

6. CHLORAMINES

The disinfectant potential of chlorine-ammonia compounds or chloramines was identified in the early 1900s. The potential use of chloramines was considered after observing that disinfection by chlorine occurred in two distinct phases. During the initial phase, chlorine reducing compounds (i.e., demand) cause the rapid disappearance of free available chlorine. However, when ammonia was present bactericidal action was observed to continue [even though free chlorine residual was dissipated]. The subsequent disinfection phase occurs by the action of the inorganic chloramines.

6.1 Chloramines Chemistry

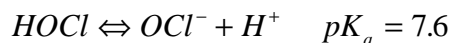
Chloramines are formed by the reaction of ammonia with aqueous chlorine (i.e., HOCl). Initially, chloramines were used for taste and odor control. However, it was soon recognized that chloramines were more stable than free chlorine in the distribution system and consequently were found to be effective for controlling bacterial regrowth. As a result, chloramines were used regularly during the 1930s and 1940s for disinfection. Due to an ammonia shortage during World War II, however, the popularity of chloramination declined. Concern during the past two decades over chlorinated organics (e.g., THM and HAA formation) in water treatment and distribution systems, increased interest in chloramines because they form very few disinfection byproducts (DBPs).

6.1.1 Equilibrium, Kinetic, and Physiochemical Properties

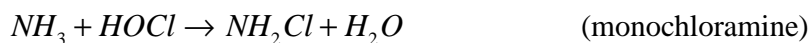
Chloramines are formed from the reaction of chlorine and ammonia. The mixture that results may contain monochloramine (NH₂Cl), dichloramine (NHCl₂), or nitrogen trichloride (NCl₃). When chlorine is dispersed in water, a rapid hydrolysis occurs according to the following reaction:

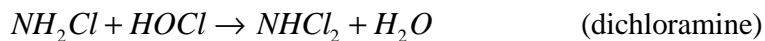


The equilibrium constant (K_{eq}) at 25°C is $3.94 \times 10^4 \text{ M}^{-1}$ for this reaction. In dilute solutions at pH greater than 3, the forward reaction is essentially complete. Hypochlorous acid (HOCl) is a weak acid that dissociates as follows:



Relative proportions of HOCl and OCl⁻ are dependent upon pH. Both of the chlorine species in the above reaction are powerful oxidants, capable of reacting with many substances present in water. In aqueous solutions with pH 7.0 to 8.5, HOCl reacts rapidly with ammonia to form inorganic chloramines in a series of competing reactions (White, 1992). The simplified stoichiometry of chlorine-ammonia reactions are as follows:





These competing reactions, and several others, are primarily dependent on pH and controlled to a large extent by the chlorine:ammonia nitrogen ($\text{Cl}_2:\text{N}$) ratio. Temperature and contact time also play a role. Figure 6-1 shows the typical relationships between the chloramine species at various $\text{Cl}_2:\text{N}$ ratios for pHs ranging from 6.5 to 8.5. This figure shows that monochloramine is predominately formed when the applied $\text{Cl}_2:\text{N}$ ratio is less than 5:1 by weight. As the applied $\text{Cl}_2:\text{N}$ ratio increases from 5:1 to 7.6:1, breakpoint reaction occurs, reducing the residual chlorine level to a minimum. Breakpoint chlorination results in the formation of nitrogen gas, nitrate, and nitrogen chloride. At $\text{Cl}_2:\text{N}$ ratios above 7.6:1, free chlorine and nitrogen trichloride are present. Figure 6-2 shows the relationship between chloramine species as the pH changes (Palin, 1950). The Figure shows that dichloramine becomes a dominant species at low pH.

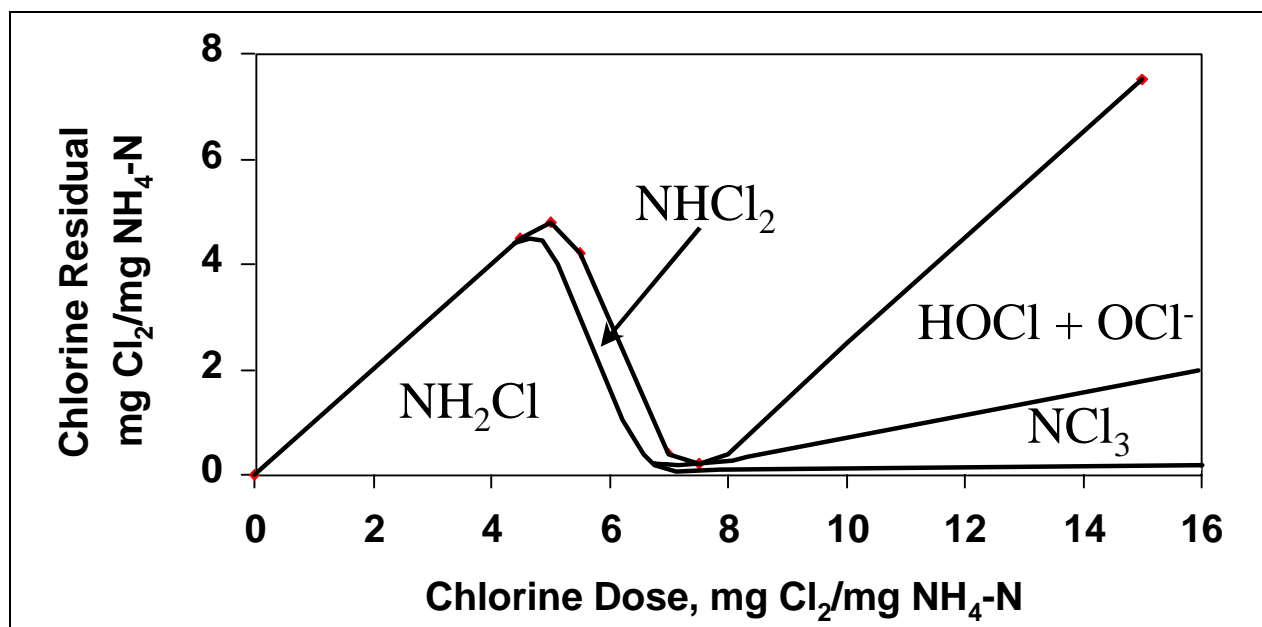
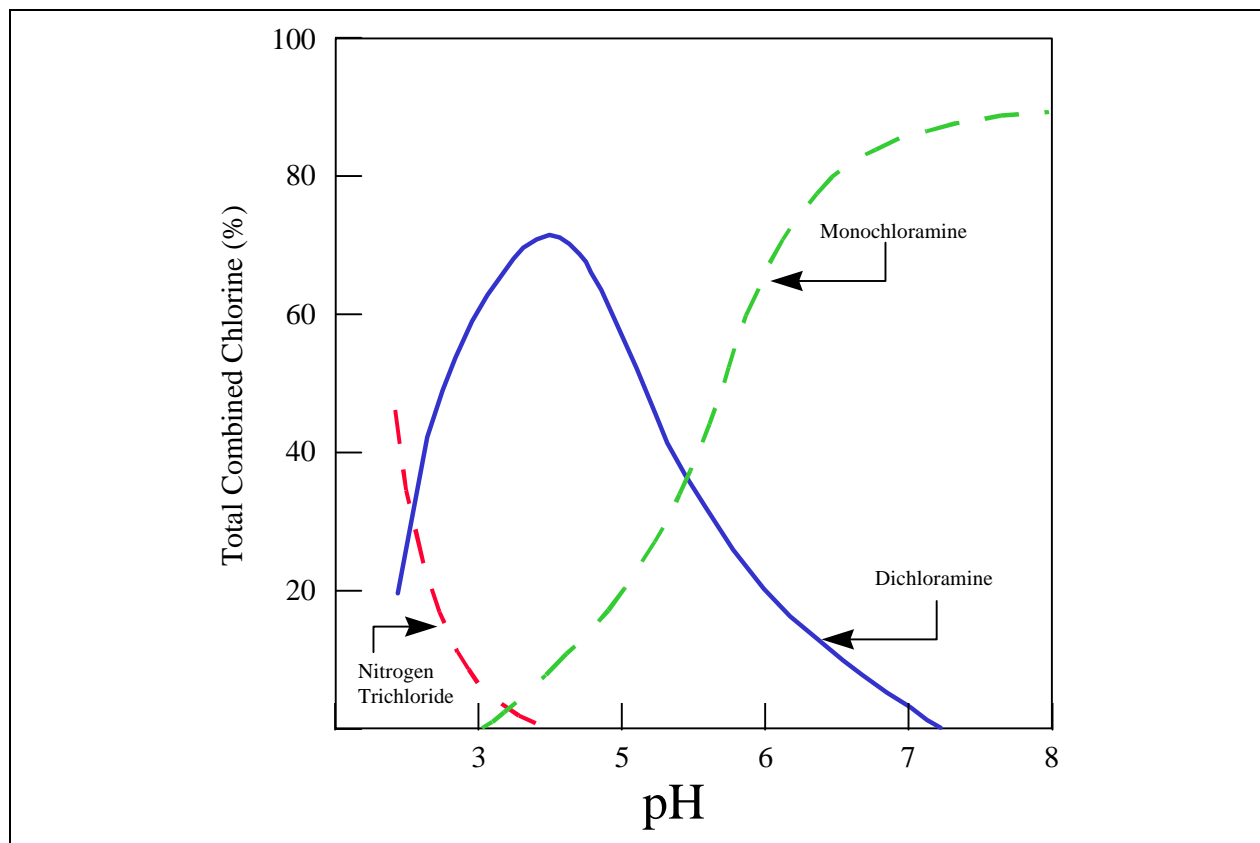


Figure 6-1. Theoretical Breakpoint Curve

To avoid breakpoint reactions, utilities should maintain a $\text{Cl}_2:\text{N}$ ratio between 3 and 5 by weight. A ratio of 6 is actually optimum for disinfection, but it is difficult to maintain a stable operation at that point in the breakthrough curve. Therefore, a $\text{Cl}_2:\text{N}$ ratio of 4 is typically accepted as optimal for chloramination.

