Determining The Properties of Colloidal Silver

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INTRODUCTION

The *properties* of substances are their characteristic qualities, many of which can be measured precisely and expressed in numbers. Accurately quantifying such properties requires:
1. A scientifically valid theoretical approach.
2. Consistent process implementation.
3. Calibration values that can be traced to recognized standards.

This document will specifically address the properties of colloidal silver solutions that define the overall quality of the solution. The operative definition of a colloid is a solution containing suspended particles whose sizes range from 1 micron down to 0.001 microns (1 nanometer). The particles are suspended in pure water.

This document is intended for those seeking a scientific description of how to measure the relevant properties that define the quality of a colloidal silver solution. This may include labs that are asked to perform quantitative measurements of silver colloids, producers of colloidal silver solutions, producers of machines that make colloidal silver as well as interested consumers who are technically inclined. Recently, much has been written about colloidal silver that lacks scientific validity. This document will discuss the measurement procedures in scientific terms such that an independent lab can duplicate the results described herein.

THE PROPERTIES OF INTEREST

1. Silver Concentration – total silver
   a. Colloidal particles in ppm, percent of total.
   b. Ionic silver in ppm, percent of total.
2. Electrical conductivity
3. pH of solution
4. Tyndall Effect – light reflected by a colloid
5. Zeta potential
6. Particle size distribution
7. Contaminants

SILVER CONCENTRATION

Silver concentration is most frequently reported as *total silver* measured in milligrams per liter (mg/L), which is numerically the same as parts-per-million (ppm). The *total silver* consists of silver in two distinct forms, silver particles and silver ions. While the measurement of total silver is fairly straight forward, the measurement of the ionic silver is less so. It is important to know how much of the total silver consists of particles vs. ions because it is the particles that define the colloid. In most processes used to produce colloidal silver the particles make up only a small fraction of the total silver.

Why is it important to how much of the total is ionic?

The benefits of colloidal silver are produced by the nanometer sized metallic silver particles not the ions. In most colloidal silver products a large quantity of ionic silver is produced as a by-product of generating the silver particles. The prominent methods of production are electrochemical processes using either low voltage DC current or high voltage AC. Both the AC and DC process may employ a constant voltage or a constant current source. Both the DC and the high voltage AC produce a significant percentage of the total silver as ionic. Typically, 75 - 99% of total silver is ionic depending on process variables. In some products claiming very high concentration levels, almost the entire silver content is ionic. To state the silver concentration in ppm without specifying what percentage is ionic is misleading to say the least. Therefore, it is important to know what

percentage of the silver concentration is ionic to properly evaluate the quality and effectiveness of the product.

What is an ion?

An ion is an atom that has gained or lost one or more orbital electrons. In the case of silver ions, it is always minus a single electron. An ion is not metallic silver, and when it is in solution it does not reflect light and cannot be seen by even the most powerful electron microscope. When ions are added to a solution, the conductivity of the solution will increase. This is a property of ions but not a property of particles. Ions cannot be separated from the solution by centrifugation and will not settle out over time unlike particles, which can be separated from a solution. A silver ion is slightly smaller in diameter than a silver atom owing to the fact that it is missing an electron. The diameter of a silver ion is 0.230 nm. Since is it missing an electron, the silver ion has a positive charge and is called a *cation.* The silver ion will readily combine with certain other ions to form a salt. A chlorine (Cl) atom that takes on an additional electron becomes a chloride ion, which has a negative charge and is called an *anion*. The chloride ion readily combines with the silver ion to form silver chloride (AgCl).

Ionic silver in the human body

Upon ingestion, the ionic silver present in most colloidal silver solutions will immediately come into contact with the hydrochloric (HCl) acid that normally exists in the stomach to digest food. The chloride ion from the hydrochloric acid combines at once with the silver ion to form silver chloride. Since hydrochloric acid does not dissolve metallic silver, the silver particles remain unaffected by the stomach acid. Some of the remaining silver particles, due to their nanometer size will pass easily through the lining of the gastro-intestinal tract and will be absorbed into the blood stream. The silver chloride that precipitates in the stomach consists of large molecules that flocculate to become even larger particles of silver chloride. Compared to the metallic silver particles, these particles are enormous and will not readily pass through the lining of the GI tract, and thus will be passed out of the body as waste.

