Effects of water quality parameters on the release of silver nanoparticles from a ceramic surface using a quartz crystal microbalance

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Abstract

Ceramic water filters are used in many developing countries as a household water treatment technology, often produced locally using regionally-available materials, and constructed in various forms (i.e., as discs, candles, or pots) that all rely on similar mechanisms of filtration and disinfection. A common production technique involves application of an anti-microbial, colloidal silver coating to the porous ceramic filter. The silver coating has shown improvements in microbial log reduction values over uncoated ceramic filters both in the laboratory and in the field. However, a more complete understanding of the silver coating requires knowledge of specific characteristics of the colloidal silver solution, including particle size, composition, and charge, and to understand how these characteristics affect silver particle deposition, anti-microbial activity, and potential optimization of the silver coating. Additionally, as water passes through the ceramic filter, the silver coating will release from the ceramic surface, decreasing the disinfection effectiveness of the filter by reducing the presence of silver.

In this investigation, a colloidal silver solution was prepared according to procedures recommended for ceramic pot filter production. The colloidal silver solution was then characterized for particle size distribution, trace contaminants, and zeta potential. Silver nanoparticles were adsorbed onto representative ceramic surfaces and assessed with a quartz crystal microbalance, which monitored silver release from the surface. Experiments were conducted to determine the effects of several water quality parameters, including pH, turbidity, ionic strength, and natural organic matter, on the release of silver nanoparticles from representative ceramic surfaces. The most significant release was caused by waters containing sodium hypochlorite, suggesting that cleaning of silver-containing ceramic filters should be performed with caution.

Introduction

Certain industries have been incorporating nanoparticles into products for years. Common applications that carry over to present day include such everyday articles as pigments and dyes, batteries, electronics, photographic film developing equipment, construction materials, sporting goods, cookware, and on to personal care products such as sunscreen, and makeup (PEN 2009). In particular, silver



Figure 1: Number of commercial products containing common nanomaterials, according to the Project on Emerging Nanotechnologies

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nanoparticles have found an increasing number of uses in recent decades, all of which require an improved understanding of the lifecycle of that silver. According to the Project on Emerging Nanotechnologies, silver nanoparticles are employed in over 250 commercial products, making silver the most prevalent commercial nanoparticle (PEN 2009).

One application of silver nanoparticles is found in a somewhat unexpected role: ceramic drinking water filters produced and used in developing regions. While there are many examples of ceramic water filtration in both developed (e.g., ceramic membranes) and developing regions (e.g., ceramic candle filters) that employ silver for its known anti-microbial properties (Doulton undated), the basis of this research is specifically the ceramic pot filter (CPF). Due to the similarities of these applications, the results of this research may be applicable to a broader range of technologies, but the intention of this research was to focus on ceramic pot filters.

In the ceramic pot filter application, an aqueous solution of nanoparticle, or colloidal, silver is applied to the entire surface area of the filter. There is a general lack of understanding about that additional silver, from its deposition characteristics to its removal behavior, including factors that may impact both deposition and removal.

Studies that have monitored the release of silver have traditionally focused on the microbial efficacy of the overall filter rather than the behavior of the silver itself (Oyanedel-Craver 2008; Kohler 2009; Lantagne 2001). This approach is valuable in that the end goal of these filters is to produce safe drinking water for the end user by reducing the microbial contamination. However, a deeper look into the behavior of the silver itself may allow for improvements in the coating process, better prediction of the lifetime of the coating, and recommendations for filter handling procedures once the coating has been applied.

The investigation presented here employed a highly sensitive mass detection technique to gain insight into the effects of varied pH, turbidity, ionic strength, natural organic matter, and sodium hypochlorite content on the release of silver from a ceramic surface.

