Drinking Water Treatment Optimization Tools

Introduction
Treating water to meet today’s potable drinking water regulations requires a delicate balance between seemingly conflicting or competing regulations, financial resources and time. Treatments techniques that work favorably at one facility fail or fall short of the desired results at another plant. What is the best way to insure that the treated water is safe and meets existing regulation requirements?

This document provides a proactive approach and guidance on tools available to water treatment personnel. This toolbox approach provides test methods and equipment necessary to characterize the treatment process and to make databased decisions on treatment changes and process improvements.

Each water system is unique. Final water quality is impacted by water chemistry, changing physical water properties and the treatment process being used. It is invaluable to have the process characterized at each treatment step.

The benefits of having a treatment process characterized are:
- Documents water quality characteristics at each treatment step and provides an overall databased understanding of the treatment process.
- Establishes normal variability and baseline data of water quality at each treatment step.
- Provides a database of information to quickly respond to customer water quality complaints.
- Identifies areas of concern to be considered for treatment improvements.
- Provides a database against which the effects of treatment changes can be tracked.
- Provides Management with a reference database for training new operators and mitigating the effects of employee turnover.

The following is a partial list of parameters available from Hach Company which are used to characterize a treatment process. These parameters are highly interactive which each other and individual parameter results should be considered only as a piece of the overall treatment process characterization. Treatment changes should not be made on the results from a single parameter, but instead the test results should be used in conjunction with other test results to help understand the process. It is well documented that any single change in a treatment process will have an effect on the system, sometimes in ways not expected. The more data available for a system, the better-prepared one will be to understand or predict these changes when they occur.
**Alkalinity**

Alkalinity refers to the capacity of water to neutralize acids. The presence of carbonates, bicarbonates and hydroxides is the most common cause of alkalinity. Alkalinity is expressed as P (phenolphthalein) alkalinity or as T (total) alkalinity. Both types are determined by titration with sulfuric acid to an end point evidenced either by a visual color change of an indicator or by a pH meter. The P alkalinity is determined by titration to pH 8.3 and T alkalinity is determined by titration to a pH of 5.1, 4.8 4.5 or 3.7 depending on the amount of carbon dioxide present. The T alkalinity has also been traditionally been referred to as MO alkalinity from the methyl orange indicator that was used to signal the end point. Most current titrations for T alkalinity now use a bromcresol green-methyl red indicator to signal the visual endpoint.

The benefits obtained from quantifying alkalinity concentrations are important because:

- High alkalinity waters require a larger amount of acid to change the water pH.
- Low alkalinity waters are greatly impacted by small additions of acid.
- Alkalinity impacts coagulation and TOC removal.
- Alkalinity plays a direct role in corrosion control in distribution systems.
- Alkalinity directly impacts regulation compliance, chemical usage and treatment optimization plans.

Alkalinity is reduced by the addition of alum and ferric sulfate coagulants. Low alkalinity results in poor coagulation due to reduced iron hydroxide and aluminum complex formation. Additional alkalinity may need to be added to increase the coagulation process. Alkalinity is also important in the removal of Total Organic Carbon (TOC) by enhanced coagulation for plants using conventional treatment. The alkalinity levels are used to determine the amount of TOC that must be removed under the Stage 2 requirements of D/DBP Rule. The TOC is harder to remove during coagulation as the alkalinity increases and pH depression is required to reach the optimal TOC removal pH of 5.5 – 6.5.

Alkalinity, along with pH, also plays an important role in corrosion control. Low alkalinity waters are corrosive and pH or alkalinity may need to be increased to minimize lead and copper corrosion issues in the distribution system.

The alkalinity method is available in a rugged and convenient Digital Titrator format as well as the classical buret titration format. The Digital Titrator eliminates the need for glass burets; reducing the time required for glassware clean-up and the need for laboratory bench space. The Digital Titrator is portable and designed for on-site analysis. Use the alkalinity titration to characterize source water changes, process treatment effects on alkalinity and to measure increasing or decreasing alkalinity values in the distributed waters.
**Chlorine Demand**

Chlorine demand is a measure of the amount of chlorine that will be consumed by the water being treated.

The benefits of determining chlorine demand are:

- Chlorine demand can determine chlorine feed rates to prevent over-feeding or under-feeding of chlorine.
- Chlorine demand predicts the concentration of chlorine required to give a desired residual disinfectant level.
- Chlorine demand can indicate changing source water conditions.
- Chlorine demand helps evaluate source waters for DBP formation to assist in meeting regulations.
- Chlorine demand can predict chlorine consumption as a function of time, temperature, concentration and pH to help optimize treatment processes.