Colloidal silver can enter the blood stream directly by at least two different means. The first is through the lungs by using a nebulizer to convert the colloidal silver into nanometer size droplets and then inhaling these droplets. The small size of the silver particles and silver ions will pass through the lung tissue directly into the blood stream. Once in the blood stream, the particles will circulate with the blood but the ions will immediately combine with the plentiful supply of chloride ions in the serum. Human blood serum contains a large quantity of potassium chloride and a lesser amount of sodium chloride. The chloride ions are present in the serum in high concentration, typically 3500 ppm. The chloride ions immediately combine with the silver ions to form silver chloride. The large silver chloride molecules will be removed from the blood stream by the kidneys and passed out as waste.

The second way colloidal silver can pass directly into the blood stream is by sublingual absorption. The thin membranes under the tongue will pass the small particles and ions directly into the blood stream. Once in the blood stream, the ions will precipitate out as described above leaving the particles to circulate with the blood.

Because the silver ions cannot exist for long in the human body regardless of the entry mechanism, they really represent an undesired byproduct that is passed from the body as waste. The ideal colloidal silver would maximize the percentage of particles and minimize the percent of ions. Since typical colloidal silver products contain a very high percentage of ionic silver, there is a lot of potential for improvement by reducing the ionic content as close to zero percent as possible.

Simple demonstration of ionic silver

To demonstrate ionic silver content, all that is needed, is a chloride ion source to be added to a small amount of colloidal silver. Normal table salt is sodium chloride (NaCl). When table salt is dissolved in water it decomposes into sodium ions and chloride ions. To demonstrate: Place a small amount (1-2 ounces) of colloidal silver in a clear glass. Add a few grains of table salt. Observe that as the salt dissolves a white cloud of silver chloride forms in the solution. Eventually, the entire solution will turn cloudy. If more salt is added, the white silver chloride will become denser until all the silver ions have combined with the available chlorine ions. If no

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silver ions are present then no white cloud will form. Details on how to measure ionic silver content are discussed in the section *Measuring Ionic Silver*.

Measuring Total Silver

Total silver is the amount of silver contained in the particles plus the amount of silver contained in the ions. This represents to total amount of silver in the colloidal solution. Total silver can be measured in a chemical analytical laboratory in several different ways depending on the sophistication of the laboratory equipment available. Instruments used to measure total silver content of a colloid can be sub-divided into two generic categories based on whether the measuring instrument must have the silver particles first converted to ionic in order to be measured. Some instruments can only measure silver when it is ionic form, whiles others can measure the silver content regardless of the form it is in. Instruments that can measure silver content only when it is in ionic form would include Ion Specific Electrodes, Spectrophotometers, and colorimeters. Instruments that can measure the silver content when it contains both ions and particles would include Atomic Absorption Spectrophotometers (AAS) and Inductively Coupled Plasma (ICP) torch based systems. The AAS and the ICP instruments are generally capable of measuring the light absorbed and/or the light emitted by the silver atom when vaporizing the atoms changes their energy state. In order to use the instruments that can only measure silver in the ionic form requires that the silver particles be dissolved in nitric acid to convert the metallic particles to ions or digested in any number of other ways. This conversion process adds substantially to the time and effort required to make the measurement. The discussion will therefore focus on a method that does not require the conversion of particles to ions, namely the AAS.

It is common today to measure total silver using an Atomic Absorption Spectrophotometer. This is a sophisticated scientific instrument that has a minimum detection limit in the parts-per-billion range. It can measure trace metals in ppm to four significant digits. This measurement tool is well suited to the task and is common in analytical laboratories. The AAS will be used for some of the measurements discussed herein. Calibration of the AAS is from diluted standard silver solutions. Standard certified silver solutions for AAS calibration are available from commercial suppliers and typically come in 100 ppm and 1000 ppm concentrations with an accuracy of 0.3%. Complete details on using the AAS to measure silver are in the section *Measurement of Total Silver using Atomic Absorption.*

Measuring total silver using the minimum equipment

A less sophisticated method involves converting the silver particles to ionic form by dissolving the particles in nitric acid at which point all the silver is in ionic form. The silver ions are then precipitated into silver chloride using a small amount of hydrochloric acid to supply the chloride ion. The silver chloride is then filtered from the solution and weighed. The silver content is 75.26% of the silver chloride by weight. This is based on the ratio of the atomic weights of silver and chlorine. For example, if 100 mL of sample solution yielded 1 mg of silver content, the concentration of total silver would be 10 ppm. This method is more time consuming, and less accurate than an AAS, but it requires only an accurate analytical balance and a vacuum filtration system. In order to make such a measurement, the analytical balance must be able to accurately measure grams to five decimal places for the concentrations of interest. The least significant digit is 10 micro-grams.

