By Daryn Martin, KRWA Technical Assistant

The Importance of Adequate Chlorine Residuals. How Accurate are Your System's?

How often is the chlorine residual analyzed in a Public Water Supply (PWS) system? The correct answer, and the one I am sure most people in the water utility business knows, is DAILY. Kansas Department of Health and Environment (KDHE) regulations require every PWS to analyze and record a chlorine residual every single day that water is being served to customers. The last time I counted, there were 982 active PWS in Kansas and 869 of those are "Community" systems, meaning they serve customers daily. So, for more than 88 percent of the PWS in Kansas, that means someone has to run a chlorine analysis EVERY day.

Why is chlorine important? My water filter salesperson told me chlorine is toxic and I should pay him to filter it out of my water! What gives here? I don't agree. Chlorine IS important! The presence of free chlorine residual in drinking water indicates that: 1) a sufficient amount of chlorine was added to the water to inactivate most of the bacteria and viruses that cause diarrheal disease; and, 2) the water is protected from recontamination during transport to the system users and during storage of water in households.

In the 1997 special Millennium issue, *LIFE Magazine* famously declared that drinking water filtration and chlorination is "probably the most significant public health advance of the millennium". Chlorination in the United States was first implemented in Jersey City, NJ in 1908. Before that time, waterborne disease outbreaks were very common. Anyone who is nearing middle-age probably played the computer game "The Oregon Trail" while in grade school. In that game, settlers often died of dysentery, typhoid or cholera – usually just before completing the entire trail. All three afflictions were common waterborne diseases. It has been estimated that nearly a quarter of the Civil War deaths were due to waterborne disease.

Once chlorination was recognized as a benefit, water suppliers across the country began to chlorinate their water supply. Even though many systems in Kansas began chlorinating water in the early 1900s, the major push to require chlorination of all PWS began in the mid-1940s after the largest waterborne disease outbreak in the State occurred in Newton in 1942. A sewage line emptied into a trench

The differences in the low range glass vial (left) and the high range plastic vial are shown here. Low range analyses require a 10-mL sample while high range requires a 5-mL sample.

where a water main was being repaired, resulting in 3,000 cases of bacillary dysentery. In 1966, the last Kansas PWS began to chlorinate its water supply. Waterborne disease outbreaks began to plummet to the point where today they are nearly unheard of. However, the Center for Disease Control (CDC) recently released a report that summarizes data from 2000 – 2015 and estimates that 17 waterborne infectious diseases cause 7,150,000 illnesses annually in the US[1]. According to those numbers, two percent of Americans will experience a waterborne illness this year! Many of these infections result from pools, spas, lakes, etc., meaning they do not come from drinking water. But diseases can originate from species associated with biofilms, which are common in Kansas distribution systems.

How does an operator ensure that the water system's customers are not included in that two percent? That is accomplished by ensuring an adequate chlorine residual in

[1] Collier SA, Deng L, Adam EA, Benedict KM, Beshearse EM, Blackstock AJ, et al. Estimate of Burden and Direct Healthcare Cost of Infectious Waterborne Disease in the United States. Emerg Infect Dis. 2021;27(1):140-149. https://dx.doi.org/10.3201/eid2701.190676

the distribution system. That said, the focus of this article is not about MAINTAINING chlorine residuals, but ANALYZING them.

Ensuring accurate measurements

Most operators use a colorimeter of some brand or another to monitor chlorine residual. There are many different brands of colorimeters. The model I have is a Hach DR300 pocket colorimeter. It is a basic colorimeter that can measure free and total chlorine in two different ranges. Colorimeters use the DPD Method to measure chlorine residual. The method requires the DPD reagent to be mixed into a sample where it is oxidized by the chlorine in the sample. The sample will turn pink in direct correlation to the chlorine level. Measuring free chlorine requires a different DPD reagent than measuring for total chlorine. It is the all important first step, make sure the correct reagent is being used.

