

Accuracy, precision, usability, and cost of portable silver test methods for ceramic filter factories

Rhiana D. Meade, Anna L. Murray, Anjuliee M. Mittelman, Justine Rayner and Daniele S. Lantagne

ABSTRACT

Locally manufactured ceramic water filters are one effective household drinking water treatment technology. During manufacturing, silver nanoparticles or silver nitrate are applied to prevent microbiological growth within the filter and increase bacterial removal efficacy. Currently, there is no recommendation for manufacturers to test silver concentrations of application solutions or filtered water. We identified six commercially available silver test strips, kits, and meters, and evaluated them by: (1) measuring in quintuplicate six samples from 100 to 1,000 mg/L (application range) and six samples from 0.0 to 1.0 mg/L (effluent range) of silver nanoparticles and silver nitrate to determine accuracy and precision; (2) conducting volunteer testing to assess ease-of-use; and (3) comparing costs. We found no method accurately detected silver nanoparticles, and accuracy ranged from 4 to 91% measurement error for silver nitrate samples. Most methods were precise, but only one method could test both application and effluent concentration ranges of silver nitrate. Volunteers considered test strip methods easiest. The cost for 100 tests ranged from 36 to 1,600 USD. We found no currently available method accurately and precisely measured both silver types at reasonable cost and ease-of-use, thus these methods are not recommended to manufacturers. We recommend development of field-appropriate methods that accurately and precisely measure silver nanoparticle and silver nitrate concentrations.

Key words | ceramic water filter, drinking water, household water treatment, silver nanoparticles, silver nitrate

Rhiana D. Meade
Anna L. Murray (corresponding author)
Anjuliee M. Mittelman
Justine Rayner
Daniele S. Lantagne
Department of Civil and Environmental
Engineering,
Tufts University,
200 College Avenue,
Medford,
MA 02155, USA
E-mail: anna.murray@tufts.edu

INTRODUCTION

More than 663 million people worldwide do not have access to an improved water source and an estimated 1.2 billion more use drinking water at elevated risk of contamination at the source, or during collection, transport, and storage (Onda *et al.* 2012; WHO/UNICEF 2015). In 2010 alone, an estimated 801,000 children died from preventable and treatable diarrheal diseases, partly caused by drinking water contaminated with bacteria, viruses, and/or protozoa (UNICEF 2012). Where piped, treated water is unavailable or unreliable, a number of household water treatment

(HWT) technologies, such as disinfection products and household filters, are promoted to reduce this disease burden.

Locally manufactured ceramic water filters (CWFs) are a promising HWT technology (Sobsey *et al.* 2008). CWFs are comprised of an approximately 10 liter (L) capacity filter that rests on its rim in a lidded receptacle (CMWG 2011). Water is poured into the filter and flows via gravity at a rate of 1–3 liters per hour (L/hr) into the receptacle, which serves as a safe storage container with a tap for dispensing water. CWFs are currently manufactured at over

50 factories worldwide (PFP 2016). In the laboratory, filters effectively remove >99% of protozoan (Lantagne 2001; van Halem 2007) and 90–99.99% of bacterial organisms from drinking water (Lantagne 2001; van Halem 2007; Bielefeldt *et al.* 2010; Brown & Sobsey 2010; Lantagne *et al.* 2010). In field testing, CWFs have been shown to reduce diarrheal disease among users (Brown *et al.* 2008).

Silver has been used for centuries as a disinfection agent. Silver nitrate (AgNO_3) dissolves in water to form silver ions (Ag^+) which actively attack microbial proteins, DNA, and cell membranes (Li *et al.* 2008). Silver nanoparticles (nAg) are engineered structures with one dimension between 1 and 1,000 nanometers, large surface area to volume ratio, and high reactivity. Silver nanoparticles have been shown to damage cell membranes directly, act as a large reservoir of Ag^+ , and form reactive oxygen species that can also damage cells (Ivask *et al.* 2014). Commercial use of silver nanoparticles has increased dramatically over the past decade as its effectiveness as an antibacterial agent has been documented and production of nanoparticles has become less costly (Tolaymat *et al.* 2010).