TDS meter is not usable for measuring total silver

The use of instruments calibrated in Total Dissolved Solids (TDS) units does not measure total silver content. A TDS meter is really measuring the conductivity of the solution as expressed in micro-Siemens/cm (uS/cm) and converting the conductivity to TDS units by multiplying by a conversion factor to arrive at the ppm of total dissolved solids in the solution. The conversion factor is usually 0.5 for inorganic solutions and 0.7 for organic solutions. Conductivity measurements only respond to the ions present and not the silver particles. The TDS meter will be discussed in greater detail in the section *Use of TDS Meters.*

Measurement of Total Silver using Atomic Absorption/ Emission

Atomic absorption refers to the process whereby an atom absorbs light energy of a specific wavelength as it enters the excited state. As the number of atoms in the light path increased, the amount of light absorbed also

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increases in accordance with Beer's Law, which states that concentration is proportional to absorbance (C=kA). By measuring the amount of light absorbed, a quantitative determination of the amount of analyte can be made. The use of special light sources and careful selection of wavelengths allow the specific determination of individual elements. To cause the atoms to reach the excited state, the test sample is first atomized and then passed through an intense heat source. The heat source is an air-acetylene flame. The temperature of the flame is 2300 degrees Centigrade. The atomic absorption measurements described in this document were performed using a Perkin-Elmer Model 3030B Flame AAS.

The measurements can also be accomplished using atomic emission spectroscopy. For atomic emission, an Inductively Coupled Plasma/Atomic Emission Spectrometer (ICP/AES) would be the best choice.

The following instrument settings are selected from the Perkin-Elmer cookbook *Standard Atomic Absorption Conditions for Ag*.

Wavelength Selection – The wavelength is selected based on the concentration expected in the measured samples. Two wavelengths exist for silver. The primary wavelength of 328.1 nm has a linear range of 4.0 mg/L. and the secondary wavelength of 338.3 has a linear range of 10.0 mg/L. The tradeoff is sensitivity vs. linear range. If the more sensitive primary wavelength is selected, higher concentration solution may be diluted to keep them in the linear range of measurement. Liner range is more important for our purpose, so the secondary wavelength of 338.3 nanometers is selected.

Slit Width – 0.7 nm is specified for Ag.

Recommended Flame - Air-acetylene, oxidizing (lean, blue).

Nebulizer – Impact bead is used in lieu of flow spoiler.

Calibration - The AAS is calibrated using solutions of standard concentrations made by diluting a certified silver standard solution of 1000 ppm. The calibration values selected are 2, 5, 10, and 20 ppm. See the section *Making AAS Diluted Standards* for details on making the dilutions.

Preparing Samples for Atomic Absorption

Sample preparation is an important part of the measurement process. Consistency in preparation is essential to achieving accurate results. The samples under test consist of distilled or DI water containing silver particles in the range of a few microns down to 1-nanometer and silver ions. If larger particles were involved, acid digestion would be required to reduce the particle size to the point where they can pass through the nebulizer without causing clogging. The particles in our samples are small enough that clogging of the aspirator tubing is not an issue. The 2300 degree C flame is sufficient to vaporize the colloidal particles along with the ions and raise the silver atoms to the excited state needed to absorb light. Acid digestion is therefore not required for flame AA analysis of colloidal silver solutions.

