Science of Chloramination

Maine Water Utilities Association

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What is chloramination?

- Chloramination is the process of disinfecting water using chloramines, compounds of chlorine and ammonia.
- The use of chloramines in the United States has evolved since the early 1900’s to become a very popular water treatment alternative – second only to the use of free chlorine.
- Understanding the various aspects of chloramination enables a water system professional to effectively manage and operate a chloraminated water system.

Free chlorine vs. chloramines

- Free chlorine is a powerful oxidant and reacts rapidly with organics and inorganics.
- As a result, the strong disinfectant residual it initially provides may not persist as long as necessary within a distribution system.
- During its reaction with organic matter, free chlorine can readily form unwanted disinfection byproducts (DPBs) such as trihalomethanes (THMs) and haloacetic acids (HAAs).

Free chlorine vs. chloramines

- In comparison, chloramines offer a less aggressive disinfectant residual that reacts more slowly and 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 – especially THMs.
- Also of benefit, fewer taste and odor concerns are reported by consumers of chloraminated water.

Further considerations

- For a drinking water utility, chloramination may or may not be a good alternative to free chlorination.
- The source water type and quality and the overall treatment process required to produce potable drinking water are primary factors to consider.
- Even with the full range of benefits provided by the use of chloramines, additional consideration must be given to the secondary impacts associated with chloramination – primarily the potential for nitrification within the distribution system.

Chloramination considerations

- With chloramination, an additional chemical must be purchased, stored, and applied to the process.
- To form the preferred chloramine compound, the appropriate weight ratio of chlorine and ammonia must be determined and then carefully managed.
- Free ammonia entering the distribution system must be limited to reduce the potential for nitrification.
- Beyond that, it may be necessary to incorporate any number of steps to actively control nitrification.

Chloramination considerations

- Free chlorine in drinking water can dissipate within a short amount of time or can be removed with relative ease.
- Chloramines are more difficult to remove, and ammonia can adversely affect patients receiving kidney dialysis and aquarium fish.
- Consumers must be notified before a water system begins chloramination so that, if necessary, corrective action at point of use can be taken to minimize any risks to sensitive users.

Chloramination in practice

- If a water system has been using free chlorination and switches to chloramination, the following points should be taken into account:
- Chloramines are weaker oxidizing agents, and 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.
- The introduction of chloraminated water to unlined cast-iron pipes may result in reddish discoloration. System flushing may be necessary.

Chloramine compounds

- Chloramine is a general term that describes three related compounds:

  mono chloramine, NH_2Cl

  di chloramine, $NHCl_2$

  tri chloramine, NCl_3

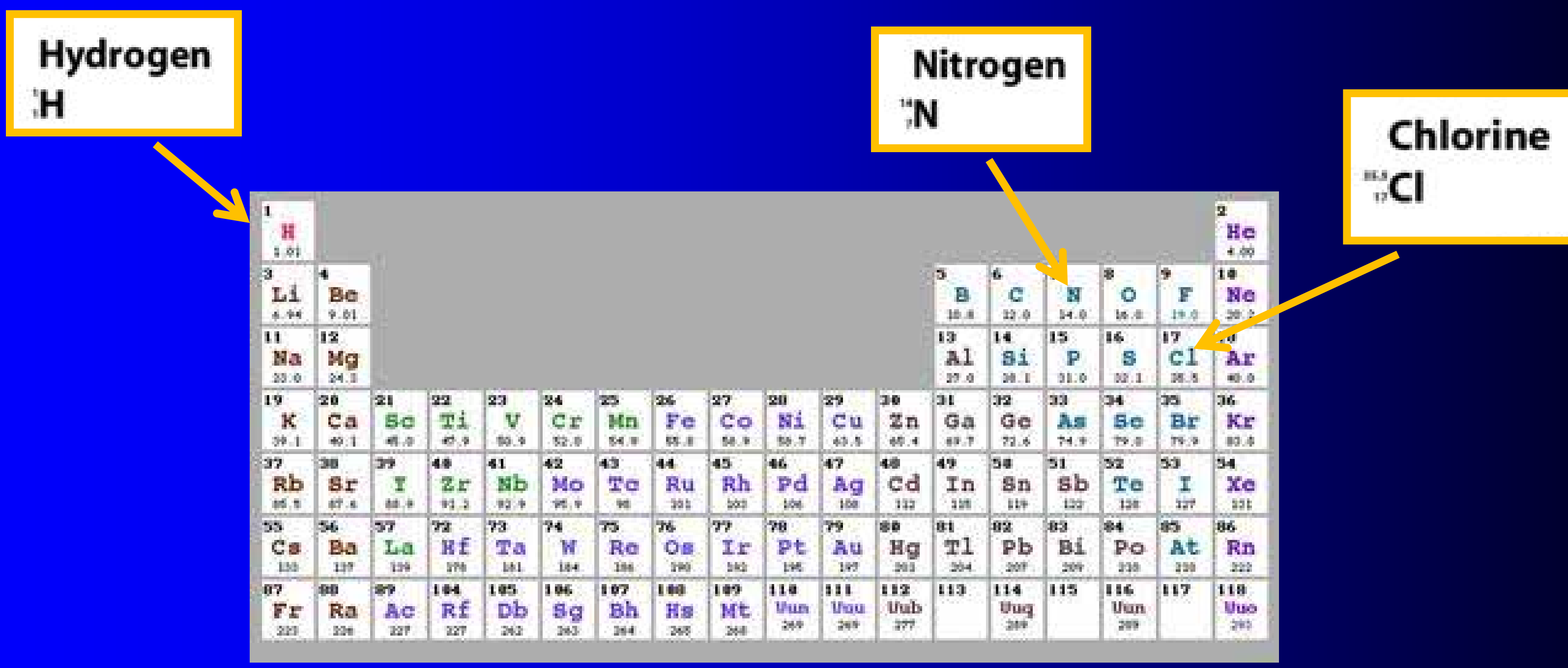
- Monochloramine is the preferred chloramine compound for drinking water disinfection.

Chloramine compounds

- The formation of di- and trichloramine is minimized by adding a particular weight ratio of chlorine and ammonia to water while maintaining a certain pH range.
- If allowed to develop, di- and trichloramines can contribute an objectionable taste and odor to the treated water.
- Monochloramines are effective biocides that contribute least to taste and odor problems.

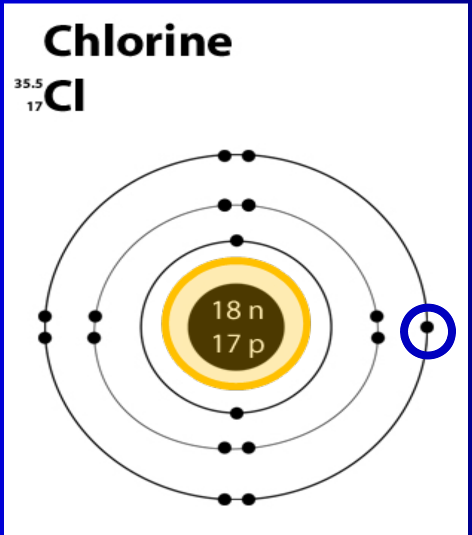
Chemistry of chloramination

- To fully understand the chemistry involved with chloramination, it is helpful to start with the basics:



Chlorine

- Chlorine, an element in the halogen family, is represented by the symbol Cl. It has one unpaired electron in its outter valence shell making it highly reactive.

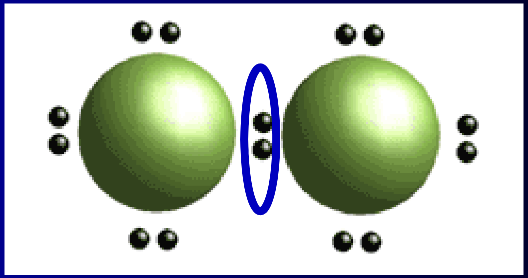


unpaired electron

Chlorine

- Elemental chlorine exists as a two-atom molecule with the symbol Cl_2. In this arrangement, each atom has 8 valence electrons in its outter shell.