Background

<u>Ceramic Pot Filter overview</u> - The ceramic pot filter is a household, or point-of-use, water treatment alternative that can provide sufficient drinking water for a family that may otherwise have no access to a safe source of drinking water (Sobsey 2008). Currently, there are over 30 operational factories in 18



Figure 2: Schematic (left) and Image (right) of a ceramic pot filter system, as promoted by Potters for Peace

different countries with a total production capacity of nearly 80,000 filters per year (Raynor 2009; Clasen 2009; CMWG 2010). Once the ceramic filter is fabricated, it is used in conjunction with a receptacle (~ 20 L bucket) and spigot as shown in Figure 2. The user pours available water into the top, 8-10 L open volume of the ceramic filter. The water passes through the ceramic element, driven by gravity at a rate of about 1-3 L/hr when full, collecting in the receptacle below. The rate of filtration slows as the quantity of water in the ceramic filter decreases, due to the decreased pressure head. The spigot then provides hygienic access to the filtered drinking water. Pot filters are produced at each factory using almost entirely locally-sourced materials. Local clay is mixed with an organic material (e.g., sawdust) such that when fired at high temperatures, the final ceramic pot contains a network of open pores created by burning off the organic material. According to Potters for Peace, a USA-based non-governmental organization (NGO) that promotes and facilitates the production of ceramic pot filters, the pores within the ceramic are targeted to a size of 0.6 to 2 micrometers (0.6-2.0 μ m) in diameter (PFP undated). A pore structure at that size will remove bacteria (and other relatively large contaminants) through size exclusion, given the characteristic dimension of many bacteria being on the order of 1-2 μ m.

<u>Silver as applied to ceramic pot filters</u> - Each filter that passes the quality control tests will then have a coating of silver applied. Potters for Peace promotes application of around 45 milligrams (mg) of silver per filter, either by brushing a colloidal solution onto the filter or by dipping the entire filter into the silver solution (Nardo 2005). Other production models exist where silver nitrate is applied to the filter instead of nanoparticle silver (Hagan 2009). Another embodiment introduces the silver as a dry powder into the dry mixture of clay and organic material (Klarman 2009). This research focuses on the application method suggested by Potters for Peace.

A quartz crystal microbalance was selected as an experimental technique to study the interactions between the colloidal silver and a ceramic surface.

<u>Quartz Crystal Microbalance Introduction</u> - The quartz crystal microbalance (QCM) is one technique used to study surface interactions. QCM devices are commonly employed in processes where high mass sensitivity is required, such as during pharmaceutical production. The fundamental piezoelectric behavior, integral to QCM measurements, was described as early as the 1880's, most notably by Jacques and Pierre Curie (Ward 1990; Mould 2007). In that seminal work, it was found that mechanical stress applied to crystals (e.g., quartz) created a proportional electrical potential. The Curies and others also experimented with the reverse effect, where an electrical potential applied across a crystal creates a mechanical strain within the structure of the crystal (Buttry 1992; O'Sullivan 1999).

Given known visco-elastic properties of the sample material, a theoretical penetration depth for each harmonic can be calculated (Rechendorff 2007). For example in water at room temperature, the decay lengths for each odd harmonic from one through thirteen are shown in Table 1 below. Decay length values for the same sensor in air are also given for perspective of the resonance damping caused by the higher density-viscosity product.

Harmonic	Air δ _N	Water δ _N
	(nm)	(nm)
1	10300	248
3	5900	143
5	4600	111
7	3900	94
9	3400	83

Table 1: Theoretical decay lengths of each harmonic frequency of interest for	or
both Air and Water at 22° C	

<u>QCM measurement and analysis</u> - Sauerbrey adopted piezoelectric resonance behavior of quartz crystals into a measurement technique with his work in 1959. In that, Sauerbrey shows that the change in

resonance frequency is directly proportional to the quantity of mass added to the sensor's surface, provided that the mass is a thin, uniform film that is rigidly attached to the quartz crystal. Those assumptions are based on the derivation of the Sauerbrey equation (Equation 1), in which additional mass on the surface of the sensor is treated as an extension of the sensor itself. Certainly, the additional mass must be well attached to the surface for the sensor to detect any changes. Also, the mass must behave similarly to the resonant properties of the quartz sensor itself, or else the equation will not accurately describe the mass added.

As can be seen by Equation 1, Sauerbrey derived a direct, linear proportion between a change in frequency and the deposited mass causing that shift. Note the terms in the equation have little to do with any characteristics of the specimen, but rather the constant of proportionality is dependent on the sensor's resonant frequency and physical properties (namely, shear modulus and density). It is also important to note that the Sauerbrey correlation is often used to arrive at an areal mass due to the inclusion of surface area in the equation. This is much less of a concern for films with good uniformity, but can cause issues in interpretation for discrete, particle-like mass additions.

