# Production of Chloramines and Chloramine Monitoring in Water Supply Systems

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## Abstract:

The use of chorine and chloramine are well understood methods for disinfecting water. However, chloramine is a weaker disinfectant than chlorine and its use can be problematic if it is not properly formed and monitored. This paper examines the most critical considerations for the production and use of chloramine as a secondary disinfectant.

## Introduction:

Source waters in many areas of the state contain elevated levels of TOC which combines with free chlorine to produce disinfection by-products (DBP). These compounds are regulated at 80 PPB and 60 PPB for total trihalomethanes and haloacetic acids. Meeting these low regulatory limits when using free chlorine as a disinfectant can be difficult.

With the increase in regulatory attention such as the new Initial Distribution System Evaluation (IDSE) that requires all public water supply systems to report critical DBP values, given problems meeting existing rules and now new rules, many water treatment systems have elected to switch to chloramines as their secondary disinfectant.

Chloramination or producing chlorine by adding ammonia in the presence of free chlorine, has been used by many water treatment systems for a number of years. The process of forming chloramines is well understood and consists of adding ammonia in the presence of free chlorine in a ratio of about 3 – 5 parts free chlorine to 1 part of ammonia.

Unfortunately, when water systems switch from free chlorine to chloramine, it brings with it new and unexpected problems. Attempting to find an explanation for what is occurring is not easy, and when problems grow worse, the system operator is left with no other option than to switch back to free chlorine disinfection and perform a “burn.” A burn is a process where superchlorinating with free chlorine is used to destroy problematic organisms and unstable conditions in the water system. When this happens, disinfection byproducts often exceed regulatory limits.

Fortunately, the use of chloramines and the control of problems in the distribution system follow predicable patterns that can be identified and corrected before conditions deteriorate to a point where a burn is needed. This paper examines the concepts in the formation and the use of chloramines and suggests preemptive techniques to identify the status of deteriorating conditions and implement corrective actions to keep the chloramination process under control.

## Understanding Chlorine Addition for Primary Disinfection:

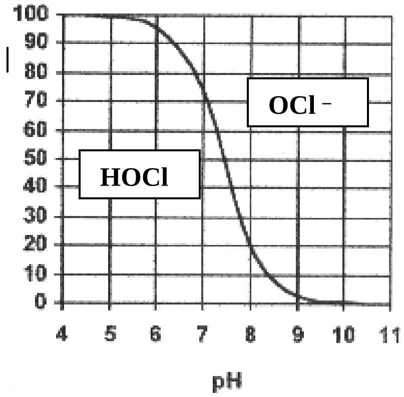
Disinfection by-products are formed when chlorine in the form of hypochlorous acid formed in the disinfection process is allowed to contact naturally occurring organic material. To control the production of disinfection by-products effectively, three methods can be employed: 1.) remove the organic precursors that are reactive with the chlorine, 2.) decrease the amount of hypochlorous acid available for the reaction and 3.) decrease the time of contact between the organic material and the hypochlorous acid. Generally, operators will accomplish all of these objectives by moving chlorine dosing points to locations that allow some precursor removal to occur within the plant and then lower free chlorine concentrations to only those levels needed to meet regulatory requirements.

When in-plant strategies are not successful, many systems have chosen to reduce the amount of hypochlorous acid available for reaction within the distribution system by switching to chloramine as a secondary disinfectant. Free chlorine is used to provide primary disinfection and meet initial chlorine demand and chloramine is used as the secondary disinfectant, i.e. in the distribution system.

It is useful to review the mechanisms of how free chlorine and chloramines are made in the disinfection process. When free chlorine ($Cl_2$) is initially added to water it goes through a series of chemical actions and eventually splits into two components. These components are hypochlorous acid (the active compound that forms the disinfection by-products) and the hypochlorite ion.

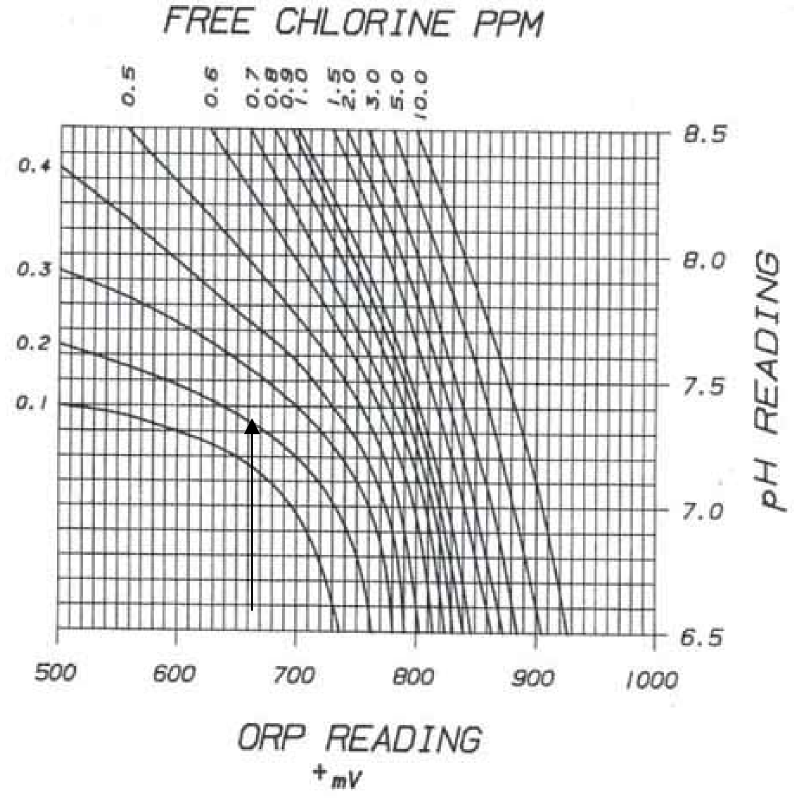
Although both hyppchlorous acid and the hypochorite ion provide disinfection, the hypochorous acid that is formed is much stronger than the ion. The amount of hypochlorous acid or the hypochlorite ion formed, is completely dependant on pH. These relationships are shown below:

**Concentration of Hypochlorous Acid and Hypchlorite Ion vs pH**



As can be seen from the above curve, when the pH of the water is around 7.5, a value near most Florida ground waters, the relative concentrations of hypochlorous acid is around 50%. Thus if pH is lowered, more hypochlorous acid is available and more DBPs form at a faster rate. Conversely, when pH is increased the available hypochlorous acid is lower and DBP formation will be slower. As the pH approaches 8, the relative portion of the hypochlorous acid is about 20%. Above a pH of 9, most all of the chlorine is in the form of the less effective hypochlorite ion and disinfectant ability will be about 1% of the disinfectant power compared to the acid form. Raising pH does have a significant drawback and that is that as the amount of hypochlorous acid is reduced disinfection ability is reduced accordingly.

The practical significance of this in water treatment is that free chlorine residual does not indicate microbial inactivation unless pH is accounted for. This limitation can be avoided when the hypochlorous acid component is directly measured. This can be accomplished by the use of an ORP meter. An ORP meter will provide an estimate of the inactivation power of chlorine at any given pH. A ORP value of 650 mV has been used since mid-1980 for municipal drinking water in Europe for water quality. The arrow below shows how this value relates to current DEP standards. At ORP values between 500 and 600 mV bacterial activation will occur but only after much longer contact times.

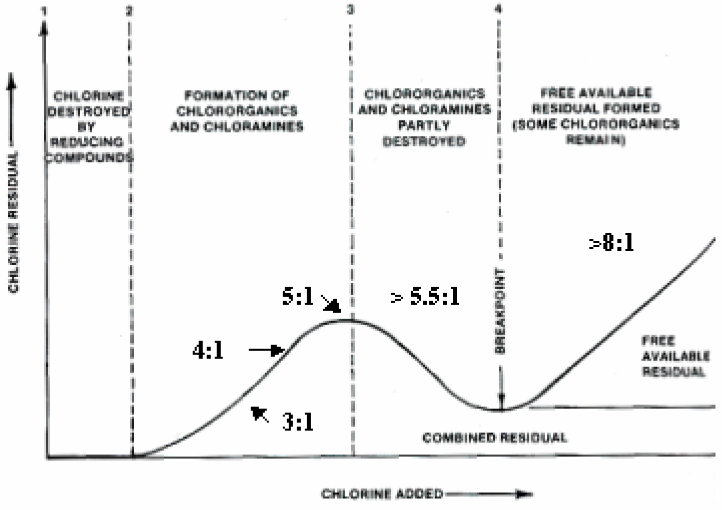


FREE CHLORINE TABLE

**Breakpoint Chlorination Curve and Chloramine Development**

To understand how chlorine forms disinfection by-products with a source water that contains chlorine demanding substances we need to develop a breakpoint chlorination curve as shown below. The X-axis shows the amount of free chlorine that is being continuously added. The Y-axis shows the total chlorine residual that is measured. Total chlorine is in a combined form (Y axis) until all the inorganic and organic demand is satisfied, in other words until the initial inorganic and organic demand has been satisfied, no hypochlorous acid is available. For each source water the breakpoint curve will be unique but it will follow the general pattern shown below.

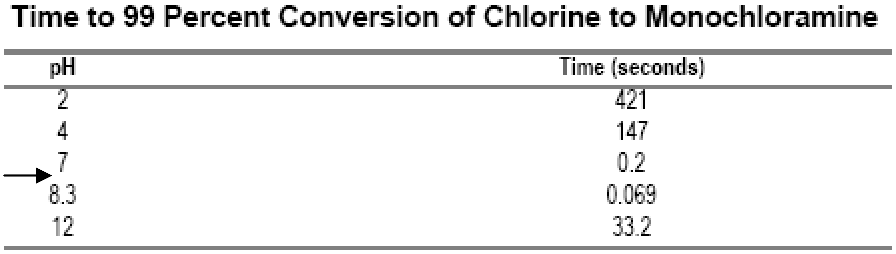
Note that between the segments labeled 1 and 2, although free chlorine has been added, no chlorine residual of any kind is shown on the left Y-axis. This is because within this range the chlorine is reacting with inorganic constituents in the water such as iron, manganese, hydrogen sulfide and any ammonia that may be naturally present. This oxidation-reduction reaction will proceed to completion until all inorganic substrate is consumed. What is important to note here is, that no reaction with organic materials present in the water will take place until all the inorganic demand has been satisfied. Within this range, free chlorine may be added to the water without producing any significant disinfection byproducts. This concept is important because many Florida water sources contain iron, hydrogen sulfide and background ammonia all inorganic demanding substances.