Chlorine demand is caused by organic materials present in the water plus inorganic compounds such as iron, manganese, ammonia, and sulfides. The chlorine demand is dependent upon water pH, temperature and the concentration of chlorine added. While the chlorine demand determination is valuable in setting chlorine feed rates it is also helpful in predicting chlorine residual levels to be expected in distributed waters. There is also a general acceptance that waters having a high chlorine demand would be expected to have higher levels of disinfection by-products (DBPs) when chlorine is the primary disinfectant. The chlorine demand value can be used to evaluate different source waters if blending is an option, can be used to monitor increases in demand levels as organics increase during warm weather seasons or may be used to monitor demand level changes due to seasonal or weather events.

The chlorine demand method is simple and straightforward to run. Several samples of the water to be tested are spiked with varying levels of chlorine and held at a fixed pH and temperature for a predetermined amount of time. The chlorine residual is then analyzed by standard DPD Chlorine methods using a colorimeter or spectrophotometer. The demand is determined by subtracting the residual chlorine value from the amount of chlorine added to the original spike. Hach Company supplies a Chlorine Dosing Ampule that eliminates the need to prepare and standardize a chlorine standard solution. The solution is manufactured to eliminate the effects of variable alkalinities and pH values that occur in using commercial bleach solutions.

Another application of the chlorine demand test is to determine the rate of chlorine consumption as a function of time, temperature, pH and concentration of chlorine added. The findings of such an application study can give insight into Contact Time (CT) calculations, disinfection efficiency, DBP formation, location of chlorine application points and the feed rates at those application points.
**Total Organic Carbon (TOC)**
TOC is a measure of the total organic compounds present in the water.

The benefits for monitoring TOC in are:
- Effective removal of TOC reduces the levels of DBPs formed.
- Effective removal of TOC eliminates the need and costs to perform enhanced coagulation under D/DBP Rule for high TOC waters.
- TOC studies on jar test settled waters can reduce costs by establishing optimum coagulant feed rates and establishing effective alkalinity levels.
- Determines DOC (dissolved organic carbon) when sample filtered.

TOC is comprised of a variety of organic compounds in various oxidation states. Most TOC in surface source waters is fulvic and humic acid originating from decaying plant materials. Most ground water source waters are low in TOC; surface waters will have higher levels, the levels of which depend on seasonal conditions, weather events and watershed topography.

Facilities using surface water or ground water under the influence of surface water are required to determine source water TOC and to remove specified amounts depending on initial TOC and water alkalinity as described in the D/DBPs Rule. Low TOC water of less than 2 mg/L C or facilities meeting the required % removal will meet the compliance guidelines and eliminate the need to move to performing enhanced coagulation. The amount of TOC present in a water sample directly correlates the amount of DBPs formed when using chlorine as a primary disinfectant.

Hach Company provides a colorimetric method for determining TOC. This method requires a sample digestion followed by colorimetric determination on a colorimeter or spectrophotometer. This method provides a low-cost alternative to TOC analyzers and is appropriate for determining TOC levels in source waters, process control of treatment processes or evaluation of pilot plant treatment changes. It may also be used following jar tests experiments to evaluate TOC removal studies versus coagulant dose and alkalinity concentrations. Additionally, sample water can be filtered and the TOC run on the filtered sample. This will give a Dissolved Organic Value (DOC) and will help characterize the TOC. DOC is harder to remove than suspended TOC particles in the treatment process.

**Organic Constituents (UV-254)**
The UV-254 method gives one a closer look at the type of TOC or organics present in source water.

The benefits that can be obtained from making UV-254 measurements are:
Determine level of organic compounds present in drinking water source water.
Determine level of organic compounds present that have a greater tendency to form DBPs.
Quickly determines change in source water quality.
Determine the UV-254 values required to calculate SUVA under the D/DBPs Rule.

The basis for this method is that organic materials which have an absorbance at 254 nm have a greater tendency to form DBPs with chlorine. Two samples having equivalent TOC levels, but having distinctly different UV-254 absorbance values will theoretically give different levels of DBPs under identical treatment conditions.

This method is best suited for monitoring source waters that are constant in water quality, relatively low in organics and for which current treatment processes are successful in meeting DBP compliance requirements. The test then becomes an indicator for detecting source water changes that would have an impact on the treatment process.