The Sauerbrey correlation is a useful description of deposited mass when the criteria mentioned above are met; another criterion bounding its application is that the shift in frequency caused by the deposited mass should be less than two percent of the baseline resonant frequency of the sensor (SRS 2005).

Equation 1: Change in frequency related to change in mass for each harmonic frequency (Sauerbrey 1959)

$$\Delta f_N = \frac{-2 \cdot \Delta m \cdot f_{N,0}^2}{A \sqrt{\rho_q \mu_q}} = -\frac{2 \cdot f_{N,0}^2}{A \sqrt{\rho_q \mu_q}} \cdot \Delta m \tag{a}$$

$$\Delta f_N = -c_N \cdot \Delta m \tag{b}$$

 Δf_N is the frequency shift, N represents the overtone (or harmonic), ρ_q is the density of the quartz, μ_q is the shear modulus of the quartz, A is the active area of the electrodes, c_N is a constant for each sensor, Δm is the associated change in mass.

As an example of QCM detection limits according to this model, consider a sensor with a 5 MHz resonant frequency. Under well-controlled conditions, a 1 Hz shift is reliably detectable by QCM measurement. According to the Sauerbrey equation, that 1 Hz shift would be caused by 6 ng/cm² of mass deposited on the surface. Assuming a common crystal geometry where the working electrode has an area of 0.24 cm², the minimum detectable mass is on the order of 1-2 ng. An upper limit for the Sauerbrey correlation may be found by assuming a frequency shift of two percent of the nominal resonant value. At that 100 kHz

frequency shift, the Sauerbrey equation yields a deposited mass of 600 μ g/ cm² corresponding to a deposited mass on the order of 150 μ g.

Much of the foundation work towards QCM measurements was hypothesized and/or conducted assuming the sensor was in a vacuum, thereby eliminating any potential effects from an ambient fluid, whether air or water. Kanazawa published an equation to describe this damping in 1985 which incorporated similar crystal properties as the Sauerbrey equation, but additionally considered the density and viscosity of the surrounding fluid. The density and viscosity of the surrounding fluid will act to dampen the resonant frequency of the quartz sensor, just as an additional mass does. This more thorough description of expected QCM behavior substantially increased the potential applications of the QCM instrument.

As in the equation derived by Sauerbrey, the theoretical frequency shift is dependent on the resonant frequency of the unloaded sensor, as well as physical properties of the sensor itself. The shift due to a liquid is also dependent on the density and viscosity of the liquid in contact with the sensor.

Equation 2: Frequency shift due to liquid loading (Kanazawa 1985)

$$\Delta f_N = -f_{N,0}^{\frac{3}{2}} \cdot \left(\frac{\rho_L \eta_L}{\pi \cdot \rho_q \mu_q}\right)^{\frac{1}{2}}$$

 Δf_N is the frequency shift, N represents the overtone (or harmonic), $f_{N,0}$ is the unloaded resonant frequency, ρ_q is the density of the quartz, μ_q is the shear modulus of the quartz, ρ_L is the density of the liquid, μ_L is the shear modulus of the liquid.

Frequency response of a deposited mass on the surface of a QCM sensor operating in a liquid may be treated as two superposed and separate effects, that due to the deposited mass and that due to the liquid damping (Kanazawa 1985). That is to say, given a certain decrease in resonant frequency caused by a deposited mass and given a certain decrease in resonant frequency caused by submersion in a viscous liquid, when that sensor with deposited mass is submerged in that liquid, the total expected frequency shift is theoretically the sum of the two components (i.e., mass and liquid).

Theoretical frequency shifts can be calculated for water flowing across the surface of a sensor (Kanazawa 1985). Using density and viscosity values for water at room temperature, the expected frequency shifts are shown in Table 2. All further results presented are in a scaled frequency format, unless otherwise stated. Data is recorded in absolute frequencies, and then scaled by normalizing by each harmonic.