**Breakpoint Chlorination Curve**
**Showing Affects of Various Chlorine to Ammonia Ratios**

Between segments 2 and 3, there is no longer any un-reacted inorganic compounds in the water and oxidation of organic contaminants that produce disinfection by-products will now occur. To prevent this undesirable situation from occurring, many water treatment plants with disinfection byproduct problems have switched to the use of chloramines. Chloramine is produced by adding ammonia, in a ratio of between 3 to 5 parts measured as free chlorine to 1 part ammonia. If chlorine is added at a higher ratio, then the chloramine will transition from the monochloramine form to the dichloramine form as shown past point 3 on the curve. Note that these ratios apply only after inorganic chlorine demand has been satisfied. This is why it is important for plants to develop their unique breakpoint chlorination curves.

It is important that the chlorine be added prior to the ammonia. Ammonia is a nutrient and adding it to a water prior to the chlorine will encourage biological growth and bacterial resistance to disinfection.

When ammonia is added to water containing hypochlorous acid, the production of chloramines occurs instantaneously with the rate of reaction controlled by pH. The reaction rates are shown in the following table. The arrow indicates the range of Florida source waters that are typically between a pH of 6.8 to 7.8. As can be seen, in this range chloramine production is instantaneous.



Time to 99 Percent Conversion of Chlorine to Monochloramine

| pH | Time (seconds) |
|---|---|
| 2 | 421 |
| 4 | 147 |
| → 7 | 0.2 |
| 8.3 | 0.069 |
| 12 | 33.2 |

**Determining Chlorine Demand for Your Water System**

It is imperative that water systems identify their chlorine demand so that free chlorine dosage can be minimized at the plant and to ensure chlorine residuals can be maintained in the distribution system at the 0.20 mg/l free chlorine or 0.60 mg/l chloramine levels that are regulatory requirements.

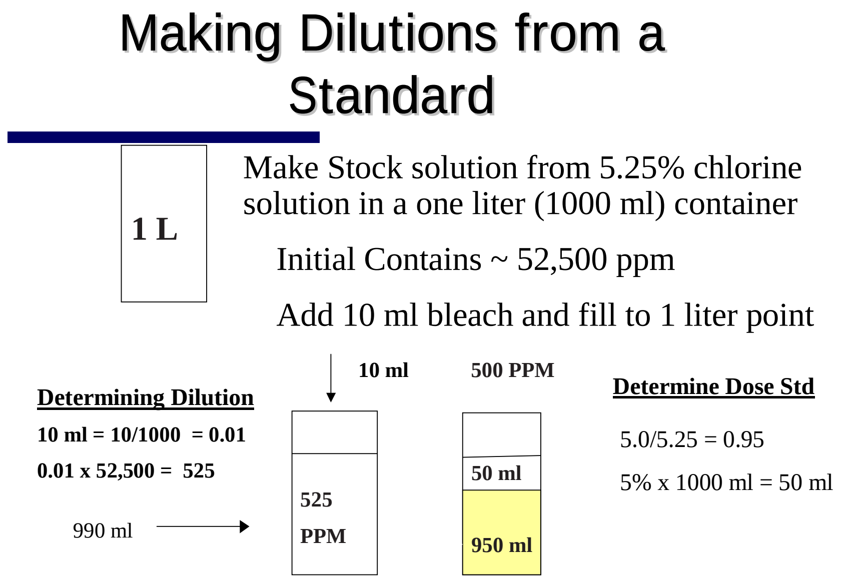
Many systems that have performed DBP analysis on their finished water at the plant, find that after implementing the controls described above, that DBP produced at the plant are 25% or less than those produced in the distribution system. By maintaining excessive free chlorine residuals in the distribution system, the reaction rates with organic material will be increased and more disinfection by-products will be produced. Conversely with chloramine, if significant excess residual is not maintained, the chloramine will have a tendency to breakdown leading to formation of disinfection by-products, slime growth and nitrification. It is important that systems check the concentration both at the entrance to the distribution system and at the regulatory monitoring point for purposes of targeting the most significant problems.

The substances that cause disinfectant demand are indicative of the source water quality and are also are the compounds that typically cause water quality customer complaints. Most source waters contain a variety of both inorganic and organic contaminants whose chlorine demand can be identified with a simple jar test without knowledge of the types of concentrations of the contaminants. The procedures illustrated below can be quickly set up and used to give a good approximation of the chlorine demand. Limiting free chlorine demand to that necessary to maintain the required residual is the most effective method of controlling disinfection by-product production.

## 1. Use of a Laboratory Jar Test Method for Plotting a Chlorine Demand Curve

**Step 1**: Determine Stock Chlorine Solution by adding about 10 ml of common bleach or a known concentration of chlorine solution used at the plant. Make up 1 liter using deionized water to a dilution that is around 500 ppm. This is accomplished by adding 10 ml of household bleach to 990 ml of distilled water.

**Step 2**: The actual concentration of the stock solution can be estimated using a DPD meter. The accuracy will be ± 0.1 mg/l which is not significant in source waters where well changes are frequent. Convert the Standard Solution into a chlorine concentration that is a whole number. This step is not necessary but makes further dilutions used for plotting the demand curve easier.



### Making Dilutions from a Standard

1 L

Make Stock solution from 5.25% chlorine solution in a one liter (1000 ml) container

Initial Contains ~ 52,500 ppm

Add 10 ml bleach and fill to 1 liter point

**Determining Dilution**

**10 ml = 10/1000 = 0.01**

**0.01 x 52,500 = 525**

990 ml

**10 ml**

**525 PPM**

**500 PPM**

**50 ml**

**950 ml**

**Determine Dose Std**

5.0/5.25 = 0.95

5% x 1000 ml = 50 ml

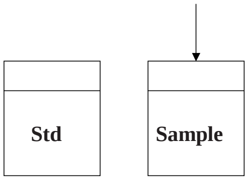
**Step 3:** Begin adding chlorine to a 1 liter source water sample 5 ml at a time and record the Total Chlorine Residual and Free Chlorine Residual using a DPD meter. The chlorine contact time should be approximately the same as in the plant. Allow about 15 minutes for the reactions to occur or use the known reaction time if known.

