroy, R.M., Wright, J.A., Moyo, S., Potgieter, N., and Gundry, S.W. (2008) Short report: use of ceramic water filtration in the prevention of diarrheal disease: a randomized controlled trial in rural South Africa and Zimbabwe. *Am. J. Trop. Med. Hyg.* 79(5) 696-701.
- Elechiguerra, J.L., Burt, J.L., Morone, J.R., Camacho-Bragado, A., Gao, X., Lara, H.H. and Yacaman, M.J. (2005) Interaction of silver nanoparticles with HIV-1. *Journal of Nanobiotechnology* 3(6): 1-10.

- Fahlin, C.J. (2003) Hydraulic Properties Investigation of the Potters For Peace Colloidal Silver Impregnated, Ceramic Filter. Unpublished Thesis, University of Colorado at Boulder, Boulder, CO, USA.
- Hach Company (2014). RapidSilver Test Kit instruction manual.  
<http://www.hach.com/rapidsilver-visual-test-kit/product?id=7640218480>
- Hanna Instruments (2014). Instruction Manual HI 96737 Silver ISM (photometer)  
[http://hannainst.com/manuals/ist96737\\_25\\_11\\_10.pdf](http://hannainst.com/manuals/ist96737_25_11_10.pdf)
- Hanna Instruments (2014). Instruction Manual HI 98185 pH/ORP/ISE Waterproof meter. [http://www.hannainst.com/manuals/manHI\\_9818x.pdf](http://www.hannainst.com/manuals/manHI_9818x.pdf)
- Housecroft, C.E., and Sharpe, A.G. Inorganic Chemistry 2<sup>nd</sup> edition. Essex: Pearson Education Limited, 2005.
- Ivask, A., Amro ElBadawy, Chitrada Kaweeteerawat, David Boren, Heidi Fischer, Zhaoxia Ji, Chong Hyun Chang, Rong Liu, Thabet Tolaymat, Donatello Telesca, Jeffrey I. Zink, Yoram Cohen, Patricia Ann Holden, and Hilary A. Godwin Toxicity Mechanisms in Escherichia coli Vary for Silver Nanoparticles and Differ from Ionic Silver ACS Nano 2014 8 (1), 374-386 <http://pubs.acs.org/doi/abs/10.1021/nn4044047>
- Jain, P. and Pradeep, T. (2004) Potential of silver nanoparticle-coated polyurethane foam as an antibacterial water filter. Biotechnology and Bioengineering 90(1): 59-63.  
<http://onlinelibrary.wiley.com.ezproxy.library.tufts.edu/doi/10.1002/bit.20368/pdf>
- Kallman E, Oyanedel-Craver V, Smith J. Ceramic filters impregnated with silver nanoparticles for point-of-use water treatment in rural Guatemala. Journal of Environmental Engineering. 2011;137:407.
- Lantagne, D.S. (2001) Investigation of the Potters for Peace Colloidal Silver Impregnated Ceramic Filter Report. Alethia Environmental: Allston, MA, USA.

- Lantagne, D.S., Quick, R., and Mintz, E.D. (2006) Household Water Treatment and Safe Storage Options in Developing Countries: A Review of Current Implementation Practices.
- Lantagne, D., Klarman, M., Mayer, A., Preston, K., Napotnik, J., & Jellison, K. (2010). Effect of production variables on microbiological removal in locally-produced ceramic filters for household water treatment. *International Journal of Environmental Health Research*, 20 (3), 171-87.
- Li. Q., M.S., Lyon. D.Y., Brunet. L., Liga. M.v., Li. D., and Alvarez. P. J.J. (2008) Antimicrobial nanomaterials for water disinfection and microbial control: Potential applications and Implications. *Water Research* 42: 4591-4602.
- Marambio-Jones, C. and Hoek, E.M.V. (2010) A review of the antibacterial effects of silver nanomaterials and potential implications for human health and the environment. *J Nanopart Res* 12:1531-1551
- Mitrano, D.M., Rimmelé, E., Wichser, A., Erni, R., Height, M. and Nowack, B. (2014) Presence of Nanoparticles in Wash Water from Conventional Silver and Nano-silver Textiles. *ACS Nano* 8 (7) 7208-7219.
- Mittelman, A.M., Lantagne, D.S., Rayner, J., and Pennel, K.D. (2015). Silver Dissolution and Release from Ceramic Water Filters. *Environ. Sci. Technol.* 49(14) 8515-8522.
- Occupational Safety and Health Administration (OSHA). (2014). Silver, Metal, and Soluble Compounds (as Ag).  
[https://www.osha.gov/dts/chemicalsampling/data/CH\\_267300.html](https://www.osha.gov/dts/chemicalsampling/data/CH_267300.html)
- Onda, K.; LoBuglio, J.; Bartram, J., Global access to safe water: accounting for water quality and the resulting impact on MDG progress (2012) *International journal of environmental research and public health* 9, (3), 880-894.

