

USING THE CORRECT ARITHMETIC TO FORM MONOCHLORAMINE

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Revision 1: February 2023 (added feed sequence for “boosting” monochloramine)

The basis for the chlorine:ammonia ratio is:

*“Measurable free available chlorine should not be present in solution at chlorine to ammonia **molar ratios** less than 1:1. On a weight basis, this ratio is approximately 5.06 mg Cl₂ to 1 mg NH₃-N (expressed as Nitrogen equivalent), and this unit convention is typically used in water treatment practices (Snoeyink and Jenkins 1980).” (Harrington et al. 2003)*

To achieve the 5.06 mg Cl₂ to 1 mg NH₃-N ratio, the stoichiometric characteristics of the ammonia or ammonium-source-chemical must be taken into consideration when expressing them in terms equivalent to N (Nitrogen).

Various references suggest use of a Chlorine:Ammonia-N ratio between 3:1 to 5.1:1. In this document, the stoichiometric Chlorine:Ammonia-N ratio of 5.06:1 is used, based on the calculations that are shown below. Using precise ratio calculations will help to form predominantly monochloramine residual and to minimize presence of undesirable free ammonia (or ammonium) in water leaving the treatment plant.

What can be done at the treatment plant to minimize potential for development of nitrification in the distribution system?

If "Ammonia" (i.e., anhydrous ammonia) is the "Ammonia-N" source chemical ...
 Require chlorine:ammonia (as NH₃) of (5.06 x 0.8224) = **4.1613:1**
 To achieve 5.06:1 chlorine:ammonia-N MOLAR ratio

Based on 1 mole Cl₂ to 1 mole NH₃ = 2(35.453) : 17.0307 = 4.163 GMW Cl to 1 GMW NH₃

Molecular weight of Chlorine, Cl₂: 2 x 35.453 = 70.906

molecular weight Ammonia-N:

$$\begin{array}{r} \text{N:} \quad 1 \times 14.007 = 14.007 \\ \text{3 H:} \quad 3 \times 1.0079 = \underline{3.0237} \\ \hline 17.0307 \end{array}$$

Then,

$$\frac{4.163 \text{ GMW Cl}}{1 \text{ GMW NH}_3} \left(\frac{17.0307 \text{ GMW NH}_3}{14.007 \text{ GMW NH}_3 \text{ expressed as N}} \right) = \frac{5.06 \text{ GMW Cl}}{1 \text{ GMW NH}_3\text{-N}}$$

GMW indicates Gram Molecular Weight

Note that the 5.06 mg Cl₂ to 1 mg NH₃-N ratio is based on expressing Ammonia in terms of Nitrogen equivalents. This is in agreement with Snoeyink and Jenkins (1980, cited at Harrington et al. (2003).

Desire Chlorine:Ammonia-N ratio to be 5.06:1 to minimize "free ammonia" in treated water:

We must express NH₃ in terms of NH₃-N (as Nitrogen):

molecular weight Ammonia-N:

$$\begin{array}{r} \text{N:} \quad 1 \times 14.007 = 14.007 \\ \text{3 H:} \quad 3 \times 1.0079 = \underline{3.0237} \\ \hline 17.0307 \end{array}$$

Molecular weight Nitrogen (N): 14.007

$$\frac{14.007 \text{ mg N/L}}{17.0307 \text{ mg NH}_3\text{/L}} = \frac{0.8224 \text{ mg N/L}}{1 \text{ mg NH}_3\text{/L}}$$

Expressed as N: multiply 1 mg NH₃/L x 0.8224 = 0.8224 mg N/L

Then the chlorine to ammonia ratio (expressed as NH₃ (as Ammonia) becomes:

$$5.06 \times 0.8224 = \mathbf{4.1613} \text{ Chlorine to Ammonia (as NH}_3\text{)}$$

Therefore, when using Ammonia (NH₃) as the source chemical, the Chlorine to Ammonia (as NH₃) ratio should be 4.16 to 1 to form a predominantly monochloramine residual and minimize free ammonia in the water leaving the treatment plant.

If ammonium sulfate or ammonium hydroxide is the “Ammonia-N” source chemical ...
 Require chlorine:ammonium (as NH₄) MOLAR ratio of (5.06 x 0.7765) = **3.93**:1
 To achieve 5.06:1 chlorine:ammonia-N ratio

Based on 1 mole Cl₂ : 1 mole NH₄ = 2(35.453) : 18.0386 = 3.931 GMW Cl : 1 GMW NH₄