# Determining Dose Rates from Stock Solution

Adding Stock Solution to Determine Dose
for 1 Liter Container of Water

| Jar # | Amount Added | Dose |
|---|---|---|
| 1 | 5 ml | 1 ppm |
| 2 | 10 ml | 2 ppm |
| 3 | 15 ml | 3 ppm |
| 4 | 20 ml | 4 ppm |

Dose Calculations



**Step 4.** After each chlorine dose and detention, measure both total and free chlorine residual with a DPD meter. Subtract the Free from the Total to determine the amount of combined chlorine. From the data compiled, plot the total chlorine residual vs. dose which will produce the standard chlorine breakpoint curve for your water treatment system. If you want to increase the accuracy, bracket your results and repeat the test. For example if the curve requires more refinement to better observe results, you can add doses in 1 ml increments instead of the 5 ml increments, etc.

# Performing a Chlorine Demand Jar Test

**10 ml added** | **20 ml added** | **30 ml added** | **40 ml added**

**Use 1- liter samples**

**Note: Combined = Total - Free**

**Record Total and Free Chlorine**

**Results of Chlorine Test**

| Sample # | Total | Free | Combined |
|---|---|---|---|
| 1 | | | |
| 2 | | | |
| 3 | | | |
| 4 | | | |

**Plot Results**

**Total Chlorine – Free Chlorine = Combined Chlorine.**

The chlorine demand test will provide the operator with a good estimate of the chlorine demanding substances that are immediately available and provide the minimum chlorine dose that can be added to achieve breakpoint. This is important because if excessive chlorine is being added, this will result in increasing the production of disinfection by-products within the treatment plant. CT tables published by DEP can be used as a guide for limiting excessive free chlorine residual concentrations.

## 2. Estimating Chlorine Demand Using Known Concentrations of Contaminants

The chlorine demand curve produced above should closely match the calculated chlorine demand from the laboratory values that identify the chlorine demanding substances. The method for computing chlorine demand is illustrated below.

**Step 1:** Determine the amount of Iron, Manganese, Hydrogen Sulfide, Ammonia, Organic Nitrogen, Nitrite and TOC in your source water. Place the values in a table and use the multiplication factors shown below to determine your chlorine demand as shown in the example below.

**Example: A source water has the following chemical contaminants**:

| **Chemical** | **Source Water #1** | **Source Water #2** |
|---|---|---|
| Fe | 0.3 mg/l | 0.30 mg/l |
| Mn | 0.06 mg/l | 0.06 mg/l |
| $H_2S$ | 0.2 mg/l | 1.5 mg/l |
| $NO_2$ | 0.1 mg/l | 0.1 mg/l |
| $NH_3$ | 0.1 mg/l | 1.4 mg/l |
| Org-N | 0.05 mg/l | 0.05 mg/l |
| TOC | 2.0 mg/l | 6.0 mg/l |

**Step2:** Determine Chlorine Demand using multipliers shown.

**Determining Chemical Demand from Source Water Analysis**

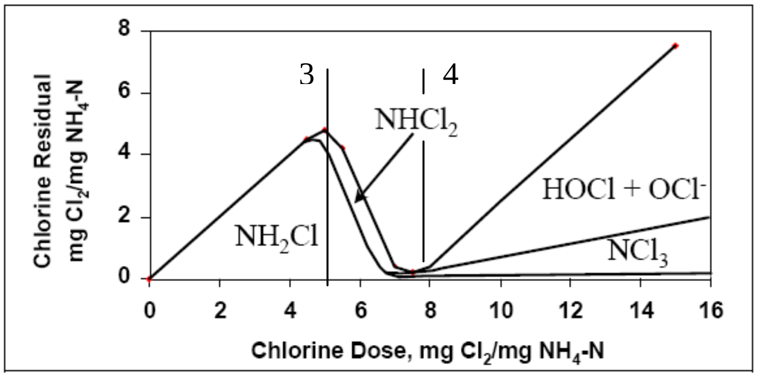
| **Chemical Constituent (mg/l)** | **Source Water #1** | **Source Water #2** | **Multiplier** | **Source Water #1** | **Source Water #2** |
|---|---|---|---|---|---|
| Fe | 0.30 | 0.30 | 0.64 | 0.19 | 0.19 |
| Mn | 0.06 | 0.06 | 1.3 | 0.08 | 0.08 |
| H2S | 0.20 | 1.5 | 2 | 0.40 | 3.00 |
| NO2 | 0.10 | 0.10 | 5 | 0.50 | 0.50 |
| NH3 | 0.10 | 1.4 | 12 | 1.20 | 16.80 |
| Org-N | 0.005 | 0.005 | 1 | 0.01 | 0.01 |
| TOC | 2.0 | 6.0 | 0.1 | 0.20 | 0.60 |
| Total | | | | 2.58 | 21.18 |

This method provide a quick check on the chlorine demanding substances. Note that the demand exerted by very small concentrations of naturally occurring ammonia is extremely high and will dominate the demand for free chlorine. Also note that the demand for organic substances is typically less than 10% of the demand total.

## Chloramine Sag with Additional Free Chlorine Addition

The examples provided above refer to the use of free chlorine. When producing chloramines, we are concerned only with the reactions that refer to the segment between points 3 and 4 on the breakpoint curve. This portion of the breakpoint curve for chloramine production is reprinted below.