Silver, as silver nitrate or silver nanoparticles, is applied to CWFs to prevent microbiological growth within the filter and increase the filter's bacterial removal efficiency (Lantagne *et al.* 2010; CMWG 2011). In addition, silver in filtered effluent water can maintain the quality of stored, filtered water (van der Laan *et al.* 2014). It is necessary to balance the amount of silver applied to maintain antimicrobial benefit while not exceeding the United States Environmental Protection Agency (EPA) and World Health Organization (WHO) guideline value of 0.1 mg/L silver in drinking water (WHO 2011; EPA 2016). In a 2009 survey of manufacturing practices in CWF factories, factories reported applying a range of silver concentrations and types of silver – including both silver nanoparticles and silver nitrate; the latter because it is less expensive and locally available. A standard amount of silver nanoparticles is recommended for use in ceramic filter manufacturing (CMWG 2011; Rayner *et al.* 2013b). Although the addition of both silver nitrate and silver nanoparticles improves microbiological performance of filters, silver is released at a faster rate from silver nitrate-treated filters, so filtered water is more likely to exceed silver guideline values and it may not

provide a long-term benefit (Rayner *et al.* 2013b; Mittelman *et al.* 2015).

Currently, filter factories do not test the silver concentration of either the application solution or the filtered effluent (Rayner *et al.* 2013b), and testing guidelines, along with recommended test methods, have not been developed (CMWG 2011). In order to develop recommendations to test silver concentrations at ceramic filter factories, we investigated the accuracy, precision, ease-of-use, and cost of commercially available portable methods to measure application and effluent silver concentrations of both nanoparticles and silver nitrate.

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

Commercially available, portable test methods were identified by searching catalogs of known environmental testing equipment manufacturers and by Google search. Methods were considered available if a price quote could be obtained and they could be ordered. Available test methods included 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]). Each of the test methods had a

Table 1 | Comparison of six silver test methods used in study

	Short name	Test method	Measurement range (mg/L)	Measurement increment (mg/L)	Equipment cost, initial	Incremental test cost	Total cost ^a (100 tests)	Total cost ^a (1,000 tests)
Waterworks Silver Check II HR	Waterworks	Test strips	0.0–1.0	0, 0.05, 0.10, 0.25, 0.50, 1.0	0	\$0.64	\$64	\$640
Machery-Nagel Quantofix Silver	Quantofix	Test strips	0–10,000	0, 1,000, 2,000, 3,000, 5,000, 7,000, 10,000	0	\$0.97	\$97	\$970
Machery-Nagel Silver Test Paper	Machery-Nagel	Test strips	≥20	Presence/absence	0	\$0.36	\$36	\$360
Hach RapidSilver™ Visual Test Kit	Hach	Test kit	0–0.05	0, 0.005, 0.01, 0.025, 0.05	\$285	\$2.68	\$285	\$2,697
Hanna HI 98185 pH/ORP/ISE Waterproof Portable Meter	Electrode	Ion selective electrode	0.11–107,900	0.001	\$1,600	\$0.50	\$1,600	\$1,850
Hanna HI 96737 Silver Portable Photometer	Photometer	Photometer	0.00–1.00	0.001	\$882	\$3.02	\$882	\$3,449

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

recommended silver concentration detection range between 0 and 10,000 mg/L (Table 1). The three test strips and one test kit method all indicated they tested for ‘silver,’ while the electrode and the photometer specified testing for silver ions in solution.

Test solution preparation

Stock silver solutions were prepared from two sources: silver nanoparticle ‘Collargol’ powder with mean diameter in solution ca. 50 nm (Mittelman *et al.* 2015) (Argenol Laboratories, Zaragoza, Spain) and silver nitrate (AlfaAesar, Ward Hill, MA).

Both silver stocks were diluted in MilliQ (MQ) water (Millipore, Darmstadt, Germany) to create six solutions in each of two concentration ranges: (1) application concentrations ranging from ~100 to 1,000 mg/L; and (2) effluent concentrations ranging from ~0.005 to 1.0 mg/L silver. Solutions were mixed in opaque Nalgene high density polyethylene (HDPE) containers, and prepared daily to minimize nanoparticle aggregation and sorption to plastic. The test solutions were pH 7.

Concentration verification

For silver nitrate solutions in the effluent concentration range, graphic furnace-atomic absorption spectroscopy (GF-AAS) (ThermoScientific, Waltham, MA) was used as the reference method. The detection limit of the GF-AAS method for Ag⁺ was determined to be 0.8 µg/L (Hubaux & Vos 1970). For silver nitrate solutions in the application concentration range, inductively coupled plasma optical emission spectrometry (ICP-OES) (7300 DV, Perkin-Elmer, Waltham, MA) in axial view mode was used as the reference method. ICP-OES samples were introduced through a cross-flow nebulizer at 0.5 mL/min and silver concentrations were determined at 328.068 nm. The detection limit for the ICP-OES was 0.1 mg/L. Samples exceeding the instruments’ detection ranges were diluted with MQ water before testing, but were otherwise unmodified.