This method requires a UV-Visible spectrophotometer with measurement capabilities at 254 nm. A quartz 1 cm cell is required. The sample is first filtered through a 0.45 μm membrane filter. Organic-free water is required to set Zero on the instrument. This is a critical step. Deionized or demineralized water from some laboratory water systems may contain traces of organic material and should be first verified with organic-free water.

The UV-254 value along with a DOC determination is also used in the calculation of SUVA or Specific Ultraviolet Absorbance. This SUVA value can also be used to determine compliance with the TOC removal requirements of the D/DBPs Rule.

**Trihalomethanes (THMs)**

Trihalomethanes are disinfection by-products (DBPs) formed in the production of potable drinking waters.

The benefits of monitoring for THMs directing on-site are:
- Identification of high concentration sites of THM compounds in distribution systems.
- Tracking of THM formation throughout the treatment process.
- Immediate feedback on process optimization studies to reduce THM levels.
- Reduction in costs of process control THM measurements.
Trihalomethanes are a group of compounds containing a single carbon bonded to three halogens usually chlorine, bromine or iodine. These THM compounds are of concern because of their potential health effects and are formed as DBPs by the reaction of chlorine with organic matter present in the water. Four of these THM compounds are regulated under the D/DBP Rule. Their formation is controlled by the disinfectant used, the amount and composition of the TOC present and pH.

THMs are analyzed by GC or GC/MS techniques. These method determine the individual THM compounds and concentrations and require instrumentation and technical expertise that is beyond the resources of most utilities. Methods such as these are not economically feasible to be used for real time process control evaluations or screening tests.

Hach Company has available a colorimetric method that is designed to screen for THMs to determine high level concentration sites in the distribution system, to track the rate of THM formation in the treatment process and to determine the effects of treatment changes on THM levels. This method, called THM Plus, does not give the individual THM speciation, but gives an aggregate value that is representative of the total THMs present. The THM Plus method is also offered as a tool by the USEPA Technical Support Center under the Area-Wide Optimization Program (AWOP) to help states comply with the compliance requirements for THMs.

**THM Formation Potential (THMFP)**
This new method is now available and is used to determine the potential of a water to form THMs under a predetermined set of reaction conditions.

The benefits to using the new method are:
- Determine the potential of source waters to form THMs.
- Monitor seasonal changes in source water and their effects on forming THMs.
- Optimize conditions to decrease THM formation in order to meet THM regulations.
- Determine results immediately on-site eliminating the cost and time-wait associated with sending samples to an outside laboratory.
- Investigate treatment options before making major capital investments.

The method is similar to the chlorine demand method in that a series of samples are spiked with varying levels of chlorine (or other oxidants) at a fixed temperature, pH and contact time. After the contact time has been reached, the residual chlorine levels are checked in each sample. The sample that has a chlorine residual representative of the treatment process is then analyzed for THMs using the THM Plus method described above.
The method can be modified to evaluate different source waters, changes in a source water due to seasonal or weather events or to evaluate treatment changes. As with the chlorine demand method, there are a wide-range of modifications which can be made to gain valuable insight into changing water conditions or changing treatment processes. Some studies that will provide an understanding of THM formation are:

- Formation potential studies on settled waters from jar tests to evaluate the effectiveness of coagulant dosage on THM formation.
- Formation potential studies vs. temperature to understand seasonal variation in THM levels.
- Formation potential studies based on chlorine dosage rates and location of chlorine application.
- Formation potential studies on the rate of THM formation at variable locations within the treatment stream.
- Formation potential studies to correlate THM levels to UV-254, TOC or SUVA values.
- Formation potential studies to study the effects of using alternative oxidants.

**Lead and Copper**

Lead and copper are normally not present in source waters, but enter the treated drinking water from corrosion, dissolution or leaching of deposits and materials present in distribution systems.

**The benefits from testing for copper and lead are:**

- **Monitor the effectiveness of corrosion management plans.**
- **Monitor concentrations to insure levels are constant and not changing due to other treatment or disinfectant changes.**
- **Screen for high lead levels in distributed waters, schools, public buildings, and residential homes.**
- **Insure compliance with the Lead and Copper Rule.**

Both lead and copper are regulated under the Lead and Copper Rule. The concentration of these two metals is dependent on materials used in the distribution systems, alkalinity and pH, and to some degree the disinfectant being used or changes made to disinfectant types.