pH Adjustment of sample - A small amount of nitric acid is used to stabilize the solution for measurement. The sample pH needs to be adjusted to 3.0 or less by addition of nitric acid. The nitric acid causes the silver atoms to transition to the higher energy state in a more consistent and uniform fashion when the atoms are vaporized in the flame, which has been experimentally shown to stabilize the measurement. This is accomplished using 25 micro-liter (uL) of 70% strength nitric acid added to 30 mL of sample. A drop is 1/50 of a milli-liter or 20 uL, so about a drop is all that is needed. A variable volume pipette is used for consistency in dispensing the 25 uL. Stir the solution to assure complete mixing of the acid. The nitric acid is weak enough that it does not significantly affect the silver particles. If left long enough, any metallic silver that would be dissolved by the acid would be available as silver ions and thus would not affect the measurement. The same pH adjustment is applied to the dilute standards that are used to calibrate the AAS. Failure to adjust the pH of the sample with nitric acid will result in the AAS reading 5 to 15 percent lower than it would if the sample had been properly pH adjusted.

Calibrating the AAS

The AAS is calibrated using diluted standard solutions. The same pH adjustment that is applied to the samples is applied to standards that are used to calibrate the AAS. Nitric acid is added to the calibration standards at the rate of 25 uL of 70% nitric acid per 30 mL of standard. It is important that the samples and the standards have approximately the same pH when dealing with solutions containing silver.

Since the absorbance response of the instrument has a limited range, the calibration will use values that permit a reasonable good interpolation along the response curve. For example, if the linear range is known to be 10 ppm, and if samples containing concentrations above 10 ppm are to be measured, the calibration points may be selected as 10, 20, 30 and 50 ppm. This assumes that 50-ppm is the highest concentration of interest for samples to be measured. Alternatively, samples whose concentration is above 10 ppm can be diluted to keep the test sample within the linear range of the instrument. The instrument automatically does the interpolation between the calibration points. Once calibrated using the pH adjusted standards, the instrument is ready to make measurements.

Making the AAS measurement for total silver

Once the instrument has been calibrated using pH adjusted concentration standards it is ready to begin the measurements. The atomic absorption reading will contain a component of noise that must be considered when selecting the time interval of a single measurement and the number of samples to average to arrive at the final result. Most modern instrument will provide a *standard deviation* calculation of the averaged samples in order to assist the operator in selecting the parameters that will produce the most consistent reading. For a standard deviation calculation to have statistical validity at the 95% confidence limit, at lease 30 samples must be included in the average/standard deviation. Reasonable fast readings using a 3 second sample time and a 3-sample average will provide results generally repeatable to 3 significant digits (i.e. 10.3 ppm). For more precise measurements the sample time and number of samples in the average can be increased. For example, 10-second sample time and 30-sample average will get close to 4 significant digits of repeatable results. Some operators prefer sample times of 30 seconds or more for the ultimately repeatable reading. Very long sample times will require the instrument to aspirate a substantial amount of sample solution. The trade off is determined by how long the measurement will take and how much sample solution will be consumed in order to achieve the higher level of measurement accuracy and repeatability. If sample solution is available in unlimited amounts the accuracy probably has reached its asymptotic value at 30-second sample time and 30-sample average. Such a measurement will take 900 seconds to complete (15 min), and so is probably impractical for most users.

Measuring Ionic Silver with the AAS

The AAS measures the atomic absorption of all the silver atoms present in the sample regardless of the form they are in as was discussed in the section on measuring total silver. The advantage of using the AAS to measure the ionic silver is that the measurement is inherently more accurate than using the Ion Selective Electrode (ISE) which is at best only accurate within 2%. In order to measure just the ionic silver content, the particles must be removed leaving only the ionic silver solution that can be measured with the AAS. The most direct approach to removing the particles from a colloidal silver solution is by centrifugation. By spinning the colloid using what is called an Ultra Centrifuge, enough G-forces can be produced to effectively remove the particles. What makes this possible is the high-density ratio of particles vs. the ionic dissolved silver. Metallic silver has a density of 10.5 g/cc vs. pure water, which is 1.0g/cc. Since the ionic silver is dissolved and uniformly dispersed in the water, it only slightly raises the density of the water depending on the concentration of the ionic silver. But even at high concentration of ionic silver, the density of the water with the ions is only slightly higher than 1 making the density ratio about a 10:1, which aids in the separation by centrifugation.

