

Monochloramine Monitoring – Reliable Analysis, Safer Drinking Water

By

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Introduction

The Safe Drinking Water Act (SDWA), enacted in 1974, is the main federal law that ensures the quality of Americans' drinking water. Under SDWA, EPA sets standards for drinking water quality and oversees the states, localities, and water suppliers who implement those standards. The law was amended in 1986 & 1996 requiring many actions to protect drinking water and its sources.

In the early 1900's chloramination received attention when it was found that the cost of chlorination might be reduced. The practice of monochloramine treatment was adopted in 1916 in Ottawa, Ontario. The first installation in the United States was in 1917 in Denver, Colorado. Both locations used ammonia and hypochlorite to form monochloramine and noted improvements in taste. Chloramination is becoming more popular to mitigate unwanted disinfection by-products (DBPs).

Chemistry of Chloramines

Chloramines are less aggressive disinfectants that react more slowly than chlorine however remains longer in the distribution system. Given more stringent disinfection byproduct regulations, chloramination can be an appealing alternative to the use of free chlorine as a means of limiting DBP formation – particularly trihalomethanes (THMs). Additional benefits are fewer taste and odor concerns are reported by consumers of chloraminated water.

Chloramine is a general term that describes three related compounds:

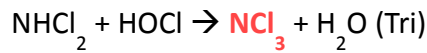
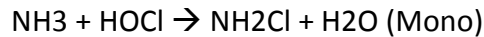
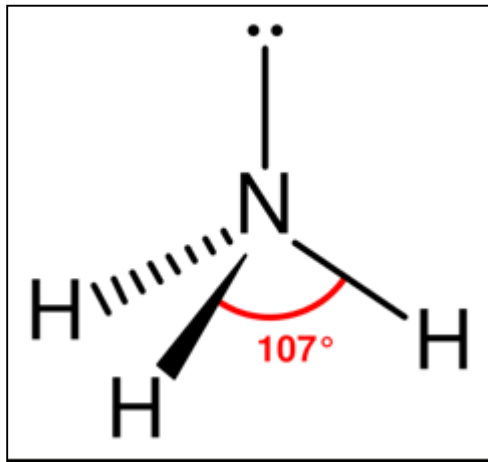
Monochloramine, NH_2Cl

Dichloramine, NHCl_2

Trichloramine, NCl_3

Monochloramine is the preferred chloramine compound for drinking water disinfection.

The molecular structure of all three chloramine compounds resembles the structure of ammonia. A chlorine atom will replace one, two, or three hydrogen atoms respectively for the formation of mono-, di-, and trichloramines as shown below.



The formation of di- and tri-chloramine is minimized by adding a specific weight ratio of chlorine and ammonia to water while maintaining the optimal pH range. Di- and tri-chloramines can contribute an objectionable taste and odor to the treated water. Monochloramines are effective biocides that contribute least to taste and odor problems.

Chloramination Process

To form the monochloramine compound, the appropriate weight ratio of chlorine and ammonia must be determined and then properly managed. Free ammonia entering the distribution system must be controlled to reduce the potential for nitrification. Chloramines are weaker oxidizing agents; therefore a higher disinfectant residual is required for similar results. A chloramine residual of 2.0 mg/L is comparable to a free chlorine residual of 0.5 mg/L.

All of the free chlorine will be converted to monochloramine when the pH is between 6.5 and 8.5 and the ratio of chlorine to ammonia is equimolar, 5:1 by weight or less. Since this reaction is pH sensitive, the rate of reaction is important.

Reaction rates for 99% conversion of free chlorine to monochloramine at 25 Degrees C.

pH-	2	4	7	8.3
Seconds-	421	147	0.2	0.009

This is why optimum pH is 6.5 to 8.5

Chlorine atoms occur in pairs and have a combined weight of just over 70 atomic mass units. The weight of ammonia is measured as N (which is why it is often expressed as $\text{NH}_3\text{-N}$), and nitrogen has an atomic mass of 14. The difference

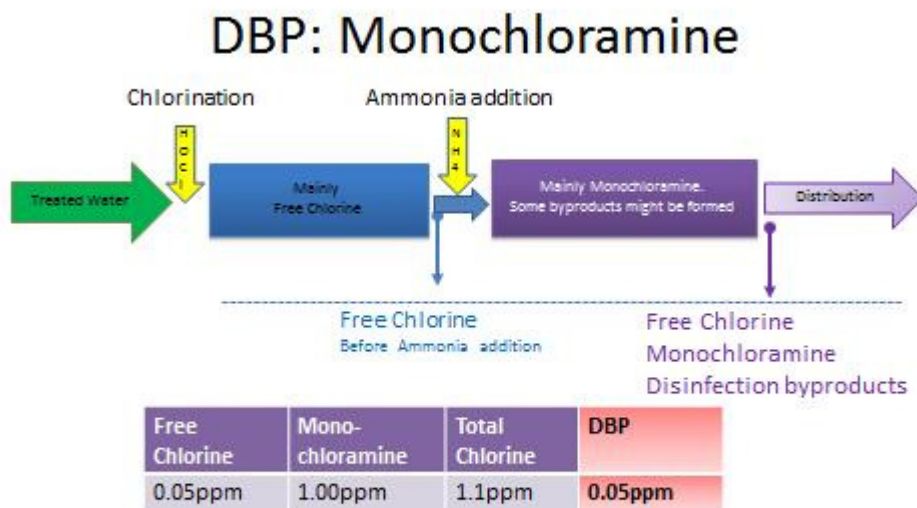
between the weight of chlorine and ammonia ($70 / 14 = 5$) establishes the chlorine to ammonia weight ratio of 5:1.