Colorimetric methods for lead and copper are available from Hach Company. The LeadTrak Method is used to screen for high lead levels at consumer taps, schools, and water coolers. The EPA-approved Copper CuVer Method is available for determining copper. Alternatively, the portable HSA-1000 Analyzer is EPA approved for determining and reporting lead and copper levels. The analyzer uses differential pulse anodic stripping voltammetry technology to determine the metals.
Monochloramine and Free Ammonia
Chloramines and more specifically monochloramine are being increasingly used as an alternative to chlorine to reduce the levels of DBPs formed.

Monitoring for monochloramine and free ammonia is beneficial because:

- Monochloramine production can be optimized to reduce costs by eliminating the over-feeding of chlorine and ammonia.
- Nitrification issues can be reduced by minimizing free ammonia levels entering the distribution system.
- Nitrification issues can be monitored directly on-site in field applications.

Monochloramine is the preferred chloramine species and Hach Company has a method (Monochlor F) available that is specific for monochloramine. Monochloramine is produced by reacting chlorine with ammonia at a ratio of 5:1 or less. The process is optimized to maintain this ratio as close as possible to minimize the amount of unreacted ammonia (free ammonia) remaining. This is critical in order to limit the amount of free ammonia entering the distribution system. While chloramines are highly effective in reducing the levels of DBPs being formed, their use has resulted in increased nitrification episodes in the distribution systems. This is attributed to the free ammonia serving as a food source for biofilm regrowth in the systems. Chlorine residual is quickly dissipated, nitrite and nitrate levels increase and HPC violations can occur under these conditions.

A technique sometimes used to determine chloramines is to determine free and total chlorine and obtain the combined chlorine or chloramines by difference. While this technique will provide some information, it does have its limitations. The chloramine value is a combination of monochloramine and dichloramine plus any trace organochloramine compounds that may react with the DPD chemistry. The other difficulty is the instability and hence the accuracy of the free chlorine value in the presence of chloramines.

The Free Ammonia method is designed to determine ammonia levels present in the presence of chloramines. The method is unique in that monochloramine does not interfere in the determination. It is important to note that most ammonia test methods such as Nesslers, Phenate and Salicylate have varying degrees of interference from chloramines and it is not possible to get an accurate determination of the free ammonia present. The Free Ammonia method is used to optimize the production of chloramines and to monitor free ammonia levels in distributed waters. The AutoCAT 9000 Amperometric Titrator can also be used to determine monochloramine.
Nitrite
Increasing nitrite concentrations in the distributed water is an indication that nitrification is taking place. It is almost never naturally occurring in the raw source water.

Monitoring for nitrite is beneficial because:
- Increasing nitrite concentrations confirms that nitrification is taking place.
- Free ammonia is rapidly converted to nitrite in the nitrification cycle which could give the false impression that the “apparent” low levels of free ammonia are within control and no nitrification is taking place.
- Nitrite is a regulated parameter in potable water systems.

NitriVer 3 is an EPA approved method for reporting nitrite levels. Nitrite is regulated in drinking water and it is theoretically possible that at the level of chloramines used in some treatment processes could approach or exceed regulatory nitrite levels during nitrification episodes.

Chlorine
Chlorine is the workhorse disinfectant most commonly used in some form in the disinfection process. Free chlorine is present as either hypochlorite or hypochlorous acid depending upon the water pH. Hypochlorite is the most effective form for disinfection at a pH of 5.5 – 6.5; however the chlorination process is typically run at a slightly higher pH to minimize the formation of HAA5s or haloacetic acids which is another class of disinfection products. Total chlorine includes free chlorine plus all combined chlorine such as the chloramines. Free chlorine and total chlorine are mostly commonly determined using the DPD Chlorine chemistry or by amperometric titration. Chlorine testing is done on-site because of its instability. A chlorine residual measured as total chlorine must be maintained throughout the distribution system.

Monitoring for free and total chlorine is beneficial because:
- Chlorine residual is required to maintain microbiologically safe drinking water.
- Chlorine residual must be maintained by regulation throughout the distribution system.
- Sudden loss of chlorine residual indicates nitrification or possible intrusion of contaminants into the treated water system.

Hach Company supplies DPD Free and Total Chlorine Reagent in powder pillow, AccuVac and the new SwifTest packaging formats. The AutoCAT 9000 Amperometric Titrator is also available to determine free and total chlorine.
**Ozone**

Ozone is used as a preoxidant to destroy organic compounds related to taste and odor and to reduce the organics present; thereby reducing the potential for forming DBPs.