Furthermore, over a period of a day or so, without any modification of pH or $\text{Cl}_2:\text{N}$ ratio, monochloramine will degrade slowly to dichloramine to a ratio of 43 percent NH_2Cl to 57 percent NHCl_2 . Dichloramine is relatively unstable in the presence of HOCl ; therefore, pure solutions of this form of monochloramine are difficult to generate and maintain.



Source: Palin, 1950.

Figure 6-2. Distribution Diagram for Chloramine Species with pH

6.2 Generation

Chloramines are formed by the reaction of hypochlorous acid and ammonia according to the equations described in Section 6.1. Table 6-1 summarizes the theoretical doses of chlorine and ammonia based on these formulas. Monochloramine is the preferred chloramine species for use in disinfecting drinking water because of taste and odor problems associated with dichloramine and nitrogen trichloride. To ensure that these compounds are not formed, common practice was to limit the chlorine to ammonia ratio to 3:1. However, because of problems such as nitrification and biofilm growth, which can be caused by excess ammonia, current practice is to use a Cl_2 :N ratio in the range of 3:1 to 5:1, with a typical value of 4:1.

Table 6-1. Chlorine Dose Required for NH_3 - Cl_2 Reaction

Reaction	mg Cl_2 /mg NH_3
Monochloramine (NH_2Cl)	4.2
Dichloramine (NHCl_2)	8.4
Nitrogen Trichloride (NCl_3)	12.5
Nitrogen (N_2)	6.3
Nitrate (NO_3)	16.7
Free residual reaction	9

Source: AWWA and ASCE, 1990.

The rate of reaction of monochloramine formation is sensitive to pH. Table 6-2 shows the calculated reaction times for monochloramine formation at 25°C, and at a chlorine:amonia ratio of 3:1 (White, 1992).

Table 6-2. 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

6.2.1 Chlorine Feed Facilities

Table 6-3 summarizes commonly used methods of chlorine addition, including their safety precautions and costs.

Table 6-3. Methods of Chlorine Addition

Method	Description	Safety precautions	Costs
Gaseous chlorine	Gas delivered in containers ranging in size from 150 lb cylinders to 90 ton rail cars. One ton cylinders are commonly used. Feed equipment consists of solution water pump/ejector to create vacuum and automatic orifice control to meter the gas. Gas can be drawn directly from storage container or be generated by an evaporator from liquid withdrawn from the container. A schematic of gaseous chlorine feed system is shown in Figure 6-3.	Gaseous chlorine is classified by the Uniform Fire Code as an oxidizing, highly toxic, compressed gas. New gaseous chlorine facilities should be designed with enclosures and air scrubbers to capture and neutralize any gas that leaks. Risk management prevention plans should be prepared. Personnel safety equipment and training should be provided for operators.	The cost per pound of liquid chlorine is in the range of \$0.08 to \$0.20 per pound depending on the quantity purchased.
Sodium hypochlorite	Sodium hypochlorite can be purchased bulk in quantities ranging from 55 gal drums to 4,500 gal truck loads. Bulk loads can be stored in fiberglass or plastic tanks. Solution is fed directly into the process stream. A schematic of typical hypochlorite feed system is shown in Figure 6-4.	Hypochlorite solution is toxic and classified as hazardous. Storage facilities should be designed with secondary containment.	Typical chemical cost is \$0.60 to \$1.00 per pound Cl ₂ .

6.2.2 Ammonia Feed Facilities

Ammonia feed facilities can be located on-site at the water treatment plant or at remote locations in the distribution system (Dennis et al., 1991). Most ammonia feed facilities use either gaseous (anhydrous ammonia) or liquid (aqueous) ammonia. Though anhydrous ammonia is a gas at ambient temperature and pressure, it is commonly stored and transported as a liquid in pressure vessels. In this phase, ammonia is highly soluble in water. Storage facilities and handling equipment should be kept dry (Dennis et al., 1991).

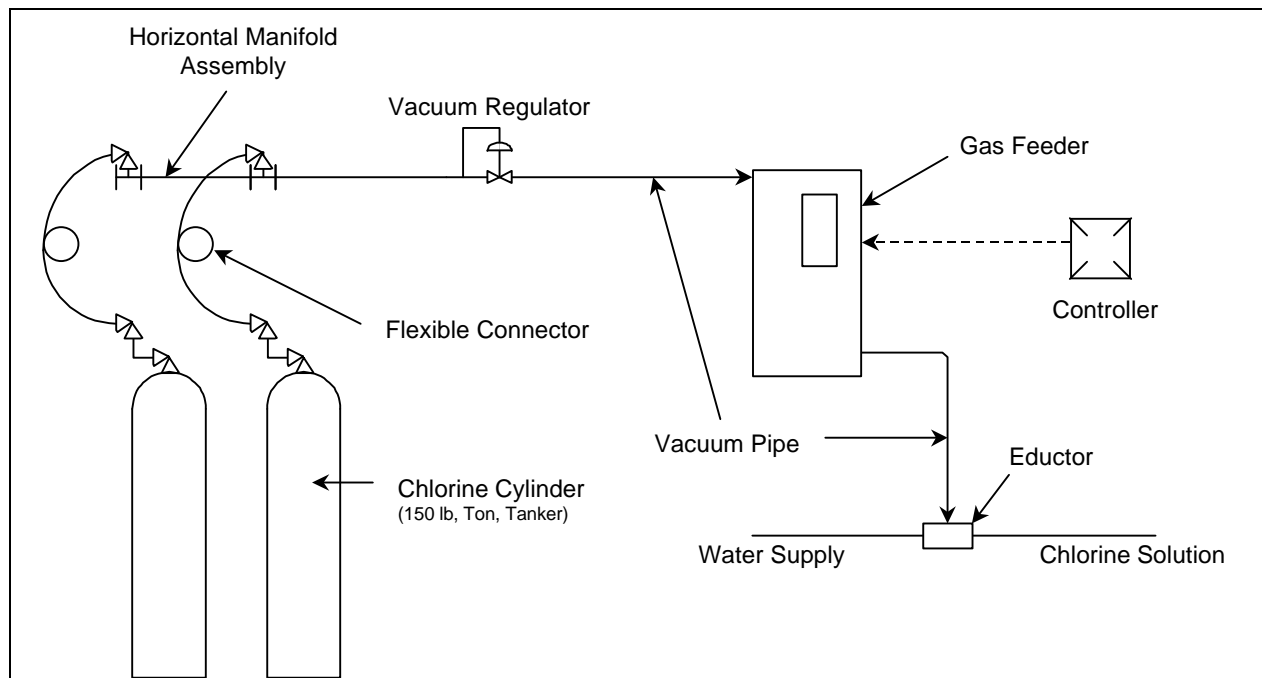


Figure 6-3. Gaseous Chlorine Feed System

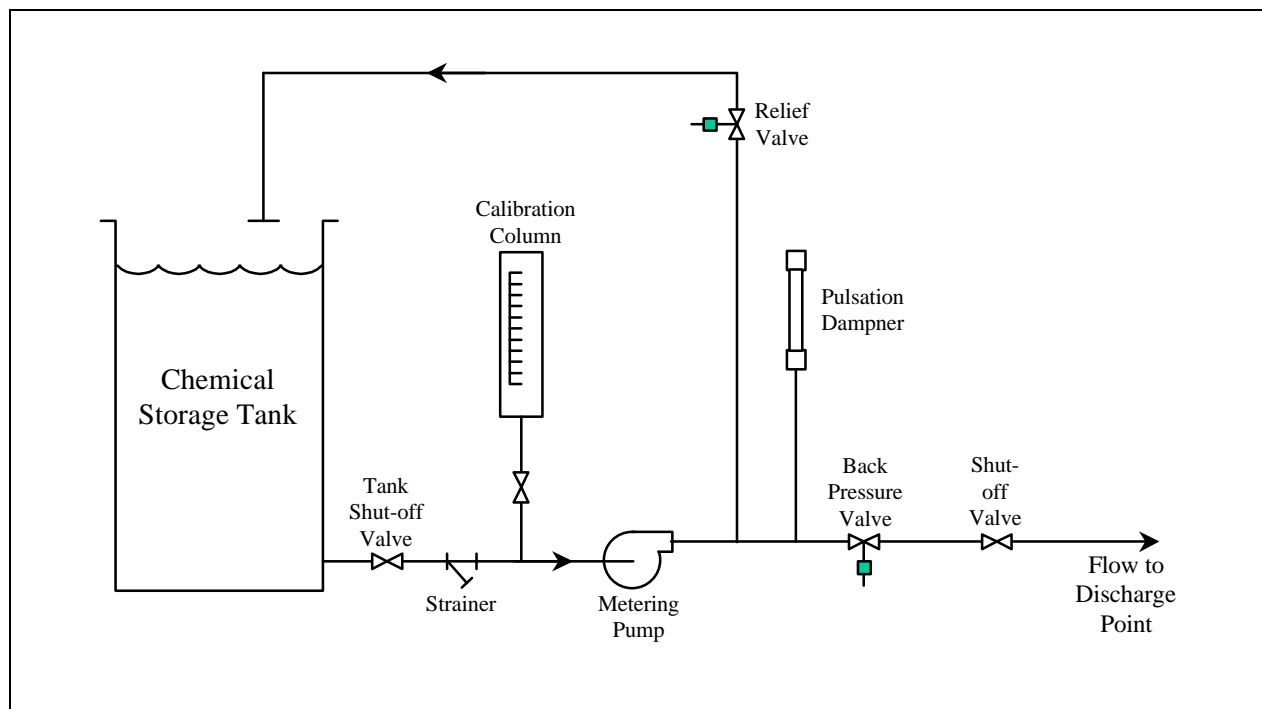


Figure 6-4. Hypochlorite Feed System

6.2.2.1 Anhydrous Ammonia

Anhydrous ammonia is stored in portable cylinders or stationary tanks. Portable cylinders are similar to chlorine cylinders and are available in 100, 150, and 800 lb sizes (Dennis et al., 1991). The cylinders are rated for a minimum service pressure of 480 psi. Stationary tanks are typically 1,000 gallon vessels that can be used on-site. These tanks are refilled by tanker trailers. The storage tanks can be located indoors or outdoors. Since each tank has a minimum working pressure of 250 psi (valves and fittings on the tanks are rated for 300 psi), a tank stored outdoors should have protection from extreme temperatures (greater than 125°F and less than 28°F) (Dennis et al., 1991). In warmer climates, an outdoor tank should be painted white and protected from sunlight. In colder climates, the tank should be wrapped with heat tape to prevent impairment of the ammonia vaporization.