For all silver nanoparticle solutions, concentrations were verified by first filtering solutions through 3 kDa centrifugal filters (Amicon 3k, Millipore, Billerica, MA) to separate silver nanoparticles from ionic silver, and then using GF-AAS or ICP-OES as described above to determine the aqueous silver concentrations. The silver nanoparticle

concentration was taken as the difference between total silver and silver ion concentration (i.e. $nAg = \text{total Ag} - Ag^+$).

Laboratory testing

All test methods were used according to the manufacturers' instructions to test all stated silver concentrations and silver types in quintuplicate, even if concentrations were outside manufacturer-reported detection ranges. All testing was completed within 24 h of silver solution preparation. Individual test methods are described below.

Waterworks test strips (0.0–1.0 mg/L) were dipped in 250 mL of sample solution for 5 seconds, removed, and shaken once to remove excess solution. 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 with a plastic eyedropper to the Machery-Nagel presence/absence test strip (lower detection limit 20 mg/L) and allowed to dry. If the paper turned red or developed a ring around the drop location, silver was recorded as present (≥ 20 mg/L). Otherwise, silver was recorded as absent.

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

For 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 the resultant color was compared to the chart provided, ranging from no color (white) (0.0 mg/L), to pink (0.005 mg/L), to blue (0.050 mg/L).

The electrode (range 0.11–107,900 mg/L) was calibrated before each test using fresh calibration standards for a five-point calibration at 0.1, 1, 10, 100, and 1,000 mg/L. Before testing samples with the electrode, 1 mL of ionic strength adjusting solution was added per 50 mL sample to increase the total ionic strength to above 10 mM and thus remove background noise. The electrode was gently swirled in 50 mL of sample solution, and results were recorded from the digital readout in mg/L upon stabilization of the reading (within 30 seconds).

For the photometer (range 0.0–1.0 mg/L), two 50 mL samples of solution were used to create a 'blank' and

'sample' by adding different proprietary reagents to each. Thus, the meter is not calibrated with a standard curve, but the sample concentration is determined by comparing the two solutions. After setting the blank solution, the sample was inserted into the meter, read, and the reading on the digital screen was recorded in mg/L.

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 silver measurements across all concentrations for each test method to the reference GF-AAS or ICP-OES results using: (1) percent measurement error, including a composite mean percent measurement error across all concentrations; and (2) the Spearman rank correlation (nonparametric test of statistical dependence between ranked variables) to determine if results were correlated at a 0.05 significance level, and Spearman's rank correlation coefficient (ρ) to rank closeness of fit. Experimental lower detection limits were identified; zero values (or those below experimental detection limits) were excluded from reported percent measurement errors, but all measurements within manufacturer-reported ranges were included in the correlation analysis. Precision was assessed by calculating the standard error and relative standard error for replicate readings at each tested concentration.

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 their experience during a 3.5 hour session. Twelve water samples, six each of silver nitrate and silver nanoparticles, were prepared at target concentrations of 0.2, 0.5, 1.0, 200, 500, and 1,000 mg/L as described above, and placed in opaque HDPE plastic bottles. To ensure sample concentrations were unknown to the participants and researcher, random numbers were generated and assigned to samples. Six stations were set up containing one test method, all necessary supplies, written instructions, three random samples of

silver nitrate solution, and three random samples of silver nanoparticle solution. Eleven volunteer participants conducted testing using all six test kits (with six samples per station), in duplicate, for a total of 72 measurements per volunteer.

Following the testing, participants completed a survey 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 subsequently calculated as described above for volunteer test results. Free and informed consent of the participants was obtained and the study protocol was approved by the Social, Behavioral, and Educational Research Institutional Review Board at Tufts University (Protocol #1501043, July 2, 2015).

Cost

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

RESULTS

The concentrations of silver nitrate solutions in the application range were verified by ICP-OES to be 139, 268, 538, 693, 802, and 955 mg/L, while concentrations in the effluent range were verified by GF-AAS to be 0.012, 0.016, 0.053, 0.12, 0.24, and 0.78 mg/L. In all silver nanoparticle solutions, 97–99% of total silver existed in nanoparticle form (nAg) rather than ionic form (Ag⁺).

None of the six test methods accurately measured silver nanoparticle concentrations, as evidenced by color changes on test strips that did not match included color keys, and results registering above or below detection limits on the electrode and photometer. 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. The electrode measured near zero, and samples were darker than the photometer's maximum detection limit. Since methods were unable to measure nanoparticles, nanoparticle results have been excluded from further analysis.