Note that when the chlorine to ammonia ratio exceeds about 5, the production of other chloramine products besides monochloramine occur simultaneously with a decrease in the measured total chlorine concentration as more free chlorine is added. This is because once the free chlorine has reacted with most all of the readily available organic contaminants in the source water, the addition of additional free chlorine oxidizes the previously formed combined chlorine compounds forming various new organic compounds and dichloramine. These reactions are causing chlorine demand and chlorine is being used up and thus is reducing the concentration of the previously measured total chlorine which was all in the monochloramine combined form. Note that when we exceed the 5:1 ratio that monochloramine ($NH_2Cl$) is being converted in to dichloramine ($NHCl_2$) and finally into nitrogen trichloride.



The most desirable form of chloramine is monochloramine ($NH_2Cl$) and it will predominate below the 5:1 free chlorine to ammonia ratio. As the amount of free chlorine exceeds the 5:1 ratio, dichloramine is produced and the total chlorine residual will fall off approaching zero total residual at point 4 on the curve.

If additional free chlorine is added beyond point 4 on the curve, “breakpoint” or the point where free ammonia will be released to the atmosphere will be reached. It can be observed from the figure that breakpoint chlorination is reached at a ratio of free chlorine to ammonia at a ratio of about 10:1 resulting in the formation of nitrogen gas, nitrate, and nitrogen chloride as well as hypochlorous and the hypochlorite ion.

Point 4 on the curve represents the point where free chlorine or hypochlorous acid and the hypochlorite ion can be measured in a water treatment plant or in a water distribution system as free chlorine. When chloramine is used as a secondary disinfectant, hypochloroous acid is not present.

## Chloramine Disinfectant Mechanisms

The mechanisms by which chloramines inactivate microorganisms have been studied to a lesser degree than with free chlorine. It is thought that monochloramine readily reacts with four genetic amino acids; cysteine, cystine, methionine and tryptophan inactivating the microbes.

The ability for chloramines to inactivate pathogens begins to degrade relatively early in a distribution system when organic material is present. The degradation will continue to occur the longer the chloramines are detained. Within a few days, monochlroramine applied to a water distribution system begins a process of autodegradation. For each 3 moles of monochloramine destroyed 1 mole of ammonia will be released. Additionally, chloramines will oxidize organic contaminants in the water releasing ammonium. Both of these processes favor nitrification.

### Natural Degradation of Monochloramine ($NH_2Cl$)

Three degradation equations for monochloramine that occur in any water system are shown below. Note that in each case that the end product is either ammonia or the ammonium ion that both contribute to nitrification.

| | |
|---|---|
| Equation #1: Autodecomposition | $3NH_2Cl \rightarrow N_2 + \mathbf{NH_3} + Cl^- + 3H^+$ |
| Equation #2: Oxidation of Organic Matter | $.1C_5H_7O_2N + NH_2Cl + .9H_20 \rightarrow$<br>$.4CO_2 + .1HCO_3^- + 1.1\ \mathbf{NH_4}^- + Cl^-$ |
| Equation #3: Reduction by Nitrite | $NH_2Cl + NO_2^- + H_20 \rightarrow \mathbf{NH_3} + NO_3^- + HCl$ |

All of these forms of degradation of monochloramine are exacerbated by long detention times such as in dead-end pipes or in storage tanks. Most water system operators do not know the residence times in their distribution systems. Studies have found that many average size water distribution systems have residence times that exceed 12 days in some places. In some smaller systems residence times as high as 24 days are not uncommon. These residence times are more than adequate to favor monochloramine degradation.

Since the mechanisms of the degradation of chloramine are well known, it is recommended that water distribution systems maintain a 2.5 mg/l level in stagnant areas of the distribution system to avoid the problems discussed above. When 2.5 mg/l of monochloramine is maintained it has been found to significantly impede nitrification.

## Monitoring Chloramine Levels in Water Distribution System

<u>Monitoring of chloramine residuals is essential if loss of disinfection, nitrification and biofilm growth in the distribution system is to be avoided</u>. Direct measurement of free

chlorine and total chlorine residual is always the preferred method of determining the concentrations and the type of disinfectants present but does not necessarily identify a problem condition unless other indicators are present..

Conventional methods of identifying chloramine breakdown and nitrification episodes include noting reduced  disinfection residual, DO depletion, reduction in pH and alkalinity, the presence of ammonia, nitrate and nitrite and the increased growth of heterotrophic bacteria. Unfortunately identification of these constituents are all indicators that a problem is in progress and possibly out of control. Thus more predictive methods must be employed as are discussed below.

## Maintaining an Oxidative Environment in a Water Distribution System

What is known about the nitrification is that it is unlikely to occur at high oxidative states since these states tend to inhibit the organisms necessary for the process to occur. Thus to minimize microbial growth, high oxidative or ORP states should be maintained as discussed in a previous section on the use of free chlorine.

All disinfectants used in water treatment inactivate microbes by oxidation. Each disinfectant used in water treatment has a relative oxidation potential that increase the oxidative state beyond what is possible using oxygen. The oxidative states for common oxidants used in water treatment are shown below in relation to the oxidation power of oxygen. Note that all oxidants used in water treatment have higher oxidation potentials than oxygen.