Anhydrous ammonia is applied using an ammoniator. An ammoniator is a self-contained modular unit with a pressure reducing valve, gas flow meter, feed rate control valve, and miscellaneous piping for controlling the flow of ammonia. Automatic paced ammoniators are available. An evaporator is used when large quantities of ammonia gas are needed. An anti-siphon valve or check valve should be used to prevent water from entering the ammoniator.

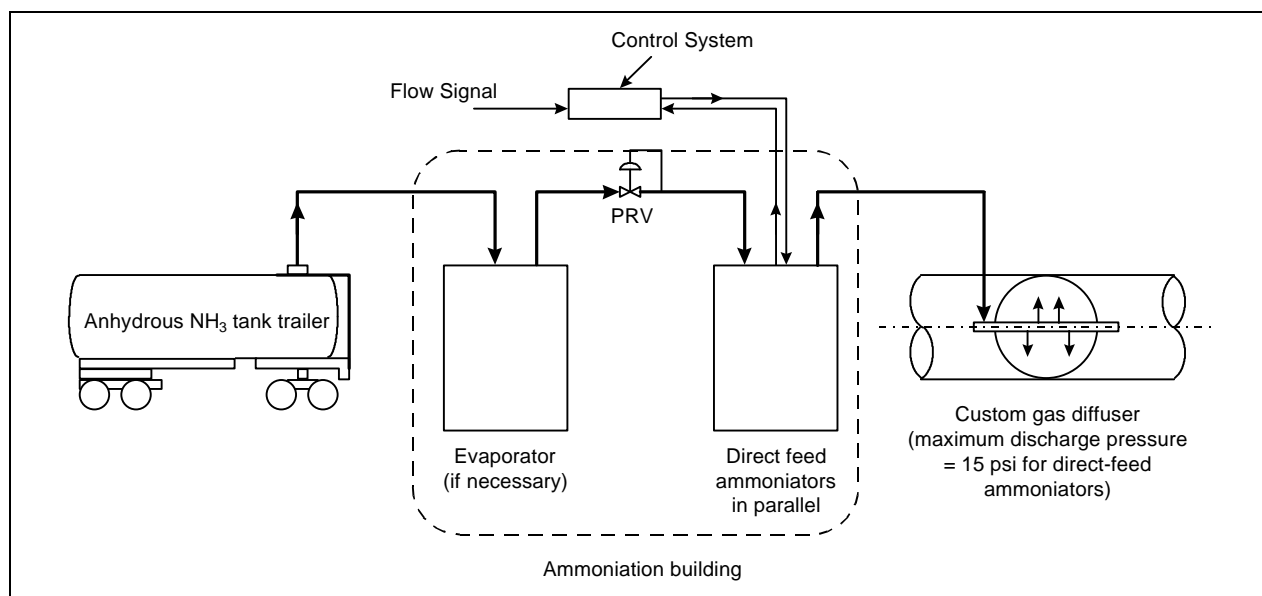
Anhydrous ammonia is usually applied by direct feed or solution feed. The direct feed method is typically used when the process stream has a low pressure and the ammonia feed rate is less than 1,000 lb per day (i.e., maximum rated feed capacity). Ammonia is drawn from the storage tank under high pressure (e.g., 200 psi), and injected directly into the process stream at a low pressure of 15 psi. The tank pressure is first reduced by a pressure reducing valve to approximately 40 psi, and

then by another pressure reducing valve in the ammoniator. Typical application points are at open channels and basin facilities. Figure 6-5 is a schematic of a direct anhydrous ammonia feed system.

The solution feed method is typically used where direct feed systems are not adequate (e.g., ammonia feed rate is greater than 1000 lb/day or where the process stream pressure is high) (Dennis et al., 1991). This type of application is similar to the chlorine vacuum feed system. The supply tank pressure is reduced by a pressure reducing valve to create a vacuum. An eductor is used to withdraw ammonia from the ammoniator where the ammonia is dissolved into a side water stream and pumped into the process stream. Solution feed ammoniators are available up to 4,000 lb/day capacities and can operate at discharge pressures up to 100 psi (Dennis et al., 1991). Softened water (i.e., hardness less than 29 mg/L as CaCO₃) is required for the carrier stream. Otherwise, the ammonia addition will precipitate scale that may plug the eductor and application point. Figure 6-6 shows a schematic of a solution feed system.

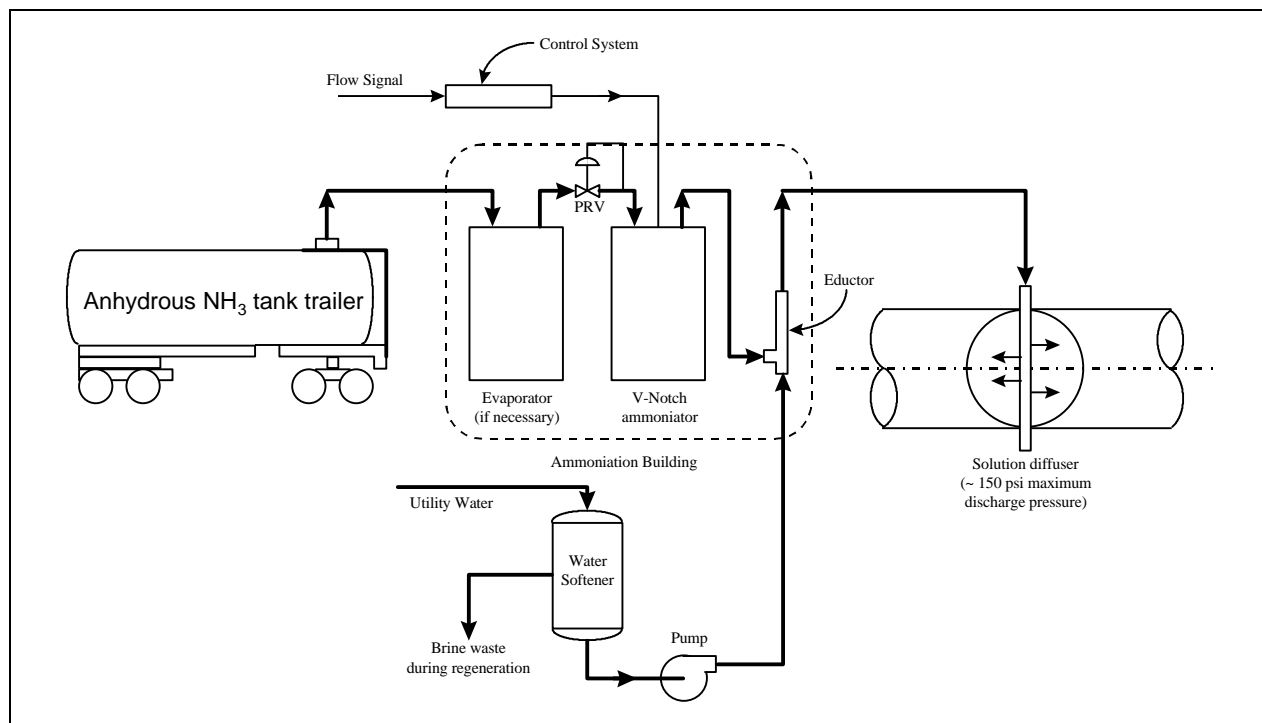
6.2.2.2 Aqueous Ammonia

Aqueous ammonia is produced by dissolving anhydrous ammonia into deionized or softened water. This form of ammonia is shipped in cargo trucks or polyethylene lined steel drums. Plastic drums are not recommended since they tend to lose their shape under the slight pressure exerted by the aqueous ammonia. Aqueous ammonia is stored in low pressure tanks, typically steel or fiberglass. Since excessive temperatures will cause ammonia gas to vaporize, each storage tank should be equipped with a water trap or ammonia scrubber to keep vapors from escaping to the atmosphere.



Source: Montgomery, 1985.