Accuracy

We found test methods had non-detectable or inaccurate data outside manufacturer-recommended ranges (Table 1). Application concentration measurements were all at the maximum reading with the Waterworks test strip; samples were unable to be filtered with the Hach test kit above the manufacturer range of 0–0.05 mg/L; and the photometer was at its maximum or produced an error for solutions above 1 mg/L, which were too dark to read. Thus, only data within manufacturer recommended ranges is presented herein. The remaining data includes results from two methods (including one presence/absence method) at application concentrations (100–1,000 mg/L), and four methods at effluent concentrations (0–1 mg/L) (Figure 1). The electrode was the only quantitative method with a detection range encompassing both concentration ranges. Additionally, two methods (the Waterworks test strip and the photometer) were found to have higher experimental detection limits than the manufacturer-reported detection ranges.

For application concentrations (100–1,000 mg/L), the electrode had a composite measurement error of 12% (range 4–26%) with Spearman's $\rho = 1.0$ ($p < 0.001$) (Figure 1(e)). The presence/absence Machery-Nagel test strips, with a lower detection limit of 20 mg/L silver, detected silver in every sample in this range. Both the electrode and Machery-Nagel test strips accurately detected silver in the application concentration range, but the electrode was the only quantitative method.

For effluent concentrations (0–1.0 mg/L), the Waterworks test strip had a composite measurement error of 27% (range 26–29%) for concentrations over 0.2 mg/L (found to be the method's lower detection limit, although the manufacturer's reported range goes to 0.0 mg/L), with Spearman's $\rho = 0.764$ ($p = 0.027$) (Figure 1(a)). The Hach test kit had composite measurement error of 31% (range 5–50%) for concentrations of 0–0.05 mg/L only with Spearman's $\rho = 0.932$ ($p < 0.001$) (Figure 1(b)). The electrode had