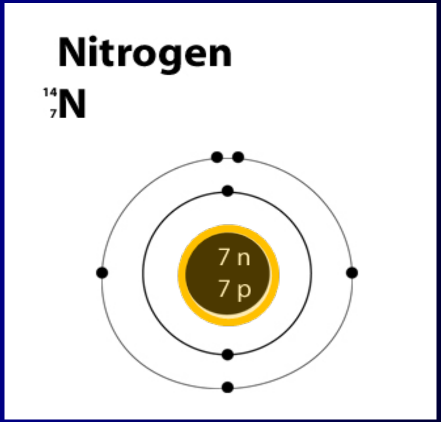
- The molecular weight of this diatomic molecule is 70.92.

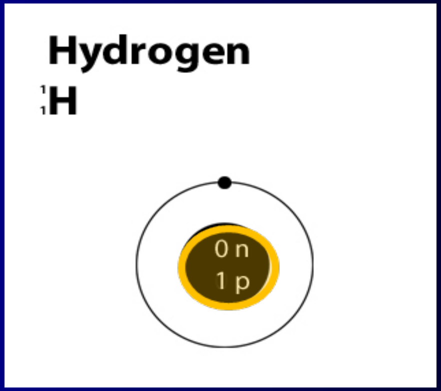


- The bonding between the two atoms is relatively weak and keeps the Cl_2 molecule highly reactive.

Ammonia

- Ammonia, NH_3, is a compound made up of one nitrogen atom and three hydrogen atoms.
- The nitrogen atom has an atomic mass of 14 and each hydrogen atom has an atomic mass of 1 giving ammonia a total molecular weight of 17.

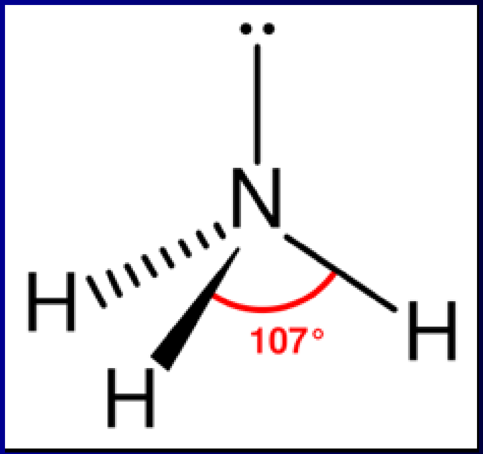




Chloramine structure

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

Monochloramine
Dichloramine
Trichloramine



Cl Cl Cl

Chlorine and water

- During hydrolysis, chlorine reacts rapidly with water to form hypochlorous acid (HOCl) and hydrochloric acid (HCl)…

$$Cl_2 + H_2O \leftrightarrows HOCl + HCl$$

- Of the two compounds, hypochlorous acid is more important in the water treatment process. It contains the active form of chlorine that will be used to disinfect organisms.

Monochloramine formation

$$Cl_2 + H_2O \leftrightarrows HOCl + HCl$$

- When ammonia is introduced under the appropriate conditions, it reacts with the hypochlorous acid to produce monochloramine:

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$$

Conditions for this reaction

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$$

- The reaction of the hypochlorous acid and ammonia will convert practically all of the free chlorine to monochloramine in less than one second provided the following conditions exist:

pH near 8

temperature near 25 ºC

Cl_2 to NH_3 -N weight ratio near 5:1

Conditions for this reaction

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$$

- This reaction is based on one molecule of chlorine combining with one molecule of ammonia.
- Once all of the chlorine and ammonia molecules combine, there is no free Cl_2 or NH_3 remaining.
- The amount of chlorine and ammonia required for this reaction to produce monochloramine is based on the ideal weight ratio of 5:1. Here is how…

Chloramine weight ratio

- 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 NH_3-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.

Weight ratio applied

- Dosing chlorine and ammonia based on the chloramine 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.
- How much of each chemical to add depends on chemical strength and volume of treated water.