Then,

Molecular weight of Chlorine, Cl₂: 2 x 35.453 = 70.906

molecular weight Ammonium:

$$\begin{array}{l} \text{N:} \quad 1 \times 14.007 = 14.007 \\ \text{4 H:} \quad 4 \times 1.0079 = \underline{4.0426} \\ \hline 18.0386 \end{array}$$

molecular weight Ammonia-N:

$$\begin{array}{l} \text{N:} \quad 1 \times 14.007 = 14.007 \\ \text{3 H:} \quad 3 \times 1.0079 = \underline{3.0237} \\ \hline 17.0307 \end{array}$$

$$\frac{3.931 \text{ GMW Cl}}{1 \text{ GMW NH}_4} \left(\frac{18.0386 \text{ GMW NH}_4}{(14.007 \text{ GMW NH}_3 \text{ expressed as N})} \right) = \frac{(5.06 \text{ GMW Cl})}{1 \text{ GMW NH}_3\text{-N}}$$

GMW indicates Gram Molecular Weight

Note that the 5.06 mg Cl₂ to 1 mg NH₃-N ratio is based on expressing Ammonia in terms of Nitrogen equivalents. This is in agreement with Snoeyink and Jenkins (1980, cited at Harrington et al. (2003).

Desire Chlorine:Ammonia-N ratio to be 5.06:1 to minimize “free ammonia” in treated water:

We must express NH₄ (Ammonium) in terms of NH₃-N (as Nitrogen):

molecular weight Ammonium:

$$\begin{array}{l} \text{N:} \quad 1 \times 14.007 = 14.007 \\ \text{4 H:} \quad 4 \times 1.0079 = \underline{4.0316} \\ \hline 18.0386 \end{array}$$

Molecular weight Nitrogen (N): 14.007

$$\frac{14.007 \text{ mg N/L}}{18.0386 \text{ mg NH}_4\text{/L}} = \frac{0.7765 \text{ mg N/L}}{1 \text{ mg NH}_3\text{/L}}$$

Expressed as N: multiply 1 mg NH₄/L x 0.7765 = 0.7765 mg N/L

Then the chlorine to ammonia ratio (expressed as NH₃(as Ammonia) becomes:

5.06 x 0.7765 = **3.93** Chlorine to Ammonium (as NH₄)

Therefore, when using Ammonium (NH₄) as the source chemical, the Chlorine to Ammonia (as NH₃) ratio should be 3.93 to 1 to form a predominantly monochloramine residual and minimize free ammonia in the water leaving the treatment plant.

Remember ... the chlorine:ammonia ratio is based on **mg/L available free chlorine residual** that is present to react with the ammonia to form monochloramine ... *not the chlorine "dosage"*.

Remember to check NH₃-N concentration in the raw water and account for it when determining ammonia feed dosage.

WHEN FORMING MONOCHLORAMINE: "START RIGHT, STAY RIGHT"

(From TCEQ-1)

- ✓ Add chlorine first. (a)
- ✓ Before adding ammonia, the free chlorine residual should equal the target monochloramine residual leaving the treatment plant. *(If ammonia is added first before the requisite chlorine residual dosage is added, undesirable dichloramine formation will occur. Once dichloramine is formed, it cannot be reverted back to monochloramine.)*
- ✓ After adding ammonia, expect to detect trace amount of free Ammonia ... must keep it low ... say not more than 0.1 mg/L as N and preferably not more than 0.05 mg/L as N.
- ✓ The total chlorine residual should equal the monochloramine residual.
 - (a) When forming monochloramine at the water treatment plant, add chlorine first.
When "boosting" the monochloramine residual out in the system, add ammonia first. By adding ammonia first, there is less chance that the chlorine being added will react with (destroy) the monochloramine that is already in the water. (TCEQ-2)

WHEN FORMING MONOCHLORAMINE: WHAT TO CHANGE

(From TCEQ-1)

- ✓ MONO TOO HIGH: reduce ammonia and reduce chlorine feed (both)
- ✓ TOTAL CHLORINE DROPS AFTER AMMONIA ADDED: Increase ammonia, or reduce chlorine feed (possibly both)
- ✓
- ✓ AMMONIA TOO HIGH: reduce ammonia, or increase chlorine (possibly both, 1 at a time)
- ✓ TOTAL CHLORINE HIGHER THAN MONO: reduce chlorine feed

References

Harrington et al., 2003

Ammonia from Chloramine Decay: Effects on Distribution System Nitrification; Gregory W. Harrington, Daniel R. Noguera, Christopher C. Bone, Alicia I. Kandou, Patrick S. Oldenburg, John M. Regan, and David Van Hoven – Dept. of Civil and Environmental Engineering, University of Wisconsin-Madison; published by AWWA Research Foundation and American Water Works Association. 2003.

Snoeyink et al., 1980

Snoeyink, V.L. and D. Jenkins, 1980. Water Chemistry.

TCEQ-1, 2015

Texas Commission on Environmental Quality; Chloramines 101; October 2015.

TECQ-2

Texas Commission on Environmental Quality; Chloramines, Training Module 5.