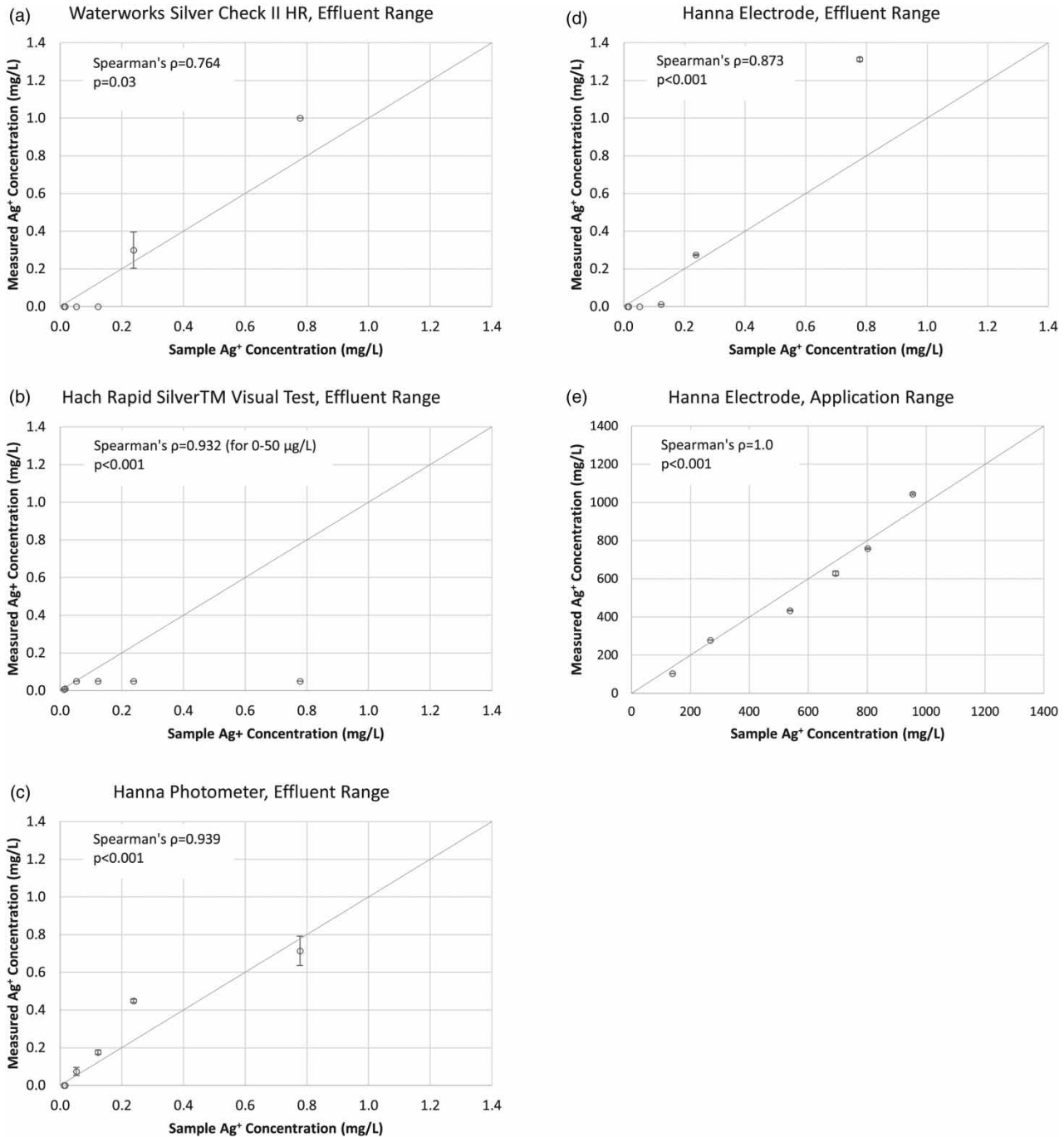


Figure 1 | Average measured ionic silver concentrations with standard error bars for each quantitative test method used to measure silver nitrate solutions. Lines represent 'ideal' readings.

composite measurement error of 58% (range 15–91%) for concentrations above 0.1 mg/L (manufacturer's reported lower detection limit) with Spearman's $\rho = 0.873$ ($p < 0.001$) (Figure 1(d)). The photometer had composite

measurement error of 45% (range 8–89%) for concentrations above 0.05 mg/L (found to be the method's lower detection limit, although the manufacturer's reported range goes to 0.0 mg/L) with Spearman's $\rho = 0.939$

($p < 0.001$) (Figure 1(c)). The presence/absence Machery-Nagel test strips did not detect silver at any concentration in this range. All of the quantitative test methods had statistically significant correlations between test results and laboratory reference results in each method's recommended range ($p < 0.05$). Based on the Spearman rank correlation coefficients, the photometer was the most accurate test for effluent silver concentrations. Based on percent measurement error, the Hach kit was most accurate, but only for concentrations ≤ 0.05 mg/L.

Precision

Precision was generally good among the test methods (Figure 1). For application concentrations (100–1,000 mg/L), replicate standard error ranged from 0.5 to 11.4 mg/L ($\leq 2\%$ relative standard error) for the electrode, which was the only quantitative method appropriate for that concentration range. For effluent concentrations (0–1.0 mg/L), replicate standard error was below 0.01 mg/L ($\leq 17\%$ relative standard error) for all methods at all concentrations except Waterworks, which had a

standard error of 0.09 mg/L at the 0.5 mg/L concentration (32% relative standard error), and the photometer, which had a standard error of 0.02 mg/L at the 0.05 mg/L concentration and a standard error of 0.08 mg/L at the 1.0 mg/L concentration (28% and 11% relative standard errors, respectively).

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% self-reported a beginner level, 25% an intermediate level, and 25% 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

Table 2 | Summary of volunteer responses to questions about test method usability

	Difficulty of test procedure ^a Mean (min, max, SD)	Confidence in test results ^b Mean (min, max, SD)	Easiest ^c (Frequency)	Most confident ^d (Frequency)	Choice for use by trained testers ^e (Frequency)	Choice for use by untrained testers ^f (Frequency)
Waterworks Silver Check II HR	1.9 (1, 3, 0.8)	2.7 (1, 5, 1.1)	2	0	0	2
Machery-Nagel Quantofix Silver	1.1 (1, 2, 0.3)	3.5 (2, 5, 1.1)	9	2	2	5
Machery-Nagel Silver Test Paper	2.3 (1, 4, 1.0)	2.0 (1, 4, 1.0)	0	1	0	0
Hach RapidSilver™ Visual Test Kit	4.6 (4, 5, 0.5)	2.3 (1, 3, 0.8)	0	0	0	0
Hanna HI 98185 pH/ORP/ISE Waterproof Portable Meter	2.8 (1, 4, 1.0)	4.0 (1, 5, 1.3)	0	6	3	3
Hanna HI 96737 Silver Portable Photometer	3.8 (3, 5, 0.8)	4.1 (2, 5, 0.9)	0	2	6	1

^aIndicate the difficulty of each test procedure on a scale of 1–5, where 1 is the simplest and 5 is the most difficult.

^bIndicate 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.

^cWhich test did you find to be the easiest to perform today?

^dWhich of the test results are you most confident in?

^eIf you were to receive silver test results from a laboratory in the United States, which test would you be most confident receiving results from?

^fIf 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?

as ‘confusing’ (7/11), and participants did not think the presence/absence results provided sufficiently detailed information. The Hach test kit was described as the most difficult because of the physical difficulty of pushing the solution through the filter membrane with the syringe. 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 also confused by the color changing on test strips to different colors than expected when testing silver nanoparticles, which may have affected their confidence in test strips.