**Oxidative States of Common Oxidants**
**Used in Water Treatment**

| Oxidant | $E^o$ Volts |
|---|---|
| Hydroxyl Radical | 2.85 |
| Ozone | 2.08 |
| Hydrogen Peroxide | 1.78 |
| Permanganate | 1.68 |
| Hypochlorous Ion | 1.64 |
| Hypochlorous Acid | 1.48 |
| Monochloramine | 1.40 |
| Dichloramine | 1.34 |
| Oxygen | 1.23 |

ORP values for free chlorine were shown for clean water to determine the amount of hypochlorous acid available. Since monochloramine is a weaker oxidant than hypochlorous acid, the ORP values for Chloramine are much lower than for Free chlorine and are provided in the following table.

**Monochloramine ORP in mV for Clean Water**

| Monochloramine in Pure Water mg/l | ORP mV |
|---|---|
| Tap Water no Cl2 | 350 |
| 0.2 | 375 |
| 0.4 | 410 |
| 0.6 | 440 |
| 0.8 | 445 |
| 1.0 | 450 |
| 1.5 | 460 |
| 2.5 | 480 |
| 3.0 | 490 |
| 4.0 | 500 |

**Note: Careful use of a portable ORP device is necessary since readings can easily fluctuate by 25 mV. See manufacture's recommendations for proper use.**

As can be observed, the higher values of monochloramine produces elevated ORP values near 500 mV which can effectively inactivate microbes with longer detention times than that needed with free chlorine. The stability of the oxidation state in a water system will depend on the concentration of pollutants or reducers in the finished water. When high concentrations of monchloramine is added bacterial inhibition will occur as long as a highly oxic state exists. If organic material is available the monochloramine will be destroyed as shown by the equations in the previous section. Thus high oxidation states (high mV) are indicative of an environment where nitrification and rapid degradation of chloramine is highly unlikely to occur. Where oxidation potentials are low or dropping, conditions are present that favor nitrification or nitrification may already be occurring. Thus these relationships provide a quantitative method for determining the state of the oxidation reactions and the trend toward undesirable low concentrations of disinfectants that are occurring in a water distribution system at any point in time. ORP is thus an indicator of the status of chlroramine degradation at any point in time. This allows operators to predict the rate of chloramine degradation and take steps needed to prevent further ORP reductions that will favor nitrification.

The following table shows the various chemical constituents and how they describe the stability of the chloramine that is present in a water system.

## Using Chemical Parameters to Determine Effectiveness of Chloramines in a Water Distribution System

| # | **Chemical Constituent Change** | **Likely Reason for Drop** |
|---|---|---|
| 1. | Decrease in Chloramine Residual or residual to below 1 mg/l | Age of Chloramine likely exceeds 3 days and breakdown is occurring |
| 2. | The Oxidation Reduction Potential (ORP) of the Water has changed by more than 25 mv to 50 mv. From a previous reading. | Chloramines are degrading |
| 3. | Chloramine Residual is low, can not be maintained and is dropping | Biological growth is occurring and is releasing organic products that increase demand |
| 4. | Ammonia is Present | Chloramine is breaking down and releasing ammonia |
| 5. | Nitrites are present | Nitrification is occurring |
| 6. | pH and Alkalinity is dropping | Nitrification is occurring |
| 7. | Higher levels of DBP's are occurring in the Distribution System with no other source water quality changes | Chloramines are breaking down and organic products are being produced |
| 8. | Onset of Very Hot weather with reduced chloramine residuals | High Ambient Temperatures > $90^o$ F heating up storage tanks |

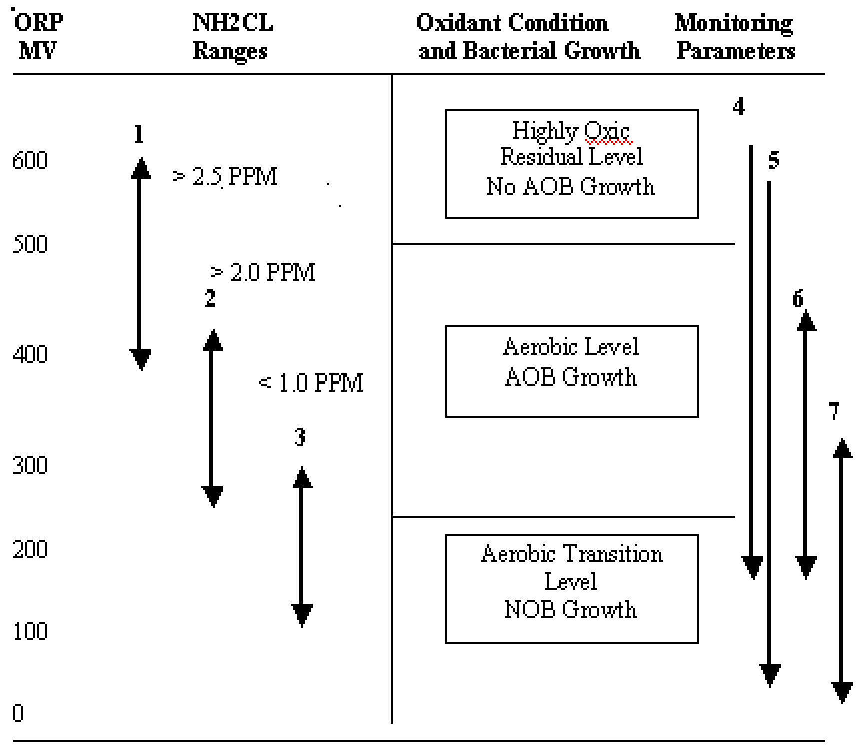
## Use of ORP for Aiding in Determining Chloramine Degradation

Use of ORP Monitoring in a Water Distribution System, in combination with other water quality parameters, provides a good indication or snapshot in time of the stability of the current system. When an ORP measurement provides an initial signature of the water system condition. ORP values can then be used to determine how fast a condition is deteriorating. The range of values provided by an ORP can indicate a problem. When ORP is used in combination of the other parameters in the above table, it provides a quantitative method for determining if distribution problems should be expected before they occur giving the operator time to adjust.