It has been empirically determined that a force-time integral in excess of 325 million G-seconds will suffice to separate out particles into the low nanometer range. When using a centrifuge that produces 1 million G-forces, it would have to dwell at that level for at least 325 seconds to insure particle separation. While a 1 million G-force centrifuges are available, they are extremely expensive and not cost effective for this purpose. Using a 365,000 G-force centrifuge the dwell time would increase to 890 seconds.

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Using an 8-place rotor and 20 mL vials will provide a total sample volume of 160 mL. Fill all the vials with the colloidal silver sample and spin at 395,000 G-forces (around 65,000 rpm using a Beckman L8-80M with a Ti80 rotor) for 15 minutes. Since the particle sizes are in the nanometer range, only a small cake of solid will form at the bottom of the vial. The supernatant is extracted using a pipette being careful to no touch the cake which is at the bottom of the vial. The extracted fluid from the vials has been tested for the presence s of silver particles using a Photon Correlation Spectrometer (PCS). This cross check is to confirm that the particles have been removed. The PCS showed a correlation function that is indistinguishable from DI water, indicating the complete removal of the particles. This sample liquid now contains only the ionic silver content from the original colloid sample. This sample is now measured for silver using the AAS. The concentration reading directly in ppm represents the ionic silver only.

Measuring Ionic Silver with the ISE

While other measurement methodologies exist, the most straightforward approach is the use of an Ion Selective Electrode (ISE). An ISE is designed to respond to a specific ion, in this case, silver. An ISE requires an instrument designed for use with such electrodes. ISE meters are generally accurate within 2%. A typical ISE capable measuring instrument is combined with a pH meter, since a glass pH electrode operates in a similar fashion. These instruments are listed in catalogs of scientific equipment suppliers as pH/ISE meters and are available from several prominent instrument manufacturers.

An ISE for the silver ion has a typical detection limit of 0.01 ppm above which the probe is linear. Below 0.01 ppm the calibration is non-linear and should be avoided. The ISE meter and probe are calibrated using a silver solution made in the lab by dissolving a know amount of silver nitrate in DI water or by purchasing a silver standard solution certified for concentration. Such solutions are available from suppliers in concentrations of 100 ppm and 1000 ppm. The standard solutions are provided with traceability certificates that specify the maximum error in concentration. For example, a 1000 ppm standard will be specified to be plus/minus 3 ppm. This translates to 0.3% allowable error.

The ISE meter must be calibrated before measurements can be taken. Calibration of the ISE meter requires that the standard solution be diluted to a range that brackets the measurements of interest. Most ISE meters allow for 3 to 5 or more points of calibration. Three calibration points are adequate for purposes of this experiment. If the ionic concentration is expected to be less that 10 ppm, three calibration points may be 0.5, 1, and 10 ppm. For each calibration point a diluted standard must be made from the certified standard. The diluted standards are created by dilution with high purity deionized (DI) water on a volumetric basis. For example to dilute the 1000-ppm certified standard down to 10 ppm requires a dilution ratio of 1:100 (1000/10=100). To make 100 ml of 10 ppm diluted standard requires 1 ml of certified 1000 ppm standard and 99 ml of DI water. The resulting 100 ml of diluted standard will contain 1 ml of certified standard in a 1:100 ratio. To make 100 ml of the 1 ppm diluted standard, use 10 ml of the 10 ppm diluted standard and 90 ml of DI water. To make 100 ml of the 0.5 ppm diluted standard, use 5 ml of the 10 ppm diluted standard and 95 ml of DI water.

While the dilutions are based on volume, a more accurate way to produce them is based on weight by using an accurate analytical balance that reads in grams to five decimal places. Accuracy of the diluted standard is improved because weight (mass) can be measured more accurately than volume, even when using volumetric flasks. When weighing the standard solutions, its weight in grams must be corrected for density of the standard. While DI water weighs 1 gram per mL at 25°C, the standard solution weighs slightly more because it has a higher density due to the dissolved salt. The exact density of the standard solution will be provided by manufacturer and specified on the calibration certificate. For example, it will appear as Density = 1.00881 g/ml.

Once the diluted standards are prepared, the Ionic Strength Adjustor (ISA) solution is added to uniformly raise the ionic activity of the standards. For silver ion electrodes the ISA is usually sodium nitrate ($NaNO_3$) dissolved in DI water. ISA solutions are available from the manufacturer of the electrodes. The ISA solution is added to both the standards and the samples using 2mL of ISA to 100 mL of samples or standards.