It is beneficial to monitor ozone levels because:

- Ozone generation is energy intensive and optimization of ozone residuals relates directly controlling costs.
- Ozone is volatile and must be monitored on-site for accurate determination of ozone levels.

Ozone testing is completed by using Hach Company’s Ozone AccuVacs based on the indigotrisulfonate chemistry. Ozone is extremely volatile and unstable; therefore chlorine or chloramines are added as a secondary disinfectant in the distribution system.

**Chlorine Dioxide**

Chlorine dioxide is another preoxidant used to destroy organics and thereby reduce DBP formation. Chlorine dioxide is generated on-site. A by-product of chlorine dioxide is chlorite which is regulated and must be checked on a daily basis. Chlorine dioxide is also extremely unstable and a secondary disinfectant of chlorine or chloramines is used in the distribution system.

It is beneficial to monitor chlorine dioxide because:

- Monitoring checks to verify that the chlorine dioxide generation is proceeding correctly.
- Monitoring confirms that chlorine dioxide levels generated are sufficient to meet the chlorine dioxide demand of the raw source water.

Chlorine dioxide can be determined using the DPD/Glycine colorimetric method. Chlorine dioxide and chlorite can also be determined amperometrically using the AutoCAT 9000 Amperometric Titrator.

**Jar Test**

The jar test is the most basic test used by water treatment plant operators to predict the amount of chemical or chemical combinations required to assure accurate coagulation and flocculation. The settled water in jar tests is often checked by “visual” measurement to see which dosage gives the clearest water. Instrumentally measuring the turbidity or the TOC of the settled jar water is a better way to check the efficiency of the chemical dosage.

Running jar tests in combination with other optimization control parameters can be beneficial by:
• Determining those properties that affect flocculation and are unique to your water system.
• Testing settled waters for TOC removal efficiency.
• Testing settled water for evaluating THM Formation Potential
• Determining optimum chemical treatment programs to reduce chemical usage and operating costs.

One of the purposes of flocculation is to remove organic materials that can cause disinfection by-products. As discussed earlier, this is the basis for the TOC removal requirements under Stage 2 of the D/DBPs Rule. The implication is that by lowering the TOC level, the DBP formation will be lowered. While this is true, there are instances where a reduction in TOC does not cause an equivalent reduction in DBP formation. The reason for this is that the TOC being removed was not the TOC that was most reactive to DBP formation.

What is most beneficial in this situation is to use the THM Formation Potential Test to evaluate the settled jar water to determine which coagulant or chemical combination is most effective in reducing the TOC responsible for forming the disinfection by-products. This becomes one additional piece of information that is helpful in characterizing and understanding the water treatment process.

**Turbidity**

Turbidity is a measurement of the cloudiness of the water and is a required reporting parameter for the production of distributed potable waters.

Monitor turbidity at several locations within the treatment process to:
• Meet the regulation requirements for finished drinking waters
• Monitor changes to incoming source waters.
• Check the efficiency or changes occurring in the coagulation process due to water temperature, alkalinity or source water changes.
• Check filter backwash water to efficiently monitor water usage and reduce costs.
• Identify water quality issues in distribution system samples.
• Signal water quality acceptance criteria following distribution system line repairs or replacements.

Hach Company provides a wide range of portable, lab and on-line turbidimeters to meet you testing needs.

**Summary**

Each water system is unique. The production of safe potable drinking water is a complex interaction of several water quality parameters. Monitoring a single water parameter cannot insure water quality. Alkalinity is related to lead and copper corrosion; alkalinity and TOC are related to DBP formation; pH and choice of oxidant are related to disinfection efficiency, nitrification issues and
THM formation. It is important that these parameters be monitored and documented. The interactions of each parameter can be studied. Water quality issues can be identified and quickly addressed.

It is important to have a system documented from a regulatory perspective, from a process control perspective and from a management perspective. Documentation of the treatment system gets the head knowledge of veteran operators down on paper. This information can be used to respond to customer complaints and to provide guidance for training of new employees.

The many simplified tools available from Hach Company are designed to be used directly on site, putting the plant operation and improvement process back into the hands of plant personnel and can help make the plant treatment documentation process a reality.

By taking a proactive approach, a water utility can develop a fully characterized and documented water treatment process to be prepared to quickly and efficiently respond to changing water quality issues, new regulatory requirements, customer complaints and employee turnover or retirement challenges.