Figure 6-5. Anhydrous Ammonia Direct Feed System

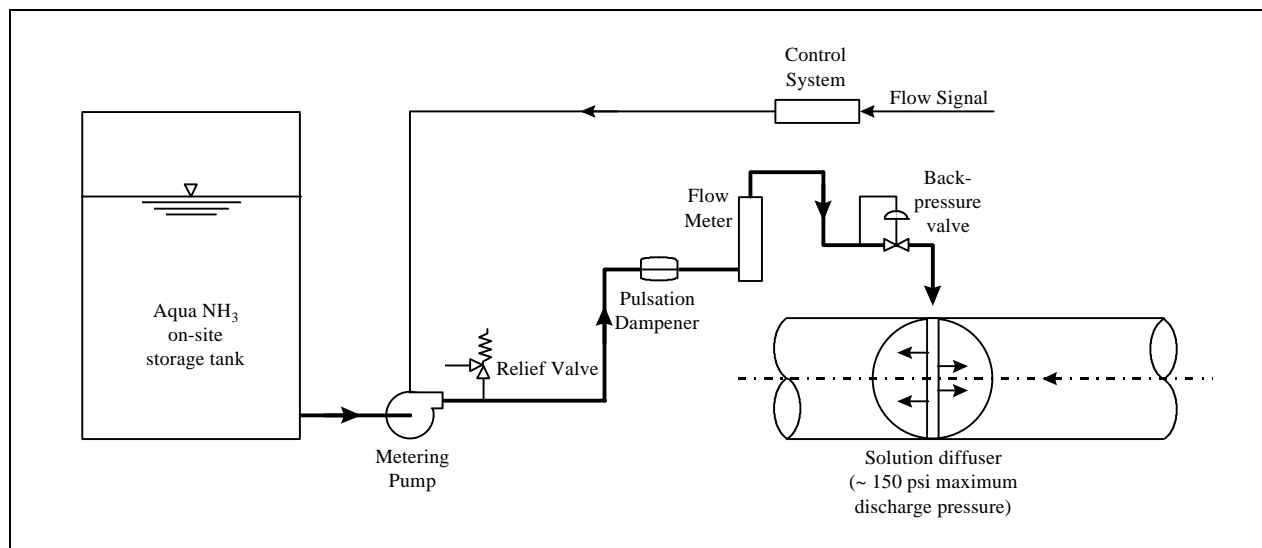


Source: Montgomery, 1985.

Figure 6-6. Anhydrous Ammonia Solution Feed System

Aqueous ammonia feed systems are similar to other liquid chemical feed systems. They require a storage tank, chemical metering pump, relief valve, pulsation dampener, flow meter, and backpressure valve. Typically, the feed pumps are positive displacement or progressive cavity type metering pumps. The feed pumps should be placed fairly close to the storage tank to minimize chances of ammonia vaporization in the piping (Dennis et al., 1991). The pump should be designed to compensate for changes in ambient temperatures, different aqueous ammonia solutions, and changes in the chlorine-to-ammonia ratio (Skadsen, 1993). When aqueous ammonia is applied to water, complete mixing is required for the ammonia to react with chlorine in the water to reduce the formation of dichloramine and nitrogen trichlorine. Figure 6-7 shows a schematic of an aqua ammonia feed system.

Metropolitan Water District of Southern California (MWDSC) uses aqueous ammonia at its chloramination facility. Ammonia is stored in unlined tanks and pumped to the ammoniator with progressive cavity pumps. During startup of its aqueous ammonia feed system, MWDSC experienced complete pump failures. Based on MWDSC's experience, EPDM rotors with adequate quality chromed finish stators are recommended for progressive cavity pumps. A mechanical seal is also recommended instead of a packing box to reduce the possibility of ammonia leaks (Skadsen, 1993). MWDSC also later installed special blow-offs and strainers in the feed pump suction line to reduce plugging at the magnetic flow meters. The pump problems prior to startup led MWDSC to install an alternative, redundant ammonia feed system. A pressurized system was designed to feed aqueous ammonia by pressurizing the ammonia tanks and by-passing the pump.



Source: Montgomery, 1985.

Figure 6-7. Aqua Ammonia Feed System

A 5.5 gpm flexible impeller centrifugal pump with a recirculation loop back to the storage tank regulates the back pressure on the by-passed feed pump. This alternative, redundant method proved to be reliable and economical. In addition, it provided a stable feed rate and required little maintenance (Skadsen, 1993).

6.2.2.3 Piping and Valving

For anhydrous ammonia, the typical piping materials for both direct and solution feed systems are stainless steel, PVC, and black iron (Dennis et al., 1991). Stainless steel or black iron pipe is used in the high pressure (i.e., greater than 15 psi) portions of the feed system. PVC pipe is used only in the low pressure portion of the feed system, after the ammoniators.

For aqueous ammonia, PVC piping should be used due to the corrosive nature of aqueous ammonia (Dennis et al., 1991).

6.2.2.4 Safety Provisions for Chloramine Generation Facilities

A chloramination facility should include some safety provisions to prevent the formation of nitrogen trichloride and the vaporization of ammonia at ambient temperatures. The possible formation of nitrogen trichloride at a chloramination facility should be considered when selecting sites for the ammonia and chlorine storage facilities.

Dennis et al. (1991) provides detailed information about safety provisions for chloramine facilities. Chlorine gas and ammonia gas should never be stored in the same room. The ammonia gas application points should be located at least 5 feet away from chlorine feed solution lines. Anhydrous ammonia is lighter than air, so any leaking vapor will rise quickly. Under pressure, anhydrous ammonia is a liquid. Great amounts of heat are absorbed when the pressurized liquid reverts to a gas.

If the storage tanks and/or chemical feed equipment are installed indoors, ventilation and vapor detection devices should be located at high points in the room. The ventilation rates will vary depending on the appropriate regulatory agency's requirements. Typically, a minimum of 6 room volume changes per minute is recommended.

Ammonia gas storage tanks should be protected from direct sunlight or direct sources of heat (i.e., greater than 125°F) to avoid pressure increases in the tank (Dennis et al., 1991). Otherwise, ammonia gas may be released into the atmosphere through the pressure relief valves. In warm regions, outdoor tanks should be covered with a shelter or outfitted with a temperature control sprinkler system. Where fugitive emissions of ammonia are a concern, fume control may be required. If the accidental release from a storage container is a concern, an emergency scrubber system similar to a chlorine gas scrubber system should be considered.

6.3 Primary Uses and Points of Application

Monochloramine is used in drinking water treatment for disinfection and nuisance organism control. Points of application are based on treatment objectives and contact time disinfection requirements.

6.3.1 Primary Uses

6.3.1.1 Disinfection

The primary use of monochloramine in water systems is as a secondary disinfectant for maintaining a residual in the distribution system. Chloramines are a good choice for secondary disinfectant because of the following potential benefits:

- Chloramines are not as reactive with organics as free chlorine in forming THMs.
- The monochloramine residual is more stable and longer lasting than free chlorine or chlorine dioxide, providing better protection against bacterial regrowth in systems with large storage tanks and dead-end water mains.
- The monochloramine residual has been shown to be more effective in controlling biofilms because of its superior ability to penetrate the biofilm. Controlling biofilms also tends to reduce coliform concentrations and biofilm induced corrosion.
- Because chloramines do not tend to react with organic compounds, many systems will experience less incidence of taste and odor complaints when using chloramines.

Water systems in Indiana and Virginia found that conversion from free chlorine to monochloramine as the secondary disinfectant significantly reduced coliform concentrations in the distribution system (Norton and LeChevallier, 1997).

The normal dosage range for monochloramine is in the range of 1.0 to 4.0 mg/L. The minimum residual of monochloramine in the distribution system is typically regulated at 0.5 mg/L (Texas

Natural Resource Conservation Commission). For prevention of nitrification in a distribution system, a minimum monochloramine dosage of 2.0 mg/L is recommended (Norton and LeChevallier, 1997).

6.3.1.2 Nuisance Organism Control

Cameron et al. (1989a) investigated the effectiveness of monochloramine to control the Asiatic clam in both the juvenile and adult phases. The adult Asiatic clam was found to be much more resistant to monochloramine than the juvenile form. Monochloramine was found to be the most effective for controlling the juvenile Asiatic clam in terms of LT_{50} (time required for 50 percent mortality). Monochloramine doses used to control the juvenile Asiatic clam range from 1.2 to 4.7 mg/L. Further research showed that the effectiveness of monochloramine increased greatly as the temperature increased (Cameron et al., 1989b).

6.3.2 Points of Application

The formation of monochloramine can be accomplished by first adding ammonia and then chlorine, or vice versa. Ammonia is added first where formation of objectionable taste and odor compounds caused by the reaction of chlorine and organic matter are a concern. However, most drinking water systems add chlorine first in the treatment plant in order to achieve the required concentration and contact time (CT) to meet EPA's SWTR disinfection requirements. Typically, the point of ammonia addition is selected to "quench" the free chlorine residual after a target period of time based on optimizing disinfection versus minimizing DBP formation.

Because the germicidal effectiveness of monochloramine is a factor of 200 less than for free chlorine, extremely long contact times are required for monochloramine to meet EPA disinfection CT requirements. Therefore, if ammonia is added first, a means of ensuring that CT requirements are met must be developed.

6.3.2.1 Impact on Other Treatment Processes

Monochloramine addition impacts other processes at the water treatment facility. These impacts include:

- Ammonia used in the chloramination process can provide nutrient ammonia for nitrifying bacteria growth in the distribution system, which can cause increased nitrate levels in the finished water where systems do not normally test for nitrate.
- Imbalances in chlorine and ammonia concentrations (in greater than an 8 to 1 ratio) can cause breakpoint chlorination reactions to occur when encountered in distribution system
- Monochloramine addition upstream of filters will reduce biological growth on filters. This has a favorable impact on the filters by keeping them clean and reducing the backwash frequency. It also has the undesirable impact of reducing BDOC removal in the filters when the filters are run in a biological mode.

The reader is referred to EPA's *Microbial and Disinfection Byproduct Simultaneous Compliance Guidance Document* (expected to be available in 1999) for additional information regarding the interaction between oxidants and other treatment processes.

6.4 Pathogen Inactivation and Disinfection Efficacy

Chloramination of drinking water has been practiced in the United States for nearly 80 years. In addition to achieving disinfection, chloramines have been used by the Denver Water Department for controlling tastes and odors since 1918 (Hazen and Sawyer, 1992). Chloramination has also been found to provide a more stable residual in water distribution system. However, because of its relatively weak disinfecting properties for inactivation of viruses and protozoa pathogens, it is rarely used as a primary disinfectant, and then only with long contact times.