Another independent parameter that can provide information about the viscosity and elasticity of any material being analyzed is dissipation. Dissipation is a term that describes the energy loss versus energy storage of the sensor and any material in contact with the sensor (Rodahl 1995). The quantity is

determined through similar electronic controls as are necessary for the detection of resonant frequency. Once the sensor is being driven at its resonant frequency, the alternating current driving the piezoelectric oscillation is stopped while the amplitude of oscillation continues to be monitored (Hook 1997). For a rigid material, with extremely low elasticity, such as quartz, the dissipation will be a very low quantity as the oscillations will not be substantially damped. A more elastic material, or highly viscous material, will have the effect to dampen the residual oscillations of the sensor through energy dissipation, yielding a much higher dissipation factor. Theoretical values for water are included in Table 2.

<u>Modeling frequency and dissipation responses</u> - There are a number of analytical approaches that have been developed to model frequency and dissipation responses of the QCM. Most fundamental of these is the Sauerbrey correlation mentioned above. Another more complex model is the Voigt model, which is based on an elasto-mechanical model of the sensor and any material in contact with the surface (Voinova 1999). The Voigt model reflects visco-elastic responses with much more accuracy than the Sauerbrey equation or any alternative approach that does not consider the viscosity of the contact material. A schematic of the Voigt physico-mechanical model is included as Figure 3 (Jaiswal 2010). As explained by Jaiswal, the frequency and dissipation shifts are dependent on the density, viscosity, elasticity, and thickness of the film, on top of the analogous sensor properties inherent in these calculations.

Keeping in mind that the dissipation factor is a measure of the visco-elastic properties of the material being analyzed, the dissipation factor can be used to determine the appropriateness of the Voigt model for the data collected. The Voigt model should only be employed when the shift in dissipation (increased by a factor of 10^6) is at least 5 to 10 percent of the frequency shift (in Hz) (Jaiswal 2010). At dissipation shifts below that threshold, the viscosity that must be input into the Voigt model approaches infinity in order to represent the stiff, inelastic material, disrupting the modeling equations.



Harmonic	Absolute ∆ f _N	Scaled Δf_N	$\Delta \mathbf{D_N}$
N	(Hz)	(Hz)	(10 ⁶ x arb. units)
1	-687	-687	278
3	-1191	-397	160
5	-1537	-307	124
7	-1819	-260	105
9	-2062	-229	93

Table 2: Theoretical frequency and dissipation shifts for a 4.95 MHz sensor in wate
at 22° C, relative to vacuum.

<u>Advantages of QCM measurements</u> - The advantage of QCM measurements is that of monitoring mass, viscosity, and density properties of a sample *at the surface* of the QCM sensor. This provides insight that may be otherwise lost by simply analyzing bulk properties of the specimen. Furthermore, the exceptional

mass sensitivity of the QCM device is a welcomed (required, perhaps) feature when investigating surface interactions of nanoparticles in an aqueous environment.

<u>QCM measurements of nanoparticle-surface interactions</u> - Quartz crystal microbalance measurement techniques are well suited to monitor and record interactions of nanoparticles with surfaces. Quantum dots are one example of a manufactured nanoparticle that have been analyzed under various conditions using the QCM. Quantum dots have found uses in a variety of commercial applications, but are most known for their encased metal structure, where the coating can be specifically designed to be compatible with a target; specifically, this has been useful for biological deployment of the metal core of the quantum dot (Quevedo 2009). The functional coating applied to a quantum dot will define its surface properties and size, and the size of the contained core will often influence the electrical and optical properties of the quantum dot. For that reason, each quantum dot needs to be specifically characterized, but in general, this class of material is manufactured to a size of between 2 and 1000 nm, depending on coatings applied.

It has been shown that ionic strength is a major factor in the deposition rate of quantum dots flowing in the solution of interest, depositing onto a silica-coated QCM sensor (Quevedo 2009). Quantum dots comprised of carboxyl-terminated cadmium-telluride at a manufacturer specified diameter of 10 nm (hydrodynamic diameters determined from dynamic light scattering to be 50 to 200 nm) were studied. The deposition rates of those quantum dots onto a silica-coated sensor were different when the ionic strength was due to either a monovalent ion (potassium) or a divalent ion (calcium), with the divalent ion causing a significantly faster rate of deposition rates in that the monovalent salt had much higher propensity to remove the quantum dots from the surface while the rate of release due to calcium was much slower (Quevedo 2009). This suggests that the divalent ion had a stronger effect of forcing the quantum dots onto the silica surface than the monovalent ion. This agrees with what would be predicted by the suspension behavior of that quantum dot according to DLVO theory.

