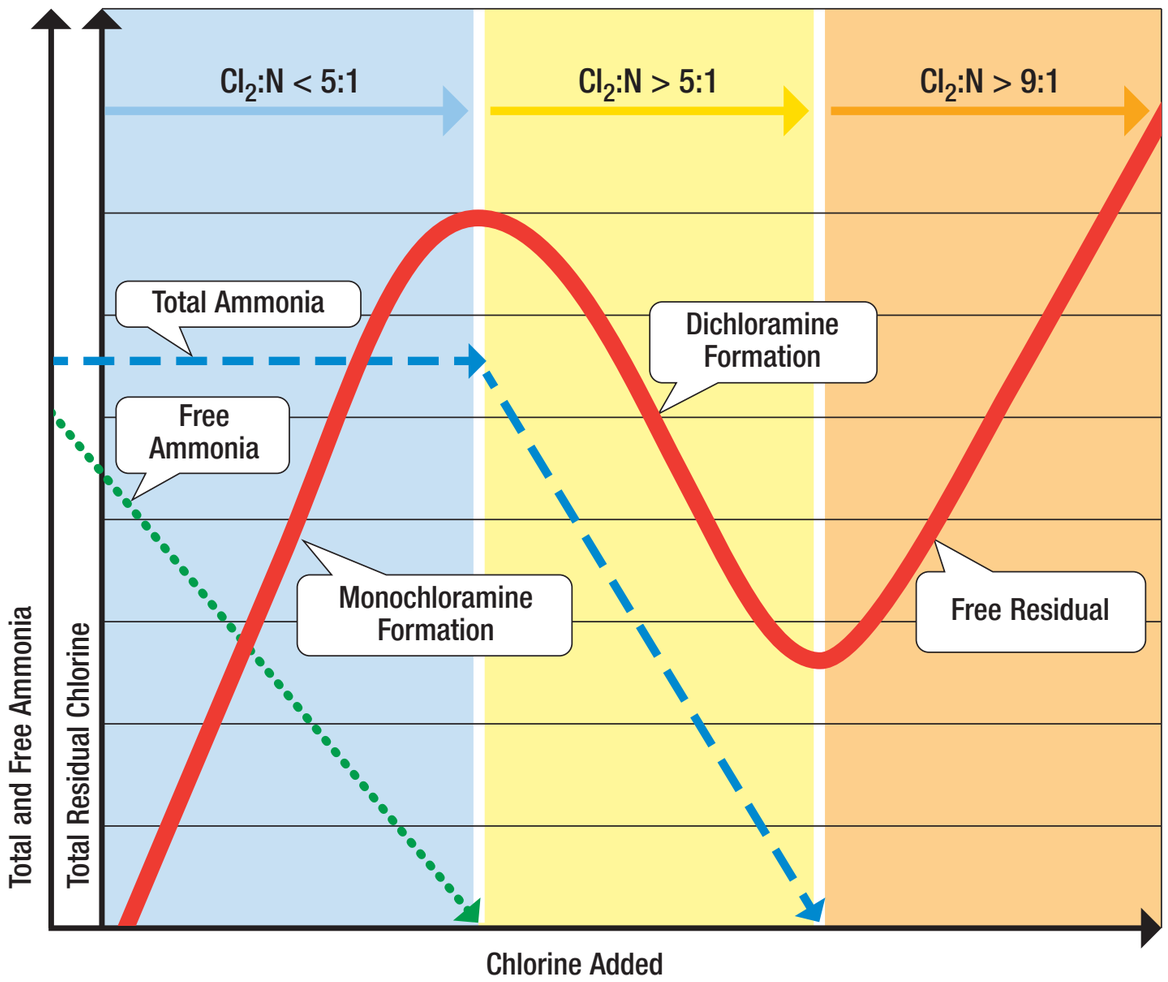
Chlorination in Drinking Water

CHLORINE BREAKPOINT CURVE



Monochloramine, Free Chlorine, Cl_2:N < 5:1 (Monochloramine predominates, Free Ammonia > 0)

- Minimises formation of chlorinated organics, specifically TTHM*.
- Less effective disinfection than free chlorine.
- Requires longer contact time and/or greater concentration than free chlorine.
- More stable than free chlorine (long distribution systems).
- Generally does not produce DBPs** (this issue is still being studied).
- Must reduce free ammonia to reduce risk of nitrification issues.

Dichloramine & Trichloramine, Cl_2:N > 5:1 (Free Ammonia = 0)

- Likely taste and odour issues.