6.4.1 Inactivation Mechanisms

The mechanisms by which chloramines inactivate microorganisms have been studied to a lesser degree than chlorine. A study of inactivation of *E. coli* by chloramines concluded that monochloramine readily reacts with four amino acids; cysteine, cystine, methionine and tryptophan (Jacangelo et al., 1987). The mechanism of inactivation for chloramine is therefore thought to involve inhibition of proteins or protein mediated processes such as respiration. Jacangelo further concluded that because of the inconsistency in rate of inactivation monochloramine should have "multiple hits" upon bacterial cells before cell death.

Few studies have been performed to determine the mechanism for viral inactivation. The initial site for destruction of bacteriophage f2 involved the RNA fragment (Olivieri et al., 1980). However, the primary mechanism for poliovirus inactivation by chloramines involved the protein coat (Fujioka et al., 1983). Similar to free chlorine, the mechanism of viral inactivation by chloramine may be dependent on factors such as virus type and disinfectant concentration.

6.4.2 Environmental Effects

Several studies have been performed to determine the effect of pH, temperature, and organic and inorganic compounds on the disinfection effectiveness of chloramines. Following is a summary of the affect these parameters have on pathogen inactivation.

6.4.2.1 pH

The effect of pH on disinfection has more to do with the organism than with the disinfectant; however, pH also impacts disinfection efficiency by controlling the chloramine species distribution. Studies have indicated that the disinfection efficacy of monochloramine and dichloramine are not equal. One study showed that the bactericidal properties of dichloramine were superior to that of monochloramine (Esposito, 1974). However, pH may be a compounding factor because changes in pH may alter the physiological response of the organism (Hoff and Geldreich, 1981). Other studies

have shown that monochloramine is superior to dichloramine with regard to virucidal ability (Dorn, 1974; Esposito, 1974; Olivieri et al., 1980). Some evidence suggests that solutions containing approximately equal concentrations of monochloramine and dichloramine may be more microbiocidal than those containing only monochloramine or dichloramine (Weber and Levine, 1944).

6.4.2.2 Temperature

Similar to most of the disinfectants discussed in this report, the bactericidal and viral inactivation efficiency of chloramine increases with increasing temperature. Moreover, the efficiency dramatically decreases under conditions of high pH and low temperature. For example, the inactivation of *E. coli* is approximately 60 times slower at pH 9.5 and temperatures of 2 and 6°C than at pH 7 and temperatures between 20 and 25°C (Wolfe et al., 1984). Similar results were obtained for poliovirus 1 inactivation (Kelley and Sanderson, 1958).

6.4.2.3 Organic Nitrogen and Other Compounds

In addition to ammonia, free chlorine reacts with organic nitrogen compounds to form a variety of organic chloramines. These organic chloramines are undesirable byproducts because they exhibit little or no microbiocidal activity (Feng, 1966). Studies have indicated that chlorine binds to amine-containing compounds more rapidly than to ammonia (Weil and Morris, 1949; Morris, 1967; Margerum et al., 1978) and that chlorine can be transferred from inorganic chloramines to amine-containing compounds (Margerum et al., 1978; Isaac and Morris, 1980)

Several other reactions may occur which divert chlorine from the formation of chloramines. These reactions can include oxidation of iron, manganese, and other inorganics such as hydrogen sulfide (Hazen and Sawyer, 1992).

6.4.3 Disinfection Efficacy

Chloramines are relatively weak disinfectants for virus and protozoa inactivation. As a consequence, it is extremely difficult to meet the SWTR CT criteria for primary disinfection of *Giardia* and viruses using chloramines because very long detention times are needed. However, given the ability of chloramines to provide a stable residual, this form of disinfection appears to be feasible for secondary disinfection protection against microbial growth in distribution systems. The following paragraphs describe the disinfection efficiency of chloramines in terms of bacteria, virus, and protozoa inactivation.

6.4.3.1 Bacteria Inactivation

A series of comprehensive experiments was initiated in the mid 1940s to determine the relative bactericidal effectiveness of free chlorine and inorganic chloramines. Results from these experiments showed conclusively that under relatively demand-free, laboratory-controlled conditions, free chlorine inactivated enteric bacteria much faster than chloramines (Wattie and

Butterfield, 1944). In this experiment, a monochloramine concentration of 0.3 mg/L required 240 minutes of contact time for 3-log inactivation of *E. coli* whereas exposure to 0.14 mg/L free Cl₂ required only 5 minutes to achieve the same level of inactivation at the same temperature and pH.

6.4.3.2 Virus Inactivation

According to reports written by Kabler et al. (1960) and the National Research Council (1980), all studies conducted prior to 1944 that compared virucidal potency of free and combined chlorine were inaccurate because the experiments failed to clearly differentiate between free and combined forms of chlorine and because high-chlorine-demand water was used in the experiments.

The majority of the experiments conducted after the mid-1940s has shown that inorganic chloramines require much higher concentrations and considerably longer contact times than free chlorine to achieve comparable levels of virus inactivation. Experiments showed that contact times between 2 and 8 hours were required at concentrations between 0.67 to 1.0 mg chloramines to achieve greater than 2-log inactivation of poliovirus 1 (Mahoney and MK500), poliovirus 2 (MEF), poliovirus 3 (Sackett), coxsackievirus B1, and coxsackievirus B5 (EA 80) (Kelley and Sanderson, 1958 and 1960). In contrast, 0.2 to 0.35 mg/L free Cl₂ required 4 to 16 minutes of contact time to achieve comparable levels of inactivation under the same conditions.

6.4.3.3 Protozoa Inactivation

Of the three predominant forms of pathogens (i.e., bacteria, viruses, and protozoan [oo]cysts), studies have shown that protozoan [oo]cysts are usually the most resistant to all forms of disinfection. Studies have indicated that free chlorine is a more effective disinfectant than chloramines for [oo]cyst inactivation (Chang and Fair, 1941; Chang, 1944; Stringer and Kruse, 1970). Chloramine concentrations of 8 mg/L were required for 2-log inactivation of *Entamoeba histolytica* cysts whereas only 3 mg/L of free chlorine was required to obtain the same degree of inactivation (Stringer and Kruse, 1970). Contact times for both disinfectants were 10 minutes.

6.4.3.4 CT Values

CT values for achieving *Giardia* cyst and virus inactivation using chloramines are shown in Table 6-4 and Table 6-5, respectively. Values contained in these tables were obtained from the *Guidance Manual for Compliance with Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources* (AWWA, 1991).

CT values shown in Table 6-4 are based on disinfection studies using in vitro excystation of *Giardia lamblia*. CT values shown in Table 6-5 were based on data using preformed chloramines at pH 8. No safety factor was applied to laboratory data used to derive the CT values shown in Table 6-4 and Table 6-5 since chloramination conducted in the field is more effective than using preformed chloramines, since monochloramine tends to degrade with time and some free chlorine is present when forming chloramines which enhances the inactivation process.

Table 6-4. CT Values for *Giardia* Cyst Inactivation Using Chloramines

Inactivation	Temperature (°C) (mg•min/L)				
	5	10	15	20	25
0.5-log	365	310	250	185	125
1-log	735	615	500	370	250
1.5-log	1,100	930	750	550	375
2-log	1,470	1,230	1,000	735	500
2.5-log	1,830	1,540	1,250	915	625
3-log	2,200	1,850	1,500	1,100	750

Source: AWWA, 1991.

Values shown in this table are based on a pH range between 6 and 9.

Table 6-5. CT Values for Virus Inactivation Using Chloramines

Inactivation	Temperature (°C) (mg•min/L)				
	5	10	15	20	25
2-log	857	643	428	321	214
3-log	1,423	1,067	712	534	356
4-log	1,988	1,491	994	746	497

Source: AWWA, 1991.

6.5 DBP Formation

The effectiveness of chloramines to control DBP production depends upon a variety of factors, notably the chlorine-to-ammonia ratio, the point of addition of ammonia relative to that of chlorine, the extent of mixing, and pH.

Monochloramine (NH_2Cl) does not produce DBPs to any significant degree, although some dichloroacetic acid can be formed from monochloramine and cyanogen chloride formation is greater than with free chlorine (Jacangelo et al., 1989; Smith et al., 1993; Cowman and Singer, 1994). The inability to mix chlorine and ammonia instantaneously allows the free chlorine to react before the complete formation of chloramines. In addition, monochloramine slowly hydrolyzes to free chlorine in aqueous solution. Therefore, halogenation reactions occur even when monochloramine is formed prior to addition in the treatment process (Rice and Gomez-Taylor, 1986). The closer the chlorine:ammonia ratio is to the breakpoint, the greater the formation of DBPs (Speed et al., 1987). In addition to controlling the formation of DBPs, chloramination results in lower concentrations of a number of the other specific organic halides generated from free chlorine, except for cyanogen chloride (Krasner et al., 1989; Jacangelo et al., 1989). Increased production of cyanogen chloride is observed when monochloramine is used as a secondary disinfectant instead of free chlorine.

The application of chloramines results in the formation of chlorinated organic material, although it occurs to a much lesser degree than from an equivalent dose of free chlorine. Little is known about the nature of these byproducts, except that they are more hydrophilic and larger in molecular size than the organic halides produced from free chlorine (Jensen et al., 1985; Singer 1993).

6.6 Status of Analytical Methods

6.6.1 Monitoring of Chloramines

There has been little development of analytical procedures for selective determination of monochloramines (Gordon, et al., 1992). Typically, the methods used for chlorine residual measurement are adapted for chloramine measurement. The DBPR promulgated on December 16, 1998 (63 FR 69390) establishes three analytical methods that are acceptable for measuring residual chloramines (combined chlorine). These methods are presented in 40 CFR § 141.131(c) and include:

- Amperometric Titration (Standard Method 4500-Cl D and ASTM Method D 1253-86);
- DPD Ferrous Titrimetric (Standard Method 4500-Cl F); and
- DPD Colorimetric (Standard Method 4500-Cl G).