Calibrating the ISE meter

The ISE meter is calibrated using the diluted standards that have been ion adjusted as described above. The exact calibration procedure will be specified in the user manual that is furnished by the manufacturer. It is recommended that the highest calibration value be above the expected sample concentration. Usually, two or three calibration points are sufficient. While calibrating the ISE, the calibration solution must be stirred. If you choose to not stir during calibration, then do not stir during sample reading. Be consistent with the stirring.

Preparing sample for ISE measurement

Samples of colloidal silver to be measured must first be ion adjusted using the ISA solution (same as standards). For 100 mL of sample, 2mL of ISA solution is added to uniformly raise the ionic activity of the sample to that of the standard. The ISA solution must be thoroughly mixed into the sample by stirring.

Making the ISE measurement

Once the ISA is added, the sample is ready to be measured by immersing the ISE probe into the sample while the sample is being stirred. After the ISE is properly calibrated using the standard solutions, it will readout the concentration of silver ions in the sample directly in parts per million. This measurement reads only the *ionic silver* present, not the silver in the *particles*.

Determining the silver content in the particles

The silver contained in the particles is determined by subtracting the ionic silver concentration from the total silver concentration. The total silver concentration is measured on the AAS and the ionic silver concentration is measured on the ISE. Therefore,

Silver particle (ppm) = Total silver (ppm) – Ionic silver (ppm)

Use of Total Dissolved Solid (TDS) Meters

TDS meters are commonly misused in an attempt to measure properties of colloidal silver. A strict scientific definition of Total Dissolved Solids is not to be found in chemistry and physics handbooks. The water testing industry as way to express water hardness uses this term. Water hardness is caused by the polyvalent metallic ions (i.e. calcium and magnesium) dissolved in water. Hardness is reported as an equivalent concentration of calcium carbonate ($CaCO_3$). A TDS meter actually measures the electrical conductivity of the sample then multiplies by a calibration factor, and expresses the result in ppm. The calibration factor of 0.5 for calcium carbonate is also commonly used as an approximation for other inorganic compounds as well. Some TDS meters allow the user to select another calibration factor (i.e. 0.7 for organic compounds) while the more sophisticated units let the user enter a calibration factor anywhere between 0.01 and 0.99. So when the 0.5 factor is used, all ions in solution are expressed in the equivalent amount of calcium carbonate. The more sophisticated instruments which allow the user to enter a wide range of calibration factors is to account for the fact that different ions require vastly different calibration factors to be properly expressed. If the user knows that an only single type of ion is present, and enters the calibration factor that applies to that particular ion, then the accuracy of the resultant reading will be improved. The TDS meter cannot distinguish between which ions it is measuring. Any and all ions present in the sample will affect the reading but will be evaluated using a single calibration factor.

Since the TDS meter is really measuring electrical conductivity, only the ions present in the solution will affect the measured value. Silver particles do not affect the electrical conductivity of the solution. The more ions present, the higher the conductivity of the solution. The standard 0.5 calibration factor has no relevance to silver ions so the ppm reading on the instrument is a meaningless number relative to silver ions. A close approximation for a silver ion calibration factor is 1.05 to 1.15 but this method is fraught with problems that arise from ionic contamination, discussed in more detail in the section on *Electrical Conductivity*.

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Even if the user believes he knows that only silver ions are present the measurement cannot be relied upon, since other factors such as temperature and pH of the sample will alter the results. As temperature goes up, conductivity goes up. Conductivity reading increase rapidly as the pH value decreases. For example, a pH value of 4.5 may cause a 300% increase in the conductivity reading from when the pH was neutral (7.0). This does not mean that there is 3 times the amount of silver ions present, only that the conductivity has increased due to the acidity of the solution. In many processes that produce silver particles, the pH of the solution drops as the process progresses, sometimes, very dramatically. Since electrical conductivity varies with temperature, it is important that the temperature of the sample be at the same temperature at which the instrument was calibrated. See the section on *Electrical Conductivity* for more details.