Chemical strength

- Various forms of chlorine and ammonia can be used for the formation of chloramines:
- Chlorine
  - gas (100% strength)
  - sodium hypochlorite solution (12% strength)
  - calcium hypochlorite tablets (65% strength)
- Ammonia
  - gas (100% strength)
  - liquid ammonium hydroxide (10 - 35% strength)

Chemical addition

$$\text{Chemical Feed Rate lbs./day} = \frac{\text{Dose mg/L} \times \text{MGD} \times \text{8.34 lbs./gal}}{\text{Chemical Strength (decimal percentage)}}$$

- The chemical feed rate equation above is used to determine the amounts of chlorine and ammonia to add. Two examples follow showing different chemical strengths…

Chemical addition example # 1

- Goal: 5:1 weight ratio to produce monochloramines
- Target chloramine residual: 3.0 mg/L
- Requires dosing: 3.0 mg/L Cl_2 and 0.60 mg/L NH_3
- Daily production: 5 MG
- Weight of water: 8.34 lbs./gal
- Chlorine: 100% strength gas
- Ammonia: 100% strength gas
- **Add 125 lbs. of chlorine and 31 lbs. of ammonia to produce the target results.**

Chemical addition example # 2

- Goal: 5:1 weight ratio to produce monochloramines
- Target chloramine residual: 3.0 mg/L
- Requires dosing: 3.0 mg/L Cl_2 and 0.60 mg/L NH_3
- Daily production: 5 MG
- Weight of water: 8.34 lbs./gal
- Chlorine: 12% strength sodium hypochlorite
- Ammonia: 19% strength ammonium hydroxide
- **Add 992 lbs. of chlorine and 159 lbs. of ammonia to produce the target results.**