If approved by the State, systems may also measure chloramines by using DPD colorimetric test kits.

6.6.1.1 Amperometric Titrations

The amperometric titration method is utilized extensively in water treatment laboratories (Gordon, et al., 1992). This method capable of differentiating the three most common forms of chlorine, namely chlorine/hypochlorous acid/hypochlorite ion, monochloramine, and dichloramine, as long as the combined forms are not present in concentrations greater than about 2 mg/L (as Cl₂). For higher concentrations, dilution of the samples is required, but differentiation is still possible (Aoki, 1989).

The amperometric titration method is a standard of comparison for the determination of free or combined chlorine. This method is not greatly affected by common oxidizing agents, temperature variations, turbidity, and color (Standard Methods, 1995). Amperometric titration requires a greater degree of skill than colorimetric methods. The differentiation of free chlorine, monochloramine, and dichloramine is possible by control of potassium iodide (KI) concentration and pH during the analysis.

Several methods are commonly used to measure chlorine species utilizing the amperometric titration including forward and back titration (Gordon, et al., 1992). The lower limit of detection of these methods varies depending on the instrumentation used and type of water sample analyzed. The lower limit of detection for commercial amperometric titrating equipment is about 30 µg/L as Cl₂ (Sugam, 1983).

Table 6-6 shows the working range, expected accuracy and precision, operator skill level required, interferences, and current status for amperometric method monochloramine analysis comparison.

6.6.1.2 Colorimetric Methods

Over the years, numerous colorimetric methods have been developed to measure free and combined chlorine in aqueous solutions (Gordon, et al., 1992). Not many of these methods would be recommended as the method of choice. Two of the colorimetric methods listed in Standard Methods (1995), are DPD methods. In addition, the colorimetric LCV method modified by Whittle and Lapteff (1974) can be used to measure free and combined chlorine species.

The DPD methods (ferrous titration and colorimetric) are operationally simpler for determining free chlorine than the amperometric titration (Standard Methods, 1995). Procedures are given for estimating separate monochloramine and dichloramine fractions, as well as combined chlorine fractions.

The LCV method modified by Whittle and Lapteff modifies the discontinued Standard Method for LCV. The maximum chlorine concentration that can be determined by this modified procedure, without dilution of the sample, is 10 mg/L as Cl₂ (Whittle and Lapteff, 1974).

See Table 6-6 for the working range, expected accuracy and precision, operator skill level required, interferences and current status for colorimetric method monochloramine analysis comparison.

6.6.2 Disinfectant Interferences

Interferences to free chlorine may impact the measurement of monochloramine since the methods use the free chlorine level in the determination of monochloramine. Many strong oxidizing agents interfere in the measurement of free chlorine in all monochloramine methods, including bromine, chlorine dioxide, iodine, permanganate, hydrogen peroxide, and ozone. However, the reduced form of these compounds (i.e. bromide ion, chloride ion, iodide ion, manganous ion, and oxygen) do not interfere. Reducing agents such as ferrous compounds, hydrogen sulfide, and oxidizable organic matter generally do not interfere (Standard Methods, 1995).

Table 6-6. Characteristics and Comparisons of Monochloramine^a Analytical Methods

Type of Test	Working Range (mg/L)	Expected Accuracy (\pm %)	Expected Precision (\pm %)	Skill Level ^b	Interferences	pH Range	Field Test	Automated Test	Current Status
Amperometric Titration, Forward	0.1 - 10	NR	0 - 10	2	dichloramine, nitrogen trichloride,	pH dependent	Yes	Yes	Recommended
Amperometric Titration, Back	0.1 - 10	NR	NF	2	dichloramine, nitrogen trichloride,	pH dependent	Yes	Yes	Recommended
Colorimetric DPD Ferrous Titration	0.01 - 10	NR	2 - 7	1	dichloramine, nitrogen trichloride, oxidizing species	Requires buffer	No	No	Recommended Lab Test
Colorimetric DPD	0.01 - 10	NR	5 - 75	1	dichloramine, nitrogen trichloride, oxidizing species	Requires buffer	Yes	No	Recommended Field Test

Source: Gordon et al., 1992.

Notes: ^a Little actual work has been carried out on selective determination of chloramines. The values reported are from extrapolated studies that had objectives other than the selective determination of chloramines.

^b Operator skill levels: 1 = minimal, 2 = good technician, 3 = experienced chemist. NR = Not reported in literature cited by referenced source.

6.6.2.1 *Amperometric Titrations*

The amperometric titration methods are unaffected by dichloramine concentrations in the range of 0 to 9 mg/L as Cl₂ in the determination of free chlorine. Nitrogen trichloride, if present, may react partially as free chlorine. The amperometric method will measure organic chloramines as free chlorine, monochloramine, or dichloramine, depending upon the activity of chlorine in the organic sample (Standard Methods, 1995). Dichloramine may also interfere with the measurement of both monochloramine and free chlorine (Marks, et al., 1951). The presence of iodide ion can be a severe problem if the titrator glassware is not washed carefully between determinations (Johnson, 1978).

Manganese dioxide, a common interference in most chlorine analytical procedures, does not interfere in the amperometric measurement of free chlorine (Bongers et al., 1977). However, because of its reaction with iodide ion, added during analysis, manganese dioxide does interfere with the amperometric measurement of combined forms of chlorine such as monochloramine (Johnson, 1978).

6.6.2.2 *Colorimetric Methods*

Sample color and turbidity may interfere in all colorimetric procedures. In the DPD colorimetric methods, high concentrations of monochloramine interfere with free chlorine determination unless arsenite or thioacetamide are added. In addition, the DPD methods are subject to interference by oxidized forms of manganese unless compensated for by a blank (Standard Methods, 1995). The DPD methods are unaffected by dichloramine concentrations in the range of 0 to 9 mg/L as Cl₂ in the determination of free chlorine. Nitrogen trichloride, if present, may react partially as free chlorine. The extent of this interference in the DPD methods does not appear to be significant (Standard Methods, 1995).

In the LCV colorimetric method, Whittle and Lapteff (1974) reported that dichloramine did not interfere with the monochloramine measurement.

6.6.3 Chloramine Monitoring for Systems Using Chloramines

Pursuant to 40 CFR §141.132(c)(1), community water systems and non-transient non-community water systems that use chloramines, must measure the residual disinfectant level at the same points in the distribution system, at the same time, and at the same frequency (based on population served) as total coliforms are sampled, as specified in 40 CFR §141.21. These systems may use the results of residual disinfectant concentration sampling conducted under §141.74(b)(6)(i) for unfiltered systems or §141.74(c)(3)(i) for systems which filter, in lieu of taking separate samples. No reduced monitoring allowances exist for these systems.

Compliance with the MRDL of 4.0 mg/L (as chlorine) is based on a running annual arithmetic average, computed quarterly, of monthly averages of all samples collected by the system under §141.132(c)(1). If the average quarterly averages covering any consecutive four-quarter period exceeds the MRDL, the system is in violation of the MRDL and must notify both the public, pursuant

to §141.32, and the State, pursuant to §141.134. Where systems switch between the use of chlorine and chloramines for residual disinfection during the year, compliance is determined by including together all monitoring results of both chlorine and chloramines in calculating compliance.

6.7 Operational Considerations

The purpose of this section is to address operational considerations in the use of chloramines in drinking water treatment. Specifically, the following topics are addressed below: the conversion of chloramination from chlorination; the potential operational impacts from chloramination disinfection; and special considerations for chloramination facilities. For a more detailed discussion of chloramine disinfection, refer to “Optimizing Chloramine Treatment” by Kirmeyer et al. 1993.

6.7.1 Conversion to Chloramination from Chlorination

6.7.1.1 Planning

Project planning and preparation are essential to ensure an efficient changeover, maintain a dependable and safe system, and preserve the public confidence in the water purveyor (Skadsen, 1993). Planning and preparation should consider the following aspects:

- Raw water composition and suitability to chloramination;
- Treatment plant and distribution system attributes and monitoring program;
- Employee training;
- Public notification and education; and
- Environmental affects from chloraminated water.

6.7.1.2 Preliminary Analysis

A bench scale study is necessary to identify the water characteristics and to determine if chloramination is suitable. White (1992) describes some of the study objectives and variables to consider. The reaction time to form free chloramine residuals varies for each water source since the reaction rate between chlorine and ammonia nitrogen depends on the water’s temperature and pH of the water. The reaction rate is also affected by the chlorine and ammonia nitrogen concentrations. To properly control the reaction time between chlorine and ammonia, the study should use different chlorine:ammonia nitrogen ratios, ammonia feed doses, and contact times.

The amount of ammonia required for chloramine residual disinfection depends on the following factors (Dennis et al., 1991):

- Organic nitrogen in the water;
- Ammonia residual desired in the distribution system; and

- Chloramine residual type and concentration required in the distribution system.

If there is organic nitrogen in the untreated water, the amount of supplemental ammonia required should be carefully determined by subtracting the background ammonia from the desired dose. The dose should also consider the amount of ammonia residual desired in the distribution system. For residual disinfection, approximately 1 to 2 mg/L of ammonia is required (Dennis et al., 1991).

For each specific water, a breakpoint curve should be developed to determine the chloramine residual type required. Monochloramine residuals are preferred for most water distribution systems. Dichloramine and nitrogen trichloride residuals may cause taste and odor problems when concentrations exceed 0.8 mg/L or 0.02 mg/L, respectively. Monochloramines are primarily formed when the theoretical chlorine to ammonia dose ratio is less than 5 to 1 (by weight ratio) and the pH is greater than 7.0 (Dennis et al., 1991). The chloramine residual concentration leaving the treatment plant will vary depending on the size of the distribution system and the chloramine demand exerted by the system. Typical chloramine residuals range from 1 to 4 mg/L (Dennis et al., 1991).