Lastly, TDS meters generally display results with less resolution than conductivity meters. The extreme case is to compare the TDS reading of a sample with the reading from a conductivity instrument designed for reading low range values of conductivity. In this extreme case the conductivity instrument will display 4 significant digits of resolution compared to a single digit of resolution on the TDS. That is an unacceptable large loss of measurement accuracy.

In summary, the TDS responds to ionic content, not just silver ions, but any ions in the solution will raise the measured TDS value. Relying on a TDS meter to determine silver concentration is bogus science in the extreme.

ELECTRICAL CONDUCTIVITY

The electrical *conductivity* of a material is an inherent property – meaning that pure water at a specific temperature will always have the same conductivity. The measurement of electrical conductivity is generally referred to as just *conductivity*. Conductivity is the reciprocal of the *resistivity* of a material. When a fluid is involved, the electrolytic conductivity is given by the ratio of current density to the electric field strength. The *conductance* of a sample of pure water depends on how the measurement was made. Things that affect conductance include how big a sample is being measured, how far apart the electrodes are, etc. Conductance is defined as the reciprocal of the resistance in ohms, measured between the opposing faces of a 1 cm cube of liquid at a specific temperature. The unit of conductance is called Siemens (S) which was formerly named the mho (ohm spelled backward). Because a measurement gives the conductance, methods have been devised to convert the measured value to the conductivity, so that results can be compared from different experiments. This requires that a *cell constant* (K) be determined for the instrument using a solution of known conductivity. Once the cell constant has been determined, then the conductivity can be calculated as follows:

Conductivity = Cell conductance x K

The cell constant is related to the physical characteristics of the measuring cell. K is defined for two flat, parallel measuring electrodes as the electrode separation distance (d) divided by the electrode area (A). Thus, for a 1 cm cube of liquid,

$K = d/A$, where $A = 1 \ cm^{-1}$

Typically, a cell with K = 0.1 cm-1 is chosen for pure water measurements, while for environmental water and industrial solutions a cell with K of 0.4 to 1 cm is used. Cells with up to K = 10 cm-1 are best for very high conductivity samples. The cell constant is calibrated using a conductivity standard solution whose value is certified to a known standard. Conductivity standards consist of sodium chloride dissolved in DI water.

The unit of conductivity is Siemens/m or in scaled form Siemens/cm. In modern conductivity meters, the measured cell value is entered into the meter and the conversion from conductance to conductivity is performed automatically. The instrument scales the value and displays the results in micro-Siemens/cm (uS/cm).

In metals, electrons carry the electrical current, while in water it is carried by charged ions. In both cases, the number of charge carriers determines the conductivity, how fast they move, and how much charge each one carries. Thus, for most water solutions, the higher the concentration of dissolved salts, which will lead to more ions, the higher the conductivity. This effect continues until the solution gets "too crowded," restricting the

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freedom of the ions to move, and the conductivity may actually decrease with increasing concentration.

Metals are extremely conductive because electrons move almost with the speed of light, while in water ions move much slowly, and the conductivity is much lower. Raising the temperature makes the ions move faster. Because the ions are of different sizes, and carry different amounts of water with them as they move, the temperature effect is different for each ion. Typically, the conductivity varies about 1-3% per degree C, and this temperature coefficient may itself vary with concentration and temperature.

Some Conductivity Values of Typical Samples measured at 25°C.

Ultra pure Water	0.055 uS/cm
Drinking Water	50
Ocean Water	53,000
31% HNO₃	865,000

Distilled water in equilibrium with carbon dioxide in the air has a conductivity of about 0.8 uS/cm.

Conductivity can be a valuable tool to help determine the properties of colloidal silver solutions when its limitations are fully understood. Because the *ion content* of water determines its conductivity, we can use this relationship to get an indication of the concentration of silver ions that are in a colloidal solution. The metallic silver particles present in the colloid do not affect the conductivity value, only the ions. To be more specific, conductivity is not an indication of the *quantity* of ions present, but of the ionic *activity* that is present. Some ions have higher activity than other ions. The higher the ionic activity, the higher the conductivity associated with that ion. A small quantity of ions of high ionic activity can cause a larger increase in conductivity than a large quantity of ions having low ionic activity. This is an important consideration when using conductivity measurements of colloidal silver solutions.