## Expected ORP ranges for Chloramination of Finished Water

The chart below shows the various ranges of chloramines that can be expected in finished well water. Chloramine concentrations are shown in ranges not in numeric values. This is because the temperature, chemistry, water quality and pH of each water will differ and thus the ORP is best used for determining acceptable chloramination ranges that results in adequate combined chlorine residual and water system stability.

### ORP Values for Chloramine Degradation in a Water Distribution System



1. Desired ORP Range to inhibit Nirtrification
2. ORP Range Supporting Nitrification and Growth of AOB
3. ORP Range Where Nitrification is Occurring and NOB Supported
4. Drop in DO level indicating conditions for Nitrification or Nitrification may have started.
5. Drop in pH/alkalinity level indicating that Nitrification is imminent or beginning
6. Detection of NH3 in this range indicates that Nitrification Process has begun
7. Detection of NO2 in this range indicates Mature Nitrification Process.

**Note: Monitoring Parameters (4, 5, 6 and 7) are useful relative to initial ORP signature.**

Note that the upper range of chloramine residual suggested (2.5 mg/l) inhibits bacterial activity and that levels of chloramine below these levels are in a range where bacteria can grow with less inhibition.

### Nitrification Bacteria and Chloramination Considerations

Nitrification takes place best in a situation where ammonia is available with elevated temperatures with a pH is between 7.0 and 8.0 but can occur within a much wider pH range under slower conditions. Decay of chloramine provides a source of ammonia and thus nitrification is fairly common in water distribution systems in Florida that use this disinfectant.

There are two types of bacteria that participate in the nitrification reaction. The first bacteria is classified as an aerobic oxidizing bacteria (AOB). In this reaction ammonia is oxidized to the nitrite form ($NO2^-$). Nitrite as we saw in the chlorine demand example, exerts a chlorine demand of 5 times its concentration. This situation will result in rapid loss of disninfection residual.

As more ammonia is oxidized, the alkalinity in the water is consumed and the pH will drop. A drop in pH is thus an indicator that nitrification is occurring. The conditions for nitrite conversion require a lower oxidation concentration as shown in the figure above. These bacteria are known as nitrogen oxidizing bacteria (NOB).

Thus the ORP can be used to determine the actual status of the nitrification reaction. The relationship among these parameters is shown in the figure above in the numbered arrows found to the right of the figure and that are described below the figure.

Lowered oxidation conditions in a water system also promote the growth of biofilm. Biofilm is active bacteria that include both AOB and NOB. These and other bacteria that proliferate under lowered oxidation conditions further complicate the problem in maintaining a chloramine residual in the water distribution system.

## Methods for Controlling Choramine Breakdown and Nitrification

<u>Raising chloramine levels are to above 2.5 mg/l is the best way to impeded nitrification but sometimes this is not possible. State drinking water rules prohibit chloramine concentrations in a distribution system to exceed 4.0 mg/l.</u> In some cases where distribution systems are several miles long with low demand a 2.5 mg/l residual can only be maintained by using an additional chloramine dosing facility located closer to the problem area. Attempting to control the concentration at a remote location to above 2.5 mg/l will require a concentration greater than 4.0 mg/l leaving the water plant.

Use of higher chloramine residuals in warmer months is recommended and "burn outs" (switching to free chlorine for 30 days) may be warranted if Nitrification is allowed to occur. Some systems have went to dichloramine to avoid nitrification, a more effective disinfectant that can also result in customer complaints of taste and odor.

## Chloramine Control Methods

The most common method of maintaining chloramine residual within a water system at remote locations is to ensure adequate turnover of the water. Unfortunately this process is very labor intensive. Manufactures have developed automated flushing valves for this purpose.

Courtesy Kupferle Foundry Co.

To keep residuals high at dead-ends automatically, many utilities use an Automatic Hydrant Flushers. These attach to any 2-1/2" NST nozzle. The flushing cycle can be selected, usually at night. Man-hour savings can be realized by flushing troublesome dead-ends without sending personnel. These devices are lockable, and can be utilized immediately by water department personnel with virtually no installation expense.

Although flushing is effective, it should not be attempted without development of a flushing plan. A flushing plan identifies the amount of water and the time that the pipe segment needs to be flushed to achieve any degree of success in increasing chloramine residual. Generally a flow velocity of 3 fps is needed to move sediment and a full pipe volume must be displaced to achieve any benefits. These estimates should be confirmed by field testing with a DPD meter to measure chloramine benefits.