The QCM platform has also been used to detect *Cryptosporidium parvum* (*C. parvum*) in water samples containing natural interferents, such as dissolved organic matter (DOM), other microbes, microbial secretions, and other broadly categorized natural colloidal particles (Poitras 2009). *C. parvum* is a protozoan oocyst approximately 2-3 µm in diameter when viable, exhibiting a negative surface charge at relevant pH values, with an isoelectric point at around 2.5 (Drozd 1996; Poitras 2009). In the work by Poitras et al, the dissipation was determined to be a better data source as a biosensor than the frequency shifts. Recall that the dissipation is directly related to the density-viscosity product of the material deposited on the surface. Microbes have a detectable viscosity that will affect the dissipation readings greater than the frequency. The authors were able to reliably detect *C. parvum* in some cases, but given interferents that mimic the viscosity effects, the QCM detection method was difficult to decipher. Of note in that same study, *E. coli* flowing across the surface of the QCM sensor was not sufficient to cause detectable shifts in either frequency or dissipation (Poitras 2009).

Materials and Methods

Unless otherwise stated, all silver used in these experiments was the commercially available product Collargol Colloidal Silver French IX Edition, produced by Laboratorios Argenol of Spain². Potters for Peace recommends mixing 2 mL of a stock 3.2 percent solution (prepared earlier from the powdered

² Commercial equipment, instruments, or materials are identified only in order to adequately specify certain procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST), nor does it imply that the products identified are necessarily the best available for the purpose.

colloidal silver) with 250 mL of filtered water, creating a solution of 0.018 percent by weight silver, calculated at a silver solids content of 70 percent, as stated by Laboratorios Argenol (Lantagne 2001; Nardo 2005).

For the purposes of this report this 0.018 percent colloidal silver solution will be called the "application solution". In this laboratory investigation, the water for the solution was purified in order to minimize additional water quality variables for each experimental run. However, the water used during actual fabrication of ceramic pot filters will generally be filtered (not purified) water, but will likely contain many other constituents from sources of contamination as well as natural organic matter. The effects of these constituents on the colloidal silver solution were not studied in this work.

Most QCM measurements were obtained using commercially available QSX-303 quartz sensors, from Q-sense®. These sensors are AT-cut quartz sensors 14 mm diameter and 0.3 mm thick. The fundamental resonance frequency is 4.95 MHz (\pm .05 MHz) with an electrode surface area of 0.24 cm². The gold electrode has a thickness on the order of 100 nm. The QSX-303 quartz sensors were selected because of the silicon dioxide, or silica, coating that is sputtered onto the working surface of the sensor, on top of the gold electrode. The thickness of that silica coating is 50 nm.

Each sensor was cleaned within 24 hours prior to the baseline measurement, and again within 24 hours prior to silver deposition. The cleaning procedure, as recommended by the manufacturer, includes UV/ozone treatment, sodium dodecylsulfate cleaning, rinsing, drying, and a final UV/ozone treatment.

Experiments were performed on a Q-sense E4 QCM device. All experiments were run at 22.0 degrees Celsius.

Data was collected through the Q-sense software package, which recorded 7 harmonic frequencies (odd harmonics from first through thirteenth), along with the dissipation of each of those 7 harmonics, for each of the 4 sensors being run simultaneously. The data was exported into



Figure 4: Flow chart of experimental procedures for all QCM measurements

Excel for statistical analysis.

During the initial resonant frequency search, if the device was unable to find any particular harmonic's maximum oscillation, or if there were multiple peaks within the scanning range, the data from that harmonic was determined to be unsuitable for further analysis; in some cases the data was still collected but not used for analysis, in other cases the data from that harmonic was not collected during the experiment. When the QCM device was unable to locate the resonant frequency, the rejection criteria was trivial. At other times, the Q-sense E4 would return a value for the resonant frequency and dissipation, but there were multiple peaks within the scanning range. Whenever at least one of the secondary peaks exceeded 50 percent of the amplitude of the primary peak (associated with the frequency value returned by the E4), the data from that harmonic was deemed unsuitable for further analysis.