In a digital colorimeter, a light is passed through the sample and an electronic eye measures the color's intensity to determine the chlorine level. The electronic eye is very sensitive to be accurate, so anything that absorbs or refracts the light beam will cause inaccuracies. It is important to maintain clean, scratch-free glassware. I am as guilty as anyone who uses their tee shirt to wipe a vial clean before putting in the colorimeter. Just like your eyeglasses, the vials will scratch with repeated tee shirt wipe-downs. Those scratches will affect the accuracy of the analysis. It's critical to make sure there are no air bubbles in the sample. Bubbles will refract light just like a smudge or scratch. This can be

The author's colorimeter kit is shown here. A small pair of scissors will be handy to open reagent packets when hands are wet.

difficult at times, especially when the water is cold during winter months. Gently inverting the vial a few times will usually clear up a majority of the bubbles. Stained glassware will cause the same issue. I have personally observed glassware so stained from DPD reagent that it read 7.0 mg/L of chlorine while the vial was empty. No one can honestly state that they believe a reading like that is accurate. Rinse those vials before and after every sample. Use lint-free cloths or wipes to polish them up. Taking care of the glassware is a very important part of accurate chlorine analyses.

If chlorine residual readings are not accurate, an operator cannot be certain an adequate residual is in the water to prevent waterborne disease.

Another essential part of ensuring accurate residual readings is to follow the instructions. Really? Well, yes, the instruction manuals have a purpose. I learned that I need the instructions for my colorimeter if I wanted to ensure consistently accurate readings. If measuring free chlorine residual, it is essential to take the reading within a minute. The DPD reaction with free chlorine is fast and the intensity of the color can increase over time, especially if there is any combined chlorine, or chloramine interference. Combined chlorine is measured with a total chlorine DPD packet. The proper wait time for a total residual test is three to six minutes as it takes longer for the chemical reaction to take place. It's important to make sure to wait the appropriate length of time.

A similar problem I have seen is reading the samples using the wrong range. On the meter I use, low range is 0.00 – 2.20 mg/L. Most systems that utilize groundwater and free chlorine will use the low range in their monitoring. The low range setting requires the glass vials and a 10-mL sample size. I have looked at daily chlorine logs showing months and months of residuals recorded as 2.20 mg/L. If the residual is over range, the display will flash 2.20. That is an indication to move to high range. High range is usually used by systems that monitor total chlorine residual. It is also recommended for systems that commonly measure residuals greater than 2.0 mg/L. High range uses the plastic vials and a 5-mL sample size and will read residuals from 0.0 – 11.0 mg/L. If it is necessary to read higher residuals than 11 mg/L while super-chlorinating or something similar, then the sample will need to be diluted below 11 mg/L or use an amperometric titrator for the analyses.

If chlorine residual readings are not accurate, an operator cannot be certain an adequate residual is in the water to prevent waterborne disease. Colorimeters need to be verified occasionally to be sure they are accurate. Each meter has instructions on how to calibrate or verify the unit officially, but operators can easily compare their meter to another for a quick check. If both meters read the same sample within a few tenths, then both meters are probably accurate.

When there are questions about a particular colorimeter, the owner's manual is usually the best place to start. Unfortunately, many of the owner's manuals read like textbooks. Feel free to call a KRWA Tech with questions about a colorimeter. KRWA staff are versed in different brands and models. KRWA also features an assortment of other meters in the new Training Trailer which will begin to be featured at various KRWA events.

The takeaway from this article is: make sure that chlorine residual readings are accurate. An adequate chlorine residual is not just a regulatory requirement for public water suppliers, it is also one of the best defenses against waterborne disease. No operator or anyone else associated with providing public drinking water wants customers getting sick from drinking the water.

Daryn Martin began work with KRWA in August 2019. He previously was a Water Program Inspector and Environmental Program Administrator at KDHE's Wichita office. Prior to joining KDHE, he worked as an operator in the El Dorado Water Treatment Plant. He holds a Class IV water operator certification.