Dosing chlorine and ammonia based on the weight ratio of 5:1 means that the required chlorine dose will be five times greater than the ammonia dose. For example, a target chloramine dose of 3.0 mg/L will require the addition of 3.0 mg/L of chlorine and 0.60 mg/L of ammonia to keep the 5:1 ratio. The amount of each chemical to add depends on chemical strength and weight of treated water.

Chlorine-Ammonia Treatment

- NH_3 is added to the chlorinated water to form monochloramines:

$$\text{HOCl} + \text{NH}_4\text{OH} \rightarrow \text{NH}_2\text{Cl} + 2 \text{H}_2\text{O}$$
- Excess of NH_3 will consume all Free Chlorine and contaminates the water
- Too little NH_3 means too much Free Chlorine is left, which will react with NH_3 to form unwanted Dichloramines and other byproducts.
- An ammonia monitor can also be employed to monitor and control ammonia.



Increasing DBP values will raise a alarm and the source can be investigated.

Monochloramine Monitoring

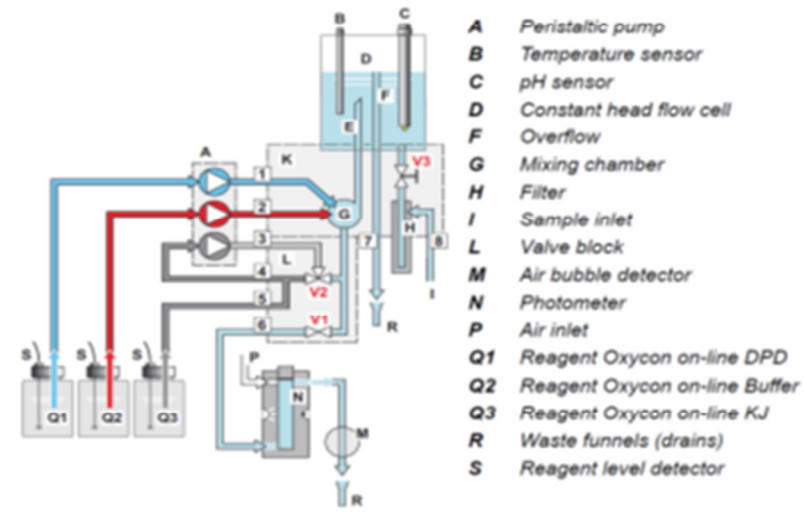
Precise and accurate measurement of the used primary disinfectant and their byproducts is an increasing concern. As the disinfection strength depends on pH it must be measured. Correct measuring equipment for the disinfectant is fundamental for the process and allows correct dosing with fewer chemicals DBPs.

AMI Codes II CC Measurement Process

- Zero measurement: Measurement of sample background to compensate for light absorption effects (turbidity, sample color) not related to red DPD color
- Free residual chlorine (FRC) measurement is 3 – 5 seconds after the addition of buffer and DPD to sample.
- Total Residual chlorine 1 (TC 1) measurement is 3 – 5 seconds after the addition of buffer, DPD, and potassium iodide to the sample. It is the sum of the free chlorine and the monochloramine. Therefore the monochloramine can be calculated by subtracting the free chlorine determined in line 2 from TC1.
- Total Residual chlorine 2 (TC 2) measurement is 120 seconds after the addition of buffer, DPD, and potassium iodide to the sample. Combined chlorine is calculated by subtracting the free chlorine determined in line 2 from TC2.

How can the AMI Codes-II CC support water utilities in optimizing their disinfection process?

- Measures Free Residual Chlorine (FRC), Total Chlorine 1 (TC1), Total Chlorine 2 (TC2)
- Calculate monochloramine (CMC, true monochloramine), Di-/ Tri-chloramines (CDC), Combined Chlorine (CCC)
- Keep a minimum Free Chlorine (0.05 ppm) to avoid Ammonia overdosing
- TC 2 should be equal [FRC & CMC] value, then the ammonia has finished the conversion
- If TC 2 is higher than [FRC&CMC], the difference is other chloramines forms, indicating an overdose of Chlorine
- Ammonia measurement or other additional instruments are not necessary but available if desired



Swan AMI Codes II Schematics



Swan AMI Codes II CC Chlorine Analyzer