The first harmonic was not used during analysis, based on its skewed results from baseline readings. Based on the criteria explained above, the data presented in this paper will not include the 11th or 13th harmonic. In very few cases did that data pass the initial assessment. There was insufficient data from these higher harmonics to group for trends.

Experimental flow overview - A flow chart is shown as Figure 4 which outlines the procedures followed for each sensor throughout the set of experiments presented here.

<u>QCM measurements</u> - Each sensor was placed into the Q-sense E4 specimen holder following the orientation guidelines. Initial resonant frequencies were determined for each sensor, each harmonic, which were used to determine the validity of the data collected, as explained above.

Data collection was carried out for a minimum of 10 minutes, seeking a stable baseline measurement. During that time, if any of the sensor's frequency readings drifted by more than 2 Hz, the measurement was started over. This was done in accordance with the manufacturer's recommendation and supported by literature (Cho 2010). It is presumed that substantial frequency drift is a measure of changing residual effects from clamping forces or from temperature equilibration, unless another effect might explain the change, which is not the case for these baseline measurements. The stable baseline measurement was sought to ensure that the reading most accurately captures the fundamental resonance frequencies of each individual sensor.

Further data analysis was conducted by using the initial resonant frequencies captured during the initial sweep. This is appropriate due to the stable measurement criteria explained above. Also, this approach will provide a better comparison to QCM measurements that were taken using an impedance analyzer, or other circuit scanning electronics, in that those measurements are instantaneous, so do not have a comparable time scale as the E4 QCM.

Flow measurements were conducted using the controlled influent waters described below. In all flow runs, the temperature was held at a constant 22.0 degrees Celsius and the flow rate, controlled by an Ismatec IPC-N4 peristaltic pump, was held at a constant 100 μ L/min through each sensor's holder.

Final QCM measurements were taken of each sensor after the silver flow run was complete and the sensor had dried, in order to compare the final shifts of frequency and dissipation relative to baseline dry measurements, both taken under ambient conditions. Visual inspection was performed after the silver flow experiment, confirming an absence of silver in cases where substantial frequency shifts were detected.

<u>Silver deposition</u> – Immediately after the sensor was cleaned according to the procedures mentioned above, colloidal silver was then deposited onto the silica surface of the sensor. Each sensor had 5 μ L of the application solution drop cast onto the center of the electrode area, equating to an expected deposited

mass of $1.27 \ \mu g$. Given that the colloidal silver product is 70-75 percent silver, the expected silver mass deposited onto each sensor was 890 ng, with the remaining mass comprised mainly of the casein stabilizer.

<u>Sample waters</u> - Table 3 below shows the sample waters used during these experiments. The baseline condition is the first line of Table 3, Millipore ultrapure water obtained from a Direct-Q3 UV system. The ionic strength and chloride content of each sample water is provided.

Sample water	рН	Ionic Strength	Cl ⁻ concentration
	(pH units)	(mM)	(mM)
Millipore ultrapure	5.8	8.8 E-04	0
51 NTU, Kaolin particles	5.6	8.8 E-04	0
HNO ₃ at pH=4.8	4.8	5.0 E-03	0
NaOH at pH=9.3	9.3	0.015	0
NaNO ₃	5.4	150	0
Ca(NO ₃) ₂	5.7	150	0
NaOCI at 8.8 mg/L	8.5	0.12	0.12
NaOCI at 525 mg/L	8.5	7	7
1% PBS	7.1	2	1
10% TSB at 1.2 g/L TOC	7.0	129	86
NOM at 15 mg/L TOC	7.1	1	-