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

Measurements from volunteers varied in accuracy. Overall, volunteers’ results had 22–148% measurement error for Waterworks, 42–53% error for Quantofix (where many volunteers recorded a value from the incorrect scale on the color chart), 75–95% error for Hach (although, because they were randomized, all tested solutions were outside the manufacturer-recommended range), 16–83% error for the electrode, and 18% error for the photometer. For the presence-absence Machery-Nagel test strip method, 18–45% of volunteers falsely recorded the presence of silver when the actual value was below the detection limit. Error variation was wide among users, but those with self-reported laboratory experience generally had smaller measurement errors. We did not identify a correlation between reported test difficulty and measurement accuracy ($R^2 = 0.047$). Standard errors across all measurements for all tested concentrations were overall higher than those found in laboratory testing, except for the Waterworks method at the 0.5 mg/L concentration. In this case, volunteer test results were more precise than laboratory results (standard error of 0.08 vs. 0.10 mg/L).

Cost

The three test strip methods contain only consumable costs, while three methods – the Hach test kit, photometer, and electrode – have both fixed equipment costs and ongoing consumable costs. Those three test methods are initially supplied with enough reagents for 100, 150, and 500 tests, respectively, after which additional reagents must be purchased. For 100 tests, costs ranged from 36 to 1,600 USD: 36 USD for Machery-Nagel, 64 USD for Waterworks, 97 USD for Quantofix, 285 USD for Hach, 1,600 USD for the electrode, and 882 USD for the photometer (Table 1). For 1,000 tests, costs ranged from 360 to 3,449 USD: 360 USD for Machery-Nagel, 640 USD for Waterworks, 970 USD for Quantofix, 2,697 USD for Hach, 1,850 USD for electrode, and 3,449 USD for the photometer.

DISCUSSION

We compared six commercially available portable 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. None of the methods were able to accurately measure silver nanoparticle concentrations, and only the electrode was appropriate according to study metrics for testing both application and effluent concentration ranges of silver nitrate relevant to ceramic filter factories. Accuracy in the laboratory ranged from 5 to 91% measurement error, with two methods found to have lower detection limits greater than manufacturer-reported limits, and the electrode being the most accurate quantitative method across both concentration ranges. Four of six test methods, including the electrode, were found to be precise with standard errors below 12 mg/L in the application concentration range and 0.01 mg/L in the effluent concentration range. Volunteers had concerns with all test methods and recognized the inaccuracy of the silver nanoparticle results; however, they reported that test strips were easiest to use, but felt most confident in results from the photometer and electrode. Costs ranged from 36 to 1,600 USD for 100 tests, with the electrode having the highest cost; and 640–3,449 USD for 1,000 tests, with the photometer having the highest cost.

Given the portable test methods currently available, developing quality control recommendations for testing silver application solution and effluent water concentrations at ceramic filter factories is difficult. The only method found to be accurate and precise across all silver nitrate application and effluent concentrations was the electrode, which was reported as moderately difficult to use and was high in cost, particularly if few tests are run. It may require personnel with some laboratory training and access to clean, silver-free water, which may not be a practical option for some ceramic filter factories. However, if factories have laboratory-trained individuals and access to a compatible meter, concerns of complexity and cost of the electrode would decrease (the probe itself is 682 USD, compared to the 1,600 USD full unit cost). Both the photometer and Hach test kit could be appropriate for both concentration ranges of silver nitrate, but would require diluting samples to a measurable concentration with clean, silver-free water, raising ease-of-use and accuracy concerns. These two also require expensive reagents, so may be cost-prohibitive if many measurements are taken.

There is not a clear recommendation for a silver test method for use in ceramic filter factories, but based on these findings, an interim recommendation to verify silver nitrate application concentrations (100–1,000 mg/L) is the Hanna electrode, if cost and personnel training are not primary concerns. Interim recommendations for effluent concentrations of silver nitrate (0.0–1.0 mg/L) include: (1) the Hanna electrode, as stated above; (2) the Hach test kit to determine silver concentrations up to 0.05 mg/L (or for higher concentrations with dilution) and if cost is not a primary concern; or (3) the less accurate, but easy-to-use and much less expensive Waterworks test strips.

Importantly, our research findings indicate the need for additional development of appropriate test methods, particularly for testing silver nanoparticle concentrations. In the laboratory, specialized instruments such as particle counters or single-particle inductively coupled plasma-mass spectroscopy are used to directly measure nanoparticles (Laborda *et al.* 2014). Silver nanoparticles or total silver (nanoparticles and ions together) can be tested in the laboratory using acid digestion, followed by ICP-OES or GF-AAS analysis as in this study. In resource-limited contexts, these methods may not be available or practical.

Despite some test methods (such as the Hach test kit and photometer) requiring solutions to be mixed with proprietary digestion solutions or indicators, it appeared that no test method effectively dissolved nanoparticles into ionic silver. The test methods were all designed to measure silver ion, not silver nanoparticles. Thus, silver nanoparticle testing would have to be precluded by acid digestion or some other treatment to convert nanoparticles to ionic silver for any of these test methods to work. There is, however, potential to use these methods to test concentrations in filtered water samples. Previous research documented that silver in effluent from silver nanoparticle-treated ceramic disks was primarily in ionic form (>90%) (Mittelman *et al.* 2015), and therefore would be detected by the methods that detected silver nitrate studied herein. However, that prior research only evaluated one filter recipe using one clay source. It is unknown if the ratio of ionic and nanoparticle silver effluent concentrations would be consistent across various raw materials and filter recipes used in CWF factories worldwide, and with different water qualities. Because of these unknowns, we recommend further research and development in the following three areas.

First, we recommend working with existing test strip and kit manufacturers to determine if: (1) color charts could be 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 silver concentration in filtered water is ≤ 0.1 mg/L to meet the EPA and WHO drinking water guideline values. With color changes for nanoparticle silver, each chart would have to correspond to specific types of silver nanoparticle, since different ligands will exhibit different color changes, and various silver synthesis methods are increasingly available.

Second, we highlight the need for the development of a portable test method specific to application concentrations of silver nanoparticles, the predominantly used silver type in ceramic filter manufacturing. This could be used to confirm application solution concentrations as a periodic quality control measure. Alternatively, procedures could be developed for digesting silver nanoparticles in the field to encourage silver nanoparticle dissolution into ionic silver, which could then be detected by available test methods. A process such as this could also be more broadly applicable,

as increased nanoparticle use in manufacturing and industry is leading to silver release into the environment, and the resulting need for environmental testing (Tolaymat *et al.* 2010).

Third, we recommend additional research comparing the ratio of silver nanoparticles to ionic silver in effluent water from a range of filter types and with varying influent water quality characteristics. If silver in filtered water from silver nanoparticle-treated filters is primarily in the ionic form, the aforementioned test methods (such as the Hach test kit or Waterworks test strips) could likely be used to measure silver concentrations in effluent water from filters coated with either silver type.

Limitations of this study include: (1) potential bias in laboratory measurements due to reliance on subjective visual color matching and solution concentration being unblinded to the researcher; and (2) all solutions were prepared with MQ water at a neutral pH and low ionic strength. Natural waters may have varied pH or high ionic strength, which will likely change the chemistry of many of the test methods. 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 multiple metrics, and volunteer test participants provided valuable data on measurement accuracy and qualitative feedback on ease-of-use for potential users new to water quality testing.

CONCLUSIONS

There are currently no recommendations for testing silver solution concentrations for quality control at CWF factories. In this research, providing test method recommendations was limited by the lack of any simple-to-use, inexpensive methods that accurately measured both application and effluent silver concentrations. Nevertheless, interim recommendations have been provided. Further research is recommended to confirm whether methods accurate for measuring ionic silver would also accurately detect silver in effluent from nanoparticle-treated filters. We also identified needs in silver test method research and development, and recommend new tests be developed to

address a targeted range of both silver nanoparticle and silver nitrate concentrations. Increased commercial use of silver nanoparticles has resulted in increased environmental release, so portable test methods could be applicable to both CWF manufacturers and the broader nanoparticle community.

ACKNOWLEDGEMENTS

Funding for this work was provided by grants from the Tufts University Faculty Research Fund and the Tufts Institute of the Environment. Partial funding was also provided by NSF grant EEC-1444926. The authors would also like to thank the volunteer testers who participated in this research.