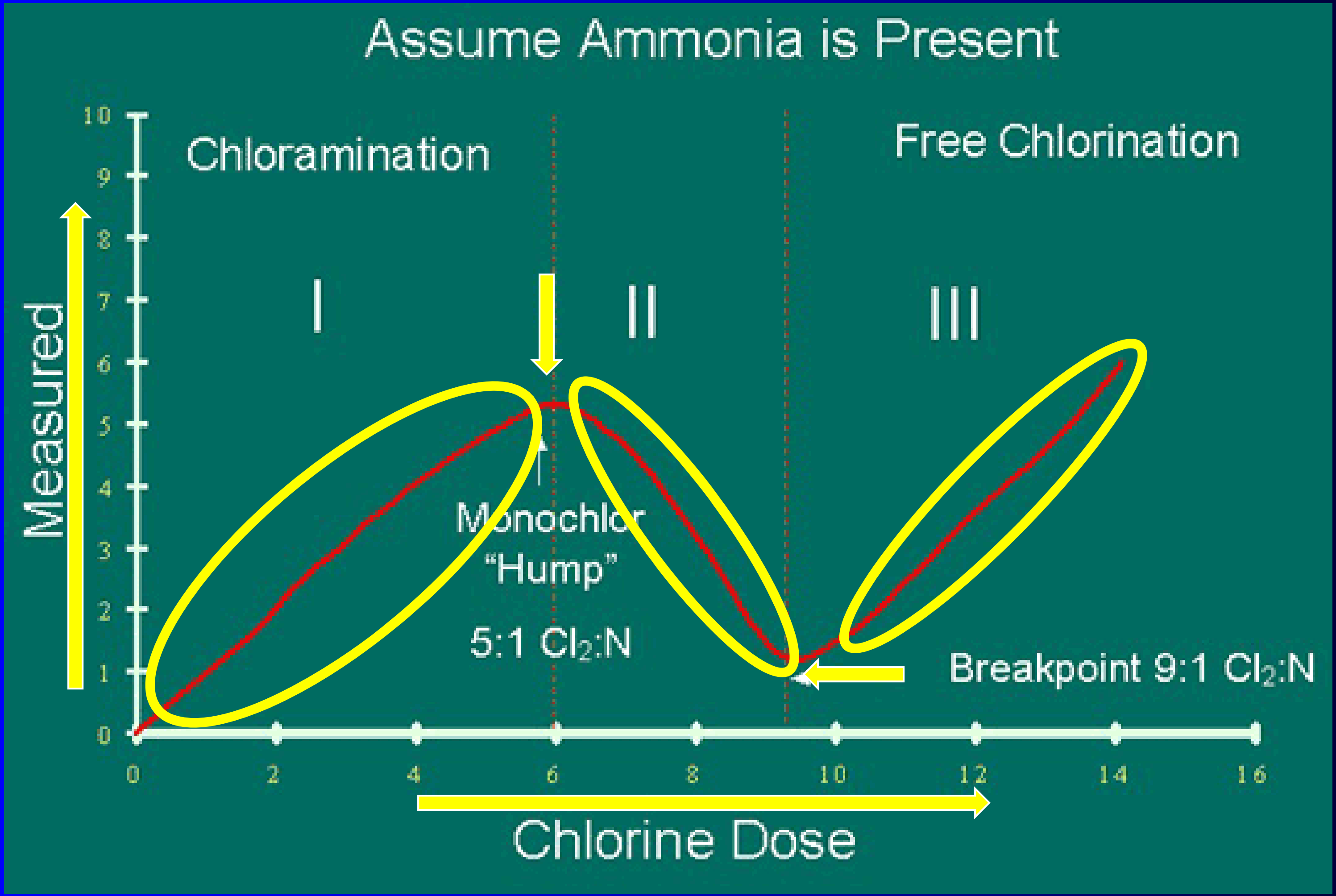
Determining the best ratio

- The 5:1 ratio was determined under controlled laboratory conditions using distilled water. As a guideline, it represents an idealistic situation and may not apply to every real world application.
- Water quality conditions, seasonal variations, and plant specific conditions may necessitate that adjustments to the 5:1 ratio be made periodically.
- In general, free ammonia leaving a treatment facility should be > 0.00 but less than 0.08 mg/L.

Importance of monitoring

- Careful monitoring of the chlorine to ammonia ratio ensures that chlorine is not underfed or overfed during the formation of monochloramines.
- An underfeeding of chlorine will result in an excess of free ammonia leaving the facility (> 0.08 mg/L).
- An overfeeding of chlorine will create the potential for di- and trichloramine formation. Consistent free ammonia concentrations of 0.00 mg/L leaving the facility would signify an overfeeding of chlorine.

Breakpoint phenomena



Awareness of nitrification

- A brief overview of the science of nitrification will follow along with some of the ways to reduce the impact of nitrification within a distribution system.

Nitrification process

- Nitrification is a bio-chemical process carried out by nitrifying bacteria under certain condititions.
- Such bacteria, commonly referred to as nitrifiers, may be found on the inside of water pipes where they are most often protected by biofilms.
- Treated water may contain an excess of free ammonia, and as water age and temperature increase, chloramine decay releases free ammonia.

Conditions for nitrification

- The main factors contributing to nitrification include:
  - excess ammonia in the distribution system
  - warm water temperatures (i.e. 15^{0}C and higher)
  - long detention times (i.e. excessive water age)
  - presence of nitrifiers
  - low disinfectant residuals to combat nitrifiers

Nitrification process

- Free ammonia fuels the nitrification process.
- Nitrosomonas bacteria oxidize the ammonia and produce nitrite, NO_2.
- While this process eliminates the actual ammonia, it supplies the nitrite necessary for the next step.
- Nitrobacter bacteria convert nitrite into nitrate, NO_3.

Free Ammonia NH_3 → Nitrite NO_2 → Nitrate NO_3

Health concerns

- Health concerns associated with excess levels of nitrite and/or nitrate relate to the capacity of blood to carry oxygen.
- Short-term exposure to drinking water with nitrite and/or nitrate levels above the health standard is a potential problem especially for babies.
- Drinking water standards for nitrite and nitrate have been established at 1 mg/L and 10 mg/L respectively.

Other impacts of nitrification

- Chloramine residuals will be depleted at a rate of 5:1 compared to nitrite.
- For example, a 0.40 mg/L nitrite concentration will consume 2.0 mg/L of the chloramine residual.
- The depletion of chloramine residuals could leave a system vulnerable to bacteriological contamination.
- A reduction in pH and alkalinity often accompanies nitrification. An increase in the potential for corrosion of lead and copper could follow.

Nitrification control measures

- Maintain an adequate disinfection residual especially during the warmer months.
- Limit free ammonia entering the distribution system.
- Flush the system periodically to reduce water age at dead-ends and areas of low circulation.
- Establish booster stations and apply additional treatment at storage facilities and/or at pumping stations to re-establish monochloramines.

References

- Connell, G. F., 1996. *The Chlorination/ Chloramination Handbook*. American Water Works Association. Water Disinfection Series.

- *Fundamentals and Control of Nitrification in Chloraminated Drinking Water Systems*. 2006. American Water Works Association. Manual of Water Supply Practices, M56. 1st ed.

Questions

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