Free Chlorine, Cl_2:N > 9:1 (Total Ammonia = 0)

- Most effective disinfection, least taste and odour occurs with free residual chlorine.
- Free chlorine may lead to formation of DBP**.

NOTE: Shape of the curve is dependent upon amount of ammonia and other chlorine demand substances in the water, temperature, pH, and contact time.

* TTHM = total trihalomethanes ** DBP = disinfection byproducts

Key Reactions

1. When chlorine is combined with water, forms hypochlorous (HOCl) and hydrochloric (HCl) acids:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

2. Reaction is reversible. Above pH 4, reaction is to the right.

3. HOCl dissociates to the hydrogen ion*** and hypochlorite ion (OCl^-) varying with temperature and pH:

$$HOCl \rightleftharpoons H^+ + OCl^-$$

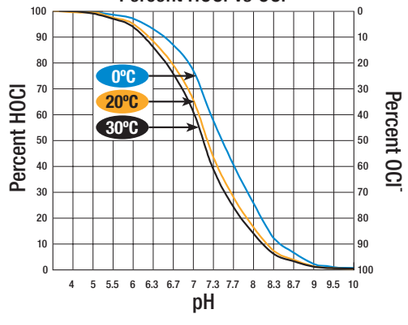
(See Table and Graph to the right.)

4. Chlorine (HOCl and OCl^-) reacts with ammonia to form chloramines, commonly referred to as “combined chlorine.”

5. The predominate species are monochloramine and dichloramine. A small fraction is trichloramine or nitrogen trichloride.

*** Hydronium ion, H_3O^+

Effect of pH on Chlorine Species



Proportions of HOCl and OCl^- at varying temperature and pH levels

pH	HOCl	OCl	HOCl	OCl	HOCl	OCl
	0 °C	0 °C	20 °C	20 °C	30 °C	30 °C
4	100	0	100	0	100	0
5	99.85	0.15	99.4	0.6	99.68	0.32
6	98.53	1.47	97.45	2.55	96.92	3.08
7	87.04	12.96	79.29	20.71	75.9	24.1
8	40.18	59.82	27.69	72.31	23.95	76.05
9	6.29	93.71	3.69	96.31	3.05	96.95
10	0.67	99.33	0.38	99.62	0.31	99.69

Chloramine Species

- Monochloramine – NH_2Cl

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O$$

- Dichloramine – $NHCl_2$

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O$$

- Trichloramine (Nitrogen Trichloride) – NCl_3

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O$$

- Definition of unreacted (free) ammonia:

NH_3 Free ammonia gas dissolved in water

and/or

NH_4^+ The ammonium ion

Nitrification Process

Formation of Nitrate

Conversion of free ammonia to nitrite.

$$NH_3 + O_2 \rightleftharpoons NO_2^- + 3H^+ + 2e^-$$

Ammonia converts to Nitrite

Nitrosomonas, Nitrosococcus, and Nitrosospira

Conversion of nitrite to nitrate.

$$NO_2^- + H_2O \rightleftharpoons NO_3^- + 2H^+ + 2e^-$$

Nitrite converts to Nitrate

Nitrobacter, Nitrospina, Nitrococcus, and Nitrospira

Signs and Consequence of Nitrification

Early Indicators

Control strategies can be applied.

- ▲ Free Ammonia
- ▼ Monochloramine
- ▲ Nitrite (just detectable)
- ▲ ATP
- ▼ pH
- ▼ DO
- ▼ Alkalinity
- ▲ Temperature

Late Indicators

A significant problem exists and remedial action must be implemented – extensive flushing, cleaning of storage tanks, free chlorine “burnout.”

- ▲ Nitrite
- ▲ Nitrate
- ▲ Turbidity
- ▲ Bacterial count
- ▲ Customer observations

Effect of Temperature on Nitrification

0 °C	10 °C	25 °C	26 to 39 °C	40 to 50 °C
Nitrification Ceases	Nitrification Slows	Favorable for Nitrification	Most Favorable for Nitrification	Nitrification Slows and Ceases

Control Strategies

Areas of Control	Action
pH	▲
Free Ammonia	▼
Water Age (flushing, decrease storage level, etc.)	▼
Monochloramine Residual	▲
TOC	▼
Improve Tank Mixing	▲

Use this panel to identify the areas of correction for your distribution system or storage tank when you begin to experience the signs of nitrification. ▲ = Increase ▼ = Decrease

HACH®
Be Right™