6.7.1.3 The Metropolitan Water District (MWDSC)

MWDSC of Southern California converted from free chlorine to chloramine disinfection in 1985 to assist its 27 member agencies in complying with the EPA's total trihalomethane regulation. MWDSC serves approximately 15 million people and operates five treatment plants, with a combined capacity of 1,670 MGD. Raw water is taken from two sources: the Colorado River and California state project water.

Prior to the changeover, MWDSC performed extensive investigations into the chemical, microbiological, and engineering aspects of chloramine disinfection. To prepare for the changeover, MWDSC coordinated the efforts among its treatment plants, distribution system reservoirs, laboratory personnel, and management. A formal request for approval to use chloramines as a disinfectant was submitted to the California State Department of Health Services. Next, a series of workshops was held on the engineering, chemical, and microbiological aspects of chloramine disinfection. MWDSC also prepared a manual for the type of chloramination application method and ammonia form selected. Information in the manual included the feed equipment information, project specifications, piping layouts, preliminary analysis, and safety and maintenance issues.

It was essential to notify specific sectors of the public that could be affected by the use of chloramines. MWDSC made its customers aware of the changeover and kept them apprised of the options for preventing adverse reactions through an extensive notification program that involved state and county health departments, appropriate interest groups, and the media.

6.7.2 Potential Operational Impacts from Chloramination Disinfection

6.7.2.1 Pretreatment

Ammonia in excess of the required chlorine can promote the growth of nitrifying bacteria in filter beds (i.e., rapid sand filters) (White, 1992). The excess ammonia acts as a nutrient and causes the growth of nitrifying bacteria, which convert the excess ammonia to nitrates and nitrites. Excessive levels of nitrate in drinking water have caused serious illness and sometimes death in infants under six months of age. The symptoms include shortness of breath and blueness of skin [40 CFR §141.32(e)(20)]. Prior to designing a chloramination facility, the amount of ammonia naturally occurring in the raw water should be determined. The required ammonia dosage would then be based on the anticipated naturally occurring ammonia levels.

A chloramine residual concentration should also be maintained in the discharge stream from the filters. An adequate residual concentration would be between 0.5 to 1 mg/L chloramine (White, 1992).

6.7.2.2 Nitrification

Nitrification in chloraminated drinking waters is usually partial. Partial nitrification occurs when the chloraminated water has excess ammonia present in the distribution system (Skadsen, 1993). Partial nitrification can have various adverse effects on water quality, including a loss of total chlorine and ammonia residuals and an increase in heterotrophic plate count (HPC) bacteria concentration. The excess ammonia encourages the growth of nitrifying bacteria that convert ammonia to nitrates. An intermediate step in this conversion results in a small amount of nitrite being formed. Research has shown that a chlorine demand of 5 mg/L is exerted by 1 mg/L of nitrite (Cowman and Singer, 1994). The nitrites rapidly reduce free chlorine, accelerate decomposition of chloramines, and can interfere with the measurement of free chlorine (Skadsen, 1993). Valentine (1998) found that the decay of monochloramine was increased (from a second order rate constant of 0.07 to 0.106) by the presence of 0.5 mg/L of nitrite. If nitrification episodes are allowed to continue, very low (or zero) total chlorine residual concentration levels may occur. Loss of chlorine residual allows an increase in HPC bacteria and potentially increases in total coliforms and may result in a positive sample (Cowman and Singer, 1994). Additional information on nitrification can be found in (Kirmeyer et al. 1995), "Nitrification Occurrence and Control in Chloraminated Water Systems."

Factors. Several possible factors have been implicated as contributing to nitrification. These factors include low chlorine-to-ammonia ratio, long detention times, and temperatures (Cowman and Singer, 1994). Though some articles noted that low monochloramine dosages may lead to nitrification, other research has reported nitrification occurring at monochloramine concentrations greater than 5.0 mg/L (Cowman and Singer, 1994). Nitrifying bacteria are relatively more resistant to disinfection by monochloramine than free chlorine (Cowman and Singer, 1994). The optimum conditions for nitrification would be a water system with free-ammonia, a pH of 7.5 to 8.5, a water temperature of

25 to 30°C, and a dark environment. Nitrifying bacteria exhibit slow growth and have been found in higher numbers in the sediment of distribution systems than in the biofilm (Cowman and Singer, 1994).

If the water reservoirs in the distribution system are covered, partial nitrification may occur (White, 1992). Nitrification occurred in two of MWDSC's covered reservoirs (Garvey and Orange County reservoirs) after the changeover. Approximately 10 weeks after the changeover from chlorine to chloramine, water quality degradation was occurring in the Garvey Reservoir. MWDSC increased the amounts of free chlorine added to the plant effluent to maintain a 1.5 mg/L monochloramine residual at the reservoir effluent and the chlorine to ammonia ratio was increased from 3:1 to 4:1 to decrease the amount of excess ammonia in the water. These changes were more effective than the flushing programs for the distribution system, which only helped temporarily.

Control Measures. Nitrification may pose a potential problem for any utility using monochloramine as a disinfectant (Cowman and Singer, 1994). Thus, nitrification should be carefully assessed and controlled. Nitrification may be controlled by monitoring at strategic locations throughout the distribution system for monochloramine and dichloramine residuals (White, 1992).

The chloramine free residual stability is increased throughout the distribution system when there is increased control of microbial contaminants and decreased bacterial concentrations in the raw water to acceptable levels. Recommended approaches to prevent and control nitrification in the distribution system include (Cowman and Singer, 1994):

- Decreasing the detention time;
- Increasing the pH;
- Decreasing the temperature;
- Decreasing TOC concentrations;
- Increasing chloramines residual;
- Increasing the chlorine-to-ammonia ratio; and
- Decreasing the excess ammonia concentration.

For the distribution system, the system should be evaluated to identify the low-flow or dead-end sections. The detention times in the system should be operationally minimized (Skadsen, 1993). For reservoirs, those with single inlet-outlet configurations should especially be carefully monitored and operated (Skadsen, 1993).

MWDSC stresses the importance of developing nitrification strategy control measures. In particular, a comprehensive monitoring program should be established to alert personnel to implement control measures when required. To control nitrification, MWDSC developed a control strategy where the reservoirs and distribution system were first sampled for nitrite levels (Skadsen, 1993). MWDSC

also decreased the detention times in reservoirs and distribution systems, especially during warmer weather, which helped to keep nitrite levels down.

The chloramination operation was modified to add more chlorine to the reservoir inlet and increase the chlorine-to-ammonia ratio from 3:1 to 5:1 at the plant effluent. The initial 3:1 ratio corresponded with a 1.5 mg/L monochloramine residual and 0.2 mg/L excess ammonia. At these concentrations, the agencies receiving the water had the flexibility of blending the chloraminated water with chlorinated water or adding more chlorine to those sections of the system with long detention times. Increasing the ratio further to 5:1 controlled the nitrification problem by decreasing the amount of free ammonia in the distribution system. Operating at a 5:1 ratio requires more monitoring since an overdose of chlorine can reduce the chloramine residual.

A survey of chloramine users in the United States was conducted in June 1991. This survey showed that the chlorine to ammonia ratio varied from 3:1 to 7:1 (Dennis, et al, 1991). The chloramine residual varied from 0.8 mg/L to 3 mg/L (Dennis, et al, 1991). Table 6-7 shows the results from this survey. The agencies surveyed reported excellent results with secondary chloramine disinfection (Dennis et al, 1991). EPA is in the process of collecting and evaluating chloramine use in the United States as part of the Information Collection Rule (ICR), but until those data are available, the 1991 survey appears to be the most recent national survey of chloramine use.

Each year, MWDSC also added chlorine past the breakpoint to allow a free residual for 30 days. The ideal locations for breakpoint chlorination are at the distribution reservoirs and interconnections. The increased chlorine oxidizes any nitrite and nitrifying bacteria and eliminates the excess ammonia in the distribution system. For larger water systems, MWDSC recommends maintaining chlorination stations throughout the distribution system. Both fixed and mobile chlorinators may be used. Mobile chlorinator units are self-contained and trailer-mounted with evaporators, chlorinators, generator, a booster pump for transport water, and chlorine injectors. They are designed to draw liquid chlorine directly from a 17-ton chlorine trailer and to inject a chlorine solution into the distribution system or reservoir.

Since nitrifying bacteria were found in higher numbers in the sediments of the distribution system than in the biofilm, flushing sediment from the system will help to control nitrification. The addition of a disinfectant (i.e., free or combined chlorine) is required to remove nitrification.

At the Indiana American Water Company, the distribution system is temporarily converted back to free chlorine for scheduled flushing (Lyn et al., 1995). Utilities should evaluate their flushing program to avoid consumer complaints with inappropriate flushing techniques.

6.7.2.3 Taste and Odor

If the chlorine to ammonia-nitrogen ratios are between 3:1 and 5.5:1, disagreeable tastes and odors should be evaluated at the consumer tap (White, 1992).

Fishy tastes and odors (e.g., from source waters and return washwater from the washwater treatment system) can be controlled by a 1-hour contact time with free-chlorine residual of 2 mg/L prior to the addition of ammonia (Dennis et al., 1991). This prechlorination eliminates the fishy taste and odor but may increase the THM concentrations at the plant effluent.