Table 3: Sample water summary table

Adjustement of pH was obtained by use of 1 molar nitric acid or sodium hydroxide, titrated to the desired pH. Kaolin powder (Fisher Scientific) was added to the baseline ultrapure water in order to increase the turbidity to a nominal value of 50 nepholometric turbidity units (NTU). Turbidity measurements were taken on a Hach Ratio/XR Turbidimeter, using a calibration curve obtained less than 30 days prior to these measurements from control specimens prepared by diluting a 4000 NTU StablCal® Formazin turbidity standard. Sodium nitrate (NaNO₃) was selected as a representative monovalent ion, with calcium nitrate (Ca(NO₃)₂) as a representative divalent ion. Both were mixed into solution to an ionic strength of 150 mM. Sodium hypochlorite solutions were mixed to final concentrations of 8.8 and 525 mg/L, representative of water treated for drinking and of a 1 percent dilution of household bleach, respectively. Natural organic matter was taken from Mirror Lake, Colorado in June 2010; the sample water was measured at 15 mg/L TOC with an ionic strength of 0.93 mM according to its measured specific conductivity. Other waters shown in Table 3 were used during preliminary experiments that formed the direction of this investigation.

Results and Discussion

<u>Baseline flow</u> - As discussed previously, theoretical values may be calculated for the frequency and dissipation shifts caused by a fluid with known density and viscosity (Table 2). There was good correlation between theoretical values and the measured values. The bar graph included as Figure 5 is a representation of the measured frequency of each harmonic of interest. The left-most set of bars, labeled "All", includes data from every sample water, every sensor, with a total number of 35 data points included. The other sets of data are labeled according to the condition of the influent water. The error

bars for this plot, and all other figures presented unless otherwise specified, represent the 95 percent confidence interval as determined using Student's t-test with α equal to 0.05.

The mean for all of the sensors correlates extremely well with the theoretical shift in frequency, especially the measured value for the third harmonic. A trend exists in which the first harmonic is shifted slightly more negatively than theory predicts, causing its normalized value (as plotted) to exceed one, with the third and higher harmonics shifting less than theoretical predictions (having normalized values less than one). In fact, each successively higher frequency shows a slightly larger departure from the predicted value, causing the normalized values to step down from the first to the third to the fifth harmonics, and so on. That same trend is present in all of the data sets for the individual sample waters.



Figure 5: Frequency shift during baseline flow measurements normalized to theoretical value for that harmonic

Clearly some data sets have a wide variance in the measured frequency shifts. In particular, the baseline flow data from experimental runs with varied turbidity, ionic strength, and sodium hypochlorite show a much larger range for their 95 percent confidence intervals. In some cases, the influent water itself may be interacting with the silica surface of the sensor, causing a fluctuation in the frequency reading. If that is the case, the intention of the baseline reading is to account for that type of fluctuation when running the flow experiment across the deposited silver.

Similarly, the dissipation shifts for each of those harmonics under baseline flow conditions are shown as Figure 6. The most obvious feature of these data is the major discrepancy between the theoretical and measured values for the dissipation of the first, or fundamental, resonant frequency. While the third through ninth harmonics all correlate well to predicted values, the first harmonic deviates from predicted values by around 25 percent. In all cases, its shift is greater than the predicted value of 278. Keep in mind that each harmonic frequency has a characteristic decay length for any given media, which is always greater for the first harmonic. Perhaps the larger penetration depth of the first harmonic is a cause for these substantially higher dissipation readings, by allowing for more interference from the flow regime within the sensor holder.



In this dissipation data, there is not a prevalent step-wise trend between the higher frequencies as was seen in the frequency data.

Figure 7: Dissipation shifts during baseline flow experiments, normalized to theoretical values for each harmonic



Silver deposition – Each sensor was treated identically for the silver deposition process, allowing for the

Figure 6: Frequency and dissipation shifts from silver deposition. Error bars represent 95% confidence interval (n=37). Dashed lines show the expected frequency shift given the mass of silver deposited, calculated by Sauerbrey equation

sensors. Figure 7 shows the results of the silver deposition measurements. both frequency and dissipation, across each of the harmonics up through the ninth. The mean of each harmonic is plotted and the error bars show the 95 percent confidence interval. Also included in that figure is a dashed line at 219 Hz, which is the expected shift for

to be grouped, with 37 total

each of those scaled frequencies given the known deposition process, calculated by the Sauerbrey equation.

According to the principles presented in the Background section, the silver nanoparticles as deposited behave as a sufficiently rigid mass so that visco-elastic properties may be neglected. As shown in Figure 7, the shift in dissipation values caused by the addition of silver was on the order of $5-10 \times 10^{-6}$ dissipation units. Dissipation shifts of that magnitude fall well below the threshold of around 10 percent of the magnitude of the frequency shift, meaning that elastic models (such as the Voigt model) are not well suited to describe this mass. For that reason, any comparisons of frequency shifts to mass have been calculated simply using the Sauerbrey correlation.

