

Understanding Chlorine Measurement

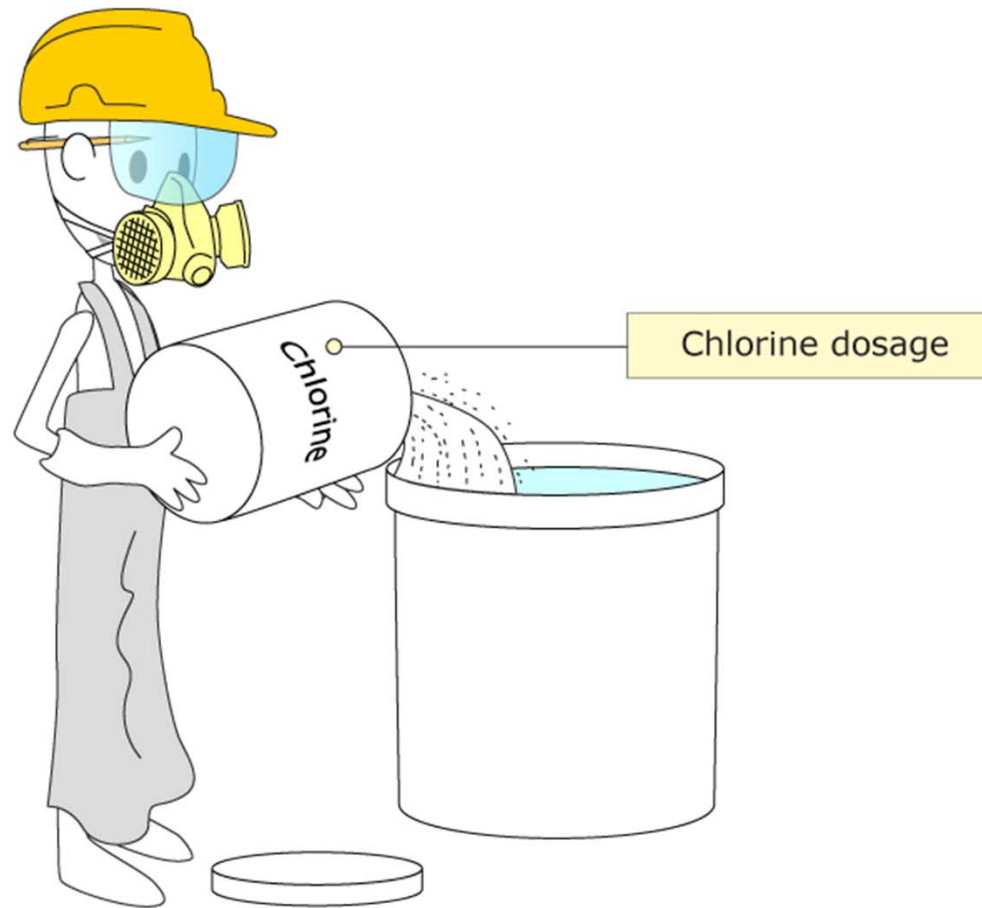


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Rebecca Luedee

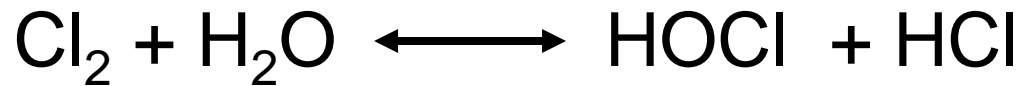
Environmental Sales

Introduction to Chlorine



Reaction with Water

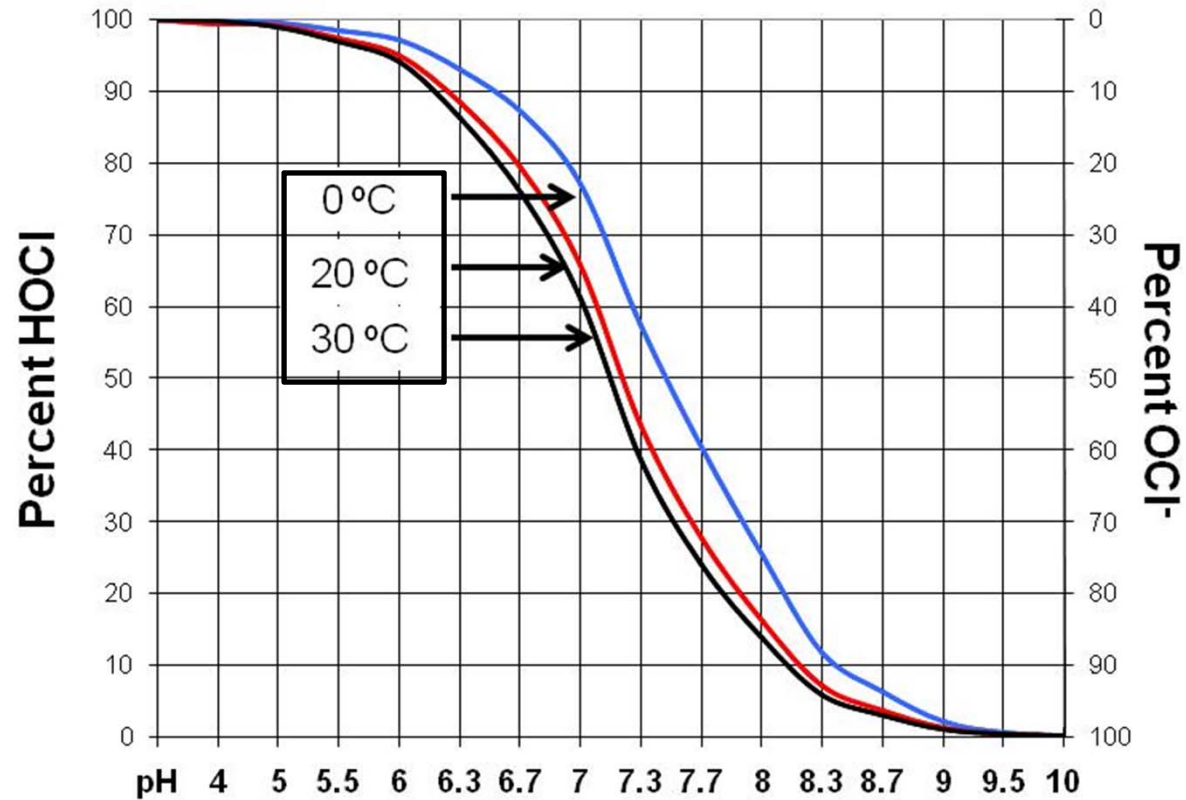
- Forms hydrochloric (HCl) and hypochlorous (HOCl) acids:



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



Percent HOCl vs OCl⁻