- Oyanedel-Craver, V.A., and Smith, J.A. (2008) Sustainable colloidal-silver-impregnated ceramic filter for point-of-use water treatment. *Environ. Sci. Technol.* 42 (3), 927-933.
- Pal, S., Tak, Y.K. and Song, J.M. (2007) Does the antibacterial activity of silver nanoparticles depend on the shape of the nanoparticle? A study of the gram-negative bacterium *Escherichia coli*. *Applied and Environmental Microbiology*: 1712-1720.
- Panacek, A., Kvitek, L., Prucek, R., Kolar, M., Vecerova, R., Pizurova, N., Sharma, V.K., Nevecna, T.J. and Zboril, R. (2006) Silver colloid nanoparticles: synthesis, characterization, and their antibacterial activity. *Journal of Physical Chemistry* 110: 16248-16253.
- R Core Team (2013). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-9000051-07-0, URL <http://www.R-project.org/>.
- Raffi, M., Hussain, F., Bhatti, T.M., Akhter, J.I., Hameed, A. and Hasan, M.M. (2008) Antibacterial characterization of silver nanoparticles against *E. Coli* ATCC-15224. *Journal of Material Science and Technology* 24(2): 192-196.
- Rayner, J., Skinner, B., and Lantagne, D. (2013a) Current practices in manufacturing locally-made ceramic pot filters for water treatment in developing countries. *Journal of Water, Sanitation and Hygiene for Development* 3 (2) 252-261.
- Rayner, J., Zhang, H., Schubert, J., Lennon, P., Lantagne, D., Oyanedel-Craver, V. (2013b). *Laboratory investigation into the effect of silver applied on the bacteriological removal efficacy of filter material for use on locally-produced ceramic water filters for household drinking water treatment.* *ACS Sustainable Chemistry & Engineering* 1(7), 737-745.
- Reed, R.B., Faust, J.j., Yang, Y., Doudrick, K., Capco, D.G., Hristovski, K., and Westerhoff, P. (2014) Characterization of Nanomaterials in Metal Colloid-

Containing Dietary Supplement Drinks and Assessment of Their Potential Interactions after Ingestion. *ACS Sustainable Chemistry & Engineering* 2 (7), 1616-1624.

Singer, R. and V. Craver (2009) Silver Nanoparticles for Water Disinfection: Water Chemistry Effect. Disinfection. Water Environmental Federation. Atlanta. Georgia.

<http://water.usgs.gov/wrri/08grants/progress/2008RI75B.pdf>

Sobsey, M.D. Stauber, C.E., Casanova, L.M., Brown, J.M., and Elliott, M.A. (2008) Point of Use Household Drinking Water Filtration: A Practical, Effective Solution for Providing Sustained Access to Safe Drinking Water in the Developing World. *Environ. Sci. Technol.* 42 (12) 4261-4267.

Song, J., Haeyoung Kang, Choonghyeon Lee, Sun Hye Hwang, and Jyongsik Jang. (2012) Aqueous Synthesis of Silver Nanoparticle Embedded Cationic Polymer Nanofibers and Their Antibacterial Activity Jooyoung Song, *ACS Applied Materials & Interfaces* 4 (1), 460-465

<http://pubs.acs.org/doi/abs/10.1021/am201563t>

The Ceramics Manufacturing Working Group (CMWG) (2011). Best Practice Recommendations for Local Manufacturing of Ceramic Pot Filters for Household Water Treatment, Ed. 1. Atlanta, GA, USA: CDC.

Tolaymat, T.M., El Badawy, A.M., Genaidy, A, Scheckel, K.G., Luxton, T.P., Suidan, M. (2010) An evidence-based environmental perspective of manufactured silver nanoparticle in syntheses and applications: a systematic review and critical appraisal of peer-reviewed scientific papers. *Sci Total Environ.* 408(5) 999-1006.

Wang, J, and Wang, W-X. (2014) Low bioavailability of silver nanoparticles presents trophic toxicity to marine medaka (*oryzias melastigma*). *Environ. Sci. Technol.* 48(14), 8152-8161.

UNICEF (2008). A simple way to make bad water safe.

[http://fieldnotes.unicefusa.org/2008/10/such\\_a\\_simple\\_way\\_to\\_make\\_bad\\_1.html](http://fieldnotes.unicefusa.org/2008/10/such_a_simple_way_to_make_bad_1.html)

UNICEF/WHO. Diarrhoea: Why Children Are Still Dying and What Can Be Done; Jensen, L., Ed.; The United Nations Children's Fund (UNICEF)/World Health Organization (WHO), 2009.

[http://whqlibdoc.who.int/publications/2009/9789241598415\\_eng.pdf](http://whqlibdoc.who.int/publications/2009/9789241598415_eng.pdf)

WHO and UNICEF (2014). Progress on Drinking Water and Sanitation. Retrieved from [http://www.unicef.org/publications/index\\_73448.html](http://www.unicef.org/publications/index_73448.html).

WHO (2011). Guidelines for drinking-water quality, fourth edition. Available from:

[http://www.who.int/water\\_sanitation\\_health/publications/dwq\\_guidelines/en/](http://www.who.int/water_sanitation_health/publications/dwq_guidelines/en/)

United State Environmental Protection Agency (EPA). (2014) Silver (CASRN 7440-22-4). <http://www.epa.gov/iris/subst/0099.htm>

Zhang, H. and Oyanedel-Craver, V. (2012). "Evaluation of the Disinfectant Performance of Silver Nanoparticles in Different Water Chemistry Conditions." J. Environ. Eng., 138(1), 58–66.

<http://ascelibrary.org/doi/full/10.1061/%28ASCE%29EE.1943-7870.0000460>