Table 6-7. Survey of Chloramine Users in the United States

Agency	Treatment Capacity	Type of Ammonia	Chlorine: Ammonia Nitrogen ratio	Chloramine Residual (mg/L)	NH ₃ Injection Point	Nitrification Control Strategies
City of Dallas, TX	730 mgd; 3 plants	Anhydrous	5:1	2.1 - 2.3	Presedimenta-tion, Post-filtration	None
City of Denver, CO	600 mgd; 3 plants	Aqueous (30%)	3:1	0.8 - 1.0	Post-filtration, prior to chlorine addition	None
Indianapolis, Water Co., IN	176 mgd; 4 plants	Anhydrous	3:1 varies	1.5 - 2.0	Post-filtration	Increase ratio in summer
Miami-Dade Water Authority, FL	300 mgd; 3 plants	Anhydrous	5:1	2.7 - 3.0	10 ft after chlorine flash mix	2 weeks free chlorine every November
City of Milwaukee, WI	305 mgd; 2 plants	Anhydrous	5:1	0.8 - 0.9	Post-filtration	None
City of Philadelphia, PA	530 mgd; 3 plants	Aqueous (30%)	3:1	2.0	Post-filtration	None
City of Portland, OR	225 mgd	Anhydrous	7:1	1.8	70 ft downstream of chlorine in conduit	None
Orleans Parish, LA	300 mgd; 2 plants	Anhydrous	3:1	2.0 - 2.5	Pre-filtration	None
St. Louis Co. Water Authority, MO	360 mgd; 4 plants	Aqueous (30%)	4:1	2.5	Concurrent with chlorine at flash mix, post-filtration	None

Source: Dennis et al., 1991.

6.7.3 Special Considerations for Chloramination Facilities

6.7.3.1 GAC Filters with Ammonia Addition

The Ann Arbor Water Treatment Plant in Michigan is a 50 mgd lime softening plant that draws its water from the Huron River (80 to 90 percent) and ground water (10 to 20 percent). When chloramination is applied to the river water, the chlorine is injected into the raw water line

immediately before ammonia is applied. The total chlorine feed averages 3.3 mg/L with an average demand of 2.0 mg/L for the river water.

Evidence of nitrification occurred immediately after a change in treatment from sand to GAC filtration. Prior to the change to GAC, the treatment plant had successfully used monochloramine as both a primary and a final disinfectant. Nitrification was not evident. The GAC received an application of approximately 1.3 mg/L ammonia. This input of ammonia to the filters constituted a nutrient source that allowed nitrifying bacteria to become established and proliferate. The GAC particles have been observed to harbor nitrifying bacteria and nitrification has been observed in GAC beds. Higher nitrifying bacteria levels have been observed in other filter beds as compared with source water. The GAC effluent also showed pronounced seasonal peaks in HPC bacteria from May to July, and percent total coliforms positive from July to August. These seasonal peaks are most probably temperature related. During periods of nitrification, GAC effluent HPC bacteria concentration was steadily decreasing while in the distribution system, HPC bacteria were increasing.

6.7.3.2 Organic Nitrogen

Concentrations of organic nitrogen and ammonia nitrogen as low as 0.3 mg/L may interfere with the chloramination process. The monochloramine residuals will hydrolyze with the organic nitrogen to form organochloramines, which are nongermicidal. This reaction would take about 30 to 40 minutes. After the monochloramine residuals disappear, free ammonia nitrogen reappears. Free ammonia nitrogen is a powerful biological nutrient. Its presence promotes biological instability in that portion of the distribution system. Biological instability usually results in foul tastes and odors plus dirty and/or colored water at the consumers tap (White, 1992).

The free chlorine residual or chloramine residual method may be used to clean an area with biological instability. Of the two methods, the free chlorine residuals method is superior (White, 1992). Free chlorine residuals restore distribution system stability quicker (i.e., a few days for free chlorine versus weeks for chloramines), the clean-up process can be monitored, and the clean-up is complete when the free chlorine residual concentration reaches 85 percent of the free chlorine concentration.

Based on their conversion to chloramination experience, MWDSC recommends that utilities employing chloramines for disinfection monitor for total organic nitrogen levels. When levels are high, the amino acid fraction is also likely to rise. This rise may impair the chloramination disinfection efficiency if high levels of organic nitrogen are not detected.

6.7.3.3 Mixing

Mixing at the point of application greatly affected the bactericidal efficiency of the chloramine process. When the pH of the water is between 7 and 8.5, the reaction time between ammonia and chlorine is practically instantaneous. If chlorine is mixed slowly into the ammoniated water, organic matter, especially organic matter prone to bleaching with chlorine solution, may react with the chlorine and interfere with chloramine formation (White, 1992).

6.7.3.4 Blending Waters

When chlorinated water is blended with chloraminated water, the chloramine residual will decrease after the excess ammonia has been combined and monochloramine is converted to dichloramine and nitrogen trichloride. The entire residual can be depleted. Therefore, it is important to know how much chlorinated water can be blended with a particular chloraminated water stream without significantly affecting the monochloramine residual. Blended residual curves should be developed for each specific blend.

6.7.3.5 Corrosion

Chloramination and corrosion control can limit bacterial biofilm development in the distribution system. If optimum corrosion of iron pipes is not controlled, the chloramination efficiency may be impacted. Corrosion inhibitors with higher phosphate concentrations may reduce corrosion rates (Lyn et al., 1995).

6.7.3.6 Formation of Nitrogen Trichloride

If water in the distribution system tends to form nitrogen trichloride, the finished water should be subjected to post-aeration, which readily removes nitrogen trichloride (White, 1992). Nitrogen trichloride is also readily destroyed by sunlight (White, 1992).

6.7.3.7 Human Health and the Environment

Users of kidney dialysis equipment are the most critical group that can be impacted by chloramine use. Chloramines can cause methemoglobinemia and adversely affect the health of kidney dialysis patients if chloramines are not removed from the dialysate water. Chloramines can also be deadly to fish. The residuals can damage the gill tissues, enter the red blood cells, and cause an acute blood disorder. Chloramine residuals should be removed from the water prior to the water contacting any fish. As such, fish hobbyists should be notified, along with pet stores and aquarium supply establishments.

6.8 Summary

6.8.1 Advantages and Disadvantages of Chloramine Use

The following list highlights selected advantages and disadvantages of using chloramines as a disinfection method for drinking water (Masschelein, 1992). Because of the wide variation of system size, water quality, and dosages applied, some of these advantages and disadvantages may not apply to a particular system.

Advantages

- Chloramines are not as reactive with organics as free chlorine in forming DBPs.

- The monochloramine residual is more stable and longer lasting than free chlorine or chlorine dioxide, thereby providing better protection against bacterial regrowth in systems with large storage tanks and dead end water mains. However excess ammonia in the network may cause biofilming.
- Because chloramines do not tend to react with organic compounds, many systems will experience less incidence of taste and odor complaints when using chloramines.
- Chloramines are inexpensive.
- Chloramines are easy to make.

Disadvantages

- The disinfecting properties of chloramines are not as strong as other disinfectants, such as chlorine, ozone, and chlorine dioxide.
- Chloramines cannot oxidize iron, manganese, and sulfides.
- When using chloramine as the secondary disinfectant, it may be necessary to periodically convert to free chlorine for biofilm control in the water distribution system.
- Excess ammonia in the distribution system may lead to nitrification problems, especially in dead ends and other locations with low disinfectant residual.
- Monochloramines are less effective as disinfectants at high pH than at low pH.
- Dichloramines have treatment and operation problems.
- Chloramines must be made on-site.

6.8.2 Summary Table

Table 6-8 summarizes the considerations for the use of chloramine.

Table 6-8. Summary of Chloramine Disinfection

Consideration	Description
Generation	<p>Chloramines are generated by the sequential addition of chlorine (hypochlorous acid) and ammonia at a Cl_2 to NH_3 ratio ranging from 3:1 to 5:1. Either chlorine or ammonia may be added first. Chlorine is normally added first to act as the primary disinfectant and after 10 to 30 minutes, ammonia is added to prevent further formation of DBPs.</p> <p>The most common methods of chlorine addition include gas feed using a dilution water reduction system or direct feed of bulk hypochlorite solution (12 percent typical commercial strength).</p> <p>The most common ammonia feed facilities include anhydrous ammonia fed either directly or via a dilution water reduction system or direct feed of bulk aqua ammonia solution (20 percent typical commercial strength).</p>
Primary uses	<p>Monochloramine is used primarily as a secondary disinfectant to provide a residual in the distribution system. It is used where elevated DBPFP levels in the treated water can cause high levels of DBP formation in the distribution system if free chlorine is used as the secondary disinfectant. Monochloramine has been found to be more effective than free chlorine in controlling biofilms and coliform bacteria in systems with long detention times due to the lower decay rate of chloramine. Monochloramine will have much less tendency to react with organics present and hence will form less taste and odor causing compounds.</p>
Inactivation efficiency	<p>At pH 7 and below, free chlorine is 200, 200, 50, and 2.5 times more effective in inactivating bacteria, viruses, spores, and cysts respectively than monochloramine.</p>
Byproduct formation	<p>Monochloramine substantially reduces the DBP formation but still forms some DBPs.</p>
Limitations	<p>Monochloramine is increasingly being used as a secondary disinfectant to provide a residual in distribution systems because of its lower decay rate than free chlorine and lesser tendency to form DBPs.</p> <p>Caution should be used in using monochloramine in distribution systems where water sources using free chlorine residual are also used. High Cl_2 to N ratios can occur where waters using different residuals combine leading to the possible formation of taste and odor causing dichloramine and nitrogen trichloride. In some cases the residual may be completely removed by the breakpoint reaction.</p>
Point of application	<p>Monochloramine is normally generated at the treatment facility with the addition of ammonia to chlorinated water. Ammonia is normally added prior to the pumping into the distribution system. In some cases, ammonia is added prior to the clearwell to minimize formation of DBPs by free chlorine residual.</p>
Special considerations	<p>Nitrification and generation of bacterial growths can occur if the Cl_2 to N ratio is too low and conditions exist for the growth of nitrifying bacteria. A minimum residual of 2.0 mg/L of monochloramine has been found effective in controlling nitrification in most systems.</p>

6.9 References

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