Generally speaking, the more apriori knowledge one has about the solution being measured the better. When measuring a solution produced in-house, there is a good likelihood of knowing what other ions may be present in the solution. This information will be missing when trying to measure a solution from an unknown source. The presents of contamination in the form of unknown ions are responsible for most of the uncertainty when trying to apply conductivity measurements to colloidal silver. An important indication of the presents of contaminating ions is the pH of the solution. The farther from neutral pH (7.0) the solution is, the less useful is the conductivity measurement for determining the silver ionic concentration. Conductivity can go up dramatically as the pH departs from a neutral value of 7.0.

Conductivity vs. silver ion concentration

Conductivity is not affected by metallic silver particles present in the solution, only the ions. Therefore, conductivity cannot be used to determine total silver content, since the particles will not influence the reading. Pure water is an electrical insulator. Adding silver particles to pure water results in the solution still being an insulator.

The empirical relationship of conductivity vs. silver ion concentration is predicated on controlling three factors; pH, temperature and contaminating ions. The pH of the solution must be neutral (pH=7.0) with the temperature at 25°C and no contamination from other ions present. When that is the case, the relationship is:

Silver ions (ppm) = Conductivity (uS/cm)   x   conversion factor

The conversion factor has been observed to range from 1.05 to 1.15 with an average value of 1.1. This has been observed over hundreds of laboratory samples produced by electrolysis. However, this works for only a very limited set of conditions and processes.

Comparing values determined by conductivity with values determined by atomic absorption/emission has shown that the results may be within 10-25% of the actual silver at best. This assumes that there is no ionic contamination. Ionic contamination may result from many causes. The most egregious errors arise when

attempting to measure ionic silver solutions that were produced using a high voltage arc. The arc renders dissolved nitrogen in the water into nitric acid which increases conductivity drastically. For these solutions, conductivity measurements have proven to be virtually worthless for determining ionic silver content. Atomic absorption/emission measurements routinely indicate only 1% or less of the silver content that would be inferred from the conductivity measured value. This experience demonstrates the futility of trying to determine ionic silver concentration by using electrical conductivity.

While many modern conductivity meters include a temperature compensation feature, this should not be relied upon when attempting to measure ionic silver concentrations. Temperature coefficients used to compensate the instrument will themselves vary with temperature and concentration.

Since this is an imprecise relationship that holds true only under very specific conditions, it is recommended that this measurement not be used a primary means of determination. It is reasonable to consider this relationship as a cross check for determination made by other means (i.e. to cross check an ISE measurement for ionic silver concentration). If the answers are in agreement, the likelihood is that the measurements were satisfactory. If they are not in agreement, something is amiss.

If the conductivity measurement results in a ppm value higher than the ISE measurement, there is probably contaminating ions and the pH will probably not be neutral. As mentioned previously, a pH value of 4.5 may cause a 300% increase in the conductivity reading from when the pH was neutral (7.0).

It is also possible to have a neutral pH and significant contamination from other ions. This would happen if the contaminants resulted in a balanced pH, which salts can do. In such a case the pH would be neutral but the conductivity could be astronomically high.

Conductivity instruments – range and resolution requirements

Most conductivity meters that are capable of measuring over a wide range are limited in the resolution that is available on the lowest range. Therefore, to adequately cover the entire measuring ranges of interest for colloidal silver requires the use of two separate instruments, a low range reading unit and a wide range reading unit.

Low range reading unit – These are usually called Ultra Pure Water testers and cover the range of 0.000 to 1.999 uS/cm with a resolution of 0.001 uS/cm. This unit is for measuring very pure de-ionized and distilled water or when ever high resolution is needed below 2.000 uS/cm. This class of instrument is available from several manufactures such as the Hanna UPW model HI 98309. The specified accuracy is 2% of full scale.

Wide range reading unit – These are usually referred to as multi-range instruments with the lowest range extending up to 199.9 uS/cm with a resolution of 0.1 uS/cm. The highest range may go to 199.9mS/cm with two ranges between the highest and the lowest. The bottom two ranges will cover most of the measurement for colloidal silver when only 0.1 uS/cm of resolution is needed. An example of this is the Hanna HI 9033. The specified accuracy is 1% of full scale.

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