The following tables were developed by the Texas Commission on Environmental Quality and are very useful in determining the amount of water to flush from each location to move water and sediment out of the pipeline. In order to determine flow from a fire hydrant it is necessary to use a pitot tube or a nozzle fitted with a pressure gauge to determine the flow rate while using a second fire hydrant to ensure a 10 psi min. pressure drop. The formula for computing fire hydrant flow is shown below. Many handbooks provide easy reference charts that solve this equation.

$$\mathbf{Q = 29.83\, cd^2\, (p)^{1/2}}$$

Q = flow rate in GPM
c = coefficient for 21/2" nozzle (rounded inside = 0.9, sharp inside =0.8, or projecting inside = 0.7)
d = outlet diameter of hydrant in inches
p = observed pressure at flow hydrant

### Methods for Flushing Fire Hydrants for Maintaining Chlorine or Chloramine Residuals

1. Flush three pipe volumes or until the disinfectant residual is restored (usually between 1 and 3 volumes of the stagnant main section)
2. Flush until color and turbidity are restored to normal levels (usually 0.5 NTU or less)
3. Flush at a rate that keeps the main pressure above 35 psi.
4. To minimize water loss, flush for the least amount of time needed.

| **Approximate Volume Needed to Flush Out One Pipe Volume** | | | | | |
|---|---|---|---|---|---|
| Main Size (Diameter) | Length of Stagnant or Dead End Main | | | | |
| | 100 feet | 200 feet | 300 feet | 400 feet | 500 feet |
| | All Flush Volumes Are in Gallons | | | | |
| 2-inches | 16 | 33 | 49 | 65 | 82 |
| 2½-inches | 25 | 51 | 76 | 102 | 127 |
| 3-inches | 37 | 73 | 110 | 147 | 184 |
| 4-inches | 65 | 131 | 196 | 261 | 326 |
| 6-inches | 147 | 294 | 441 | 587 | 734 |
| 8-inches | 260 | 522 | 783 | 1044 | 1306 |

| **Flow Rate in GPM Needed to Achieve Desired Flushing Velocity** | | | |
|---|---|---|---|
| **Main Size** Diameter | Target Flushing Velocity | | |
| | 3 fps | 4 fps | 5 fps |
| 2-inches | 29 | 39 | 50 |
| 2½-inches | 46 | 61 | 80 |
| 3-inches | 66 | 88 | 110 |
| 4-inches | 118 | 157 | 200 |
| 6-inches | 264 | 353 | 450 |
| 8-inches | 470 | 627 | 780 |

**Example:** How long would a 2 inch diameter pipe 500 feet long need to be flushed to remove sediment and stagnant water?

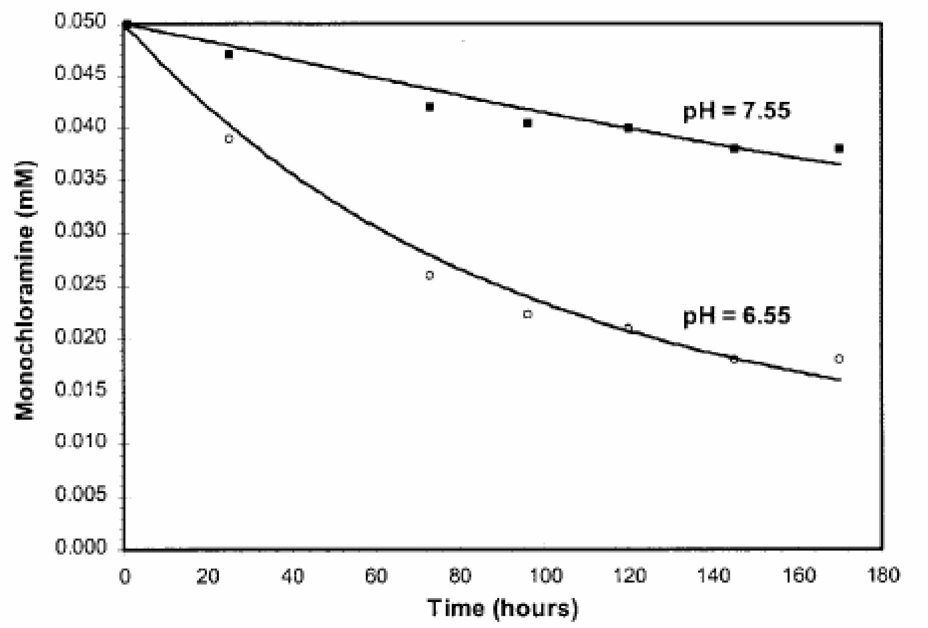
Determine Flow Rate ~ 30 gpm (> 29 GPM; flow rate is adequate to move sediment)
Volume of water = 82 gallons
82 gallons / 30 gpm ~ 3 minutes

Need to Flush ~ 3 minutes preferably 9 minutes to obtain optimal results and then check the residual with a DPD meter.

The advantage in using a fire hydrant is that the amount of water that can be discharged trough a 2 1/4 inch hydrant port can approach 500 gpm, Precautions must be taken when using flushing since operating fire hydrants during peak water demand periods can result in violations of DEP’s 20 psi minimum system pressure. Additionally the amount and velocity of water that is flushed can cause flooding and erosion problems, thus the placement of flushing valves and erosion protective devices is critical.

## Adjusting pH for Maintaining Chloramine Residuals

Another method used successfully to maintain chloramine residuals is to maintain an alkaline pH. The effects of raising pH is shown in the following figure.



The reason that pH increases are effective for maintaining chloramine residuals is because pH increase slows ammonia release from chloramine degradation.

## Managing Chloramines

It is highly recommended that systems using chloramine establish monitoring for the parameters of total chlorine, ammonia, nitrite, temperature, alkalinity and pH all parameters that can be measured using simple low cost field kits. ORP monitoring is also recommended and has wide use in the wastewater treatment industry. ORP hand-held equipment can be purchased for around $100.

Use of the concepts identified in this paper can provide the water supply operator with a information that identifies the breakdown of disinfection and resultant problems before they occur.

It is highly recommended that the operator establish signatures in critical areas of the water system and monitor the parameters suggested to observe trends in chloramine breakdown before nitrification is allowed to occur. Historical information is most valuable in predicting the likely occurrence of future chloramine breakdown occurrences.

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