Drop casting the colloidal silver solution onto the silica surface is certainly not the best manner of silver deposition to meet the criteria of the Sauerbrey correlation. Drop casting is, however, a deposition process representative of the application method used during ceramic pot filter production. Brushing the colloidal silver solution onto the walls of the ceramic pot filter allows for a similar interaction between silver nanoparticles and the ceramic surface as when a drop is placed onto the QCM sensor surface.

Two primary concerns raised by drop casting these nanoparticles onto the sensor are the location within the overlapping electrode area, and the uniformity of the mass deposited. Every effort was made to center the 5 μ L drop of the colloidal silver solution within the electrode area; in all cases, the entirety of the drop was contained within the overlapping area. A mass placed at the very outskirts of the overlapping electrode area will have a very small effect on the frequency readings, generally less than a few percent (Lu 2004). Effects caused by poor placement of the adsorbed silver are not sufficient to explain the discrepancy, relative to the calculated, expected values, in frequency shifts.

The uniformity of the deposited silver was not controlled beyond the deposition process. Localized deposits of mass may have impacted the frequency response of these readings. If localized deposits were the primary cause of the poorly correlated frequency readings, then one would expect to see extreme outliers within the data set, in that unique localized deposits could cause dramatic effects that would not be repeated. Another reason to assume that localized deposits did not have an important effect on the frequency readings is that a similar discrepancy (between theoretical or expected values, and actual values) was encountered when silver was deposited by sputtering, a method that deposits a much more uniform film than can be achieved by drop casting.

<u>Silver flow</u> – Data was recorded for each flow condition, providing a real-time glimpse of the effects that each varied water quality parameter has on the release of silver from the silica surface.

<u>Post flow</u> – These measurements indicate a major effect of sodium hypochlorite to remove silver nanoparticles from the silica surface. The removal by sodium hypochlorite was practically immediate and nearly complete (~90 percent of deposited, detected mass was removed). Optical microscopy confirmed the near complete removal of silver.

The nitrate-salt containing waters showed deposition-like behavior that needs to be analyzed further to fully understand the effects captured. All other water quality parameters showed much less of an effect on the release of silver.

Conclusions

The results presented here provide a glimpse of a colloidal silver product used worldwide in ceramic pot filter production. A novel gravimetric technique was employed to determine the effects of varied water quality parameters on the rate of release of that silver nanoparticle, once applied to a silica surface.

The results of this study show that the pH, ionic strength, and turbidity, when at environmentally relevant concentrations, have little impact on the rate of silver release. Even though the results do not show significant trends between the sample waters tested, a valuable piece of information was still gained – that the influent water quality should not greatly impact the rate of release of the colloidal silver coating from the walls of the ceramic pot filter.

On the other hand, water containing even very low concentrations of sodium hypochlorite has the effect of removing almost all of the silver from the silica surface. That is an important fact to know for the use of these ceramic pot filters.

The concentration of 8.8 mg/L NaOCl was selected based on guidelines provided by the World Health Organization (WHO) and the US Environmental Protection Agency (EPA) for drinking water purification by addition of household bleach. This concentration of sodium hypochlorite is a potential influent stream into a ceramic pot filter in areas where inconsistent municipal drinking water treatment may be provided, or where community members have been instructed to also treat their water with a few drops of bleach per liter (which is a distinct possibility given the often overlapping efforts of aid organizations and NGO's in developing regions).

Based on these experiments, it is clear that pouring water containing NaOCl into a ceramic pot filter would quickly remove the silver coating. There are at least two negative effects caused by this, including the increased silver concentration being ingested by the end-user and the decreased effectiveness of the water filter due to the removal of the anti-microbial coating.

It is extremely important that users do not clean their ceramic pot filters with water containing bleach. This could be a difficult message to deliver, as it may seemingly be in contrast to the very important procedure of cleaning the receptacle and spigot with a cleaning solution, often containing sodium hypochlorite from bleach.

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