REFERENCES

- Bielefeldt, A. R., Kowalski, K., Schilling, C., Schreier, S., Kohler, A. & Scott Summers, R. 2010 Removal of virus to protozoan sized particles in point-of-use ceramic water filters. *Water Res.* **44** (5), 1482–1488.
- Brown, J. & Sobsey, M. D. 2010 Microbiological effectiveness of locally produced ceramic filters for drinking water treatment in Cambodia. *J. Water Health* **8** (1), 1–10.
- Brown, J., Sobsey, M. D. & 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.
- CMWG 2011 *Best Practice Recommendations for Local Manufacturing of Ceramic Pot Filters for Household Water Treatment*, 1st edn. Ceramic Manufacturing Working Group, Centers for Disease Control and Prevention, Atlanta, GA, USA. Available from: <http://hwts.web.unc.edu/files/2014/09/1-3-Rayner-Best-Practice-Recommendations-for-Local-Manufacturing-of-Ceramic-Pot-Filters-for-Household-Water-Treatment.pdf>.
- EPA 2016 *Secondary Standards*. United States Environmental Protection Agency, Washington, DC, USA. Available from: www.epa.gov/dwstandardsregulations/secondary-drinking-water-standards-guidance-nuisance-chemicals.
- Hubaux, A. & Vos, G. 1970 Decision and detection limits for calibration curves. *Anal. Chem.* **42** (8), 849–855.
- Ivask, A., Elbadawy, A., Kaweeteerawat, C., Boren, D., Fischer, H., Ji, Z., Chang, C. H., Liu, R., Tolaymat, T., Telesca, D., Zink, J. I., Cohen, Y., Holden, P. A. & Godwin, H. A. 2014 Toxicity mechanisms in *Escherichia coli* vary for silver nanoparticles and differ from ionic silver. *ACS Nano* **8** (1), 374–386.

- Laborda, F., Bolea, E. & Jimenez-Lamana, J. 2014 Single particle inductively coupled plasma mass spectrometry: a powerful tool for nanoanalysis. *Anal. Chem.* **86** (5), 2270–2278.
- Lantagne, D. 2001 *Investigations of the Potters for Peace Colloidal Silver Impregnated Ceramic Filter. Report 1: Intrinsic Effectiveness*. Alethia Environmental, Allston, MA, USA. Available from: <http://web.mit.edu/watsan/Docs/Other Documents/ceramicpot/PFP-Report1-Daniele Lantagne, 12-01.pdf>.
- 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. *Int. J. Environ. Health Res.* **20** (3), 171–187.
- Li, Q., Mahendra, S., Lyon, D. Y., Brunet, L., Liga, M. V., Li, D. & Alvarez, P. J. 2008 Antimicrobial nanomaterials for water disinfection and microbial control: potential applications and implications. *Water Res.* **42** (18), 4591–4602.
- Mittelman, A. M., Lantagne, D. S., Rayner, J. & Pennell, K. D. 2015 Silver dissolution and release from ceramic water filters. *Environ. Sci. Technol.* **49** (14), 8515–8522.
- Onda, K., LoBuglio, J. & Bartram, J. 2012 Global access to safe water: accounting for water quality and the resulting impact on MDG progress. *Int. J. Environ. Res. Public Health* **9** (3), 880–894.
- PFP 2016 Home page. Available from: www.pottersforpeace.org. Retrieved March 31, 2016.
- Rayner, J., Skinner, B. & Lantagne, D. 2013a Current practices in manufacturing locally-made ceramic pot filters for water treatment in developing countries. *J. Water Sanit. Hyg. Dev.* **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 Sustain. Chem. Eng.* **1** (7), 737–745.
- Sobsey, M., Stauber, C. E., Casanova, L. M., Brown, J. & 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.
- 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.
- UNICEF 2012 *Pneumonia and Diarrhea: Tackling the Deadliest Diseases for the world's poorest Children*. UNICEF, New York City, NY, USA. Available from: www.epa.gov/sites/production/files/2015-01/documents/nanotechnology_whitepaper.pdf.
- van der Laan, H., van Halem, D., Smeets, P. W., Soppe, A. I., Kroesbergen, J., Wubbels, G., Nederstigt, J., Gensburger, I. & Heijman, S. G. 2014 Bacteria and virus removal effectiveness of ceramic pot filters with different silver applications in a long term experiment. *Water Res.* **51**, 47–54.
- van Halem, D., Heijman, S. G. J., Soppe, A. I. A., van Dijk, J. C. & Amy, G. L. 2007 Ceramic silver-impregnated pot filters for household drinking water treatment in developing countries: material characterization and performance study. *Water Science and Technology: Water Supply.* **7** (5–6), 9–17.
- WHO 2011 *Guidelines for Drinking-Water Quality*, 4th edn. World Health Organization, Geneva, Switzerland. Available from: http://apps.who.int/iris/bitstream/10665/44584/1/9789241548151_eng.pdf.
- WHO/UNICEF 2015 *Progress on Drinking Water and Sanitation: 2015 Update and MDG Assessment*. World Health Organization and UNICEF, Geneva, Switzerland and New York City, NY, USA. Available from: www.wssinfo.org/fileadmin/user_upload/resources/JMP-Update-report-2015_English.pdf.

First received 21 June 2016; accepted in revised form 24 August 2016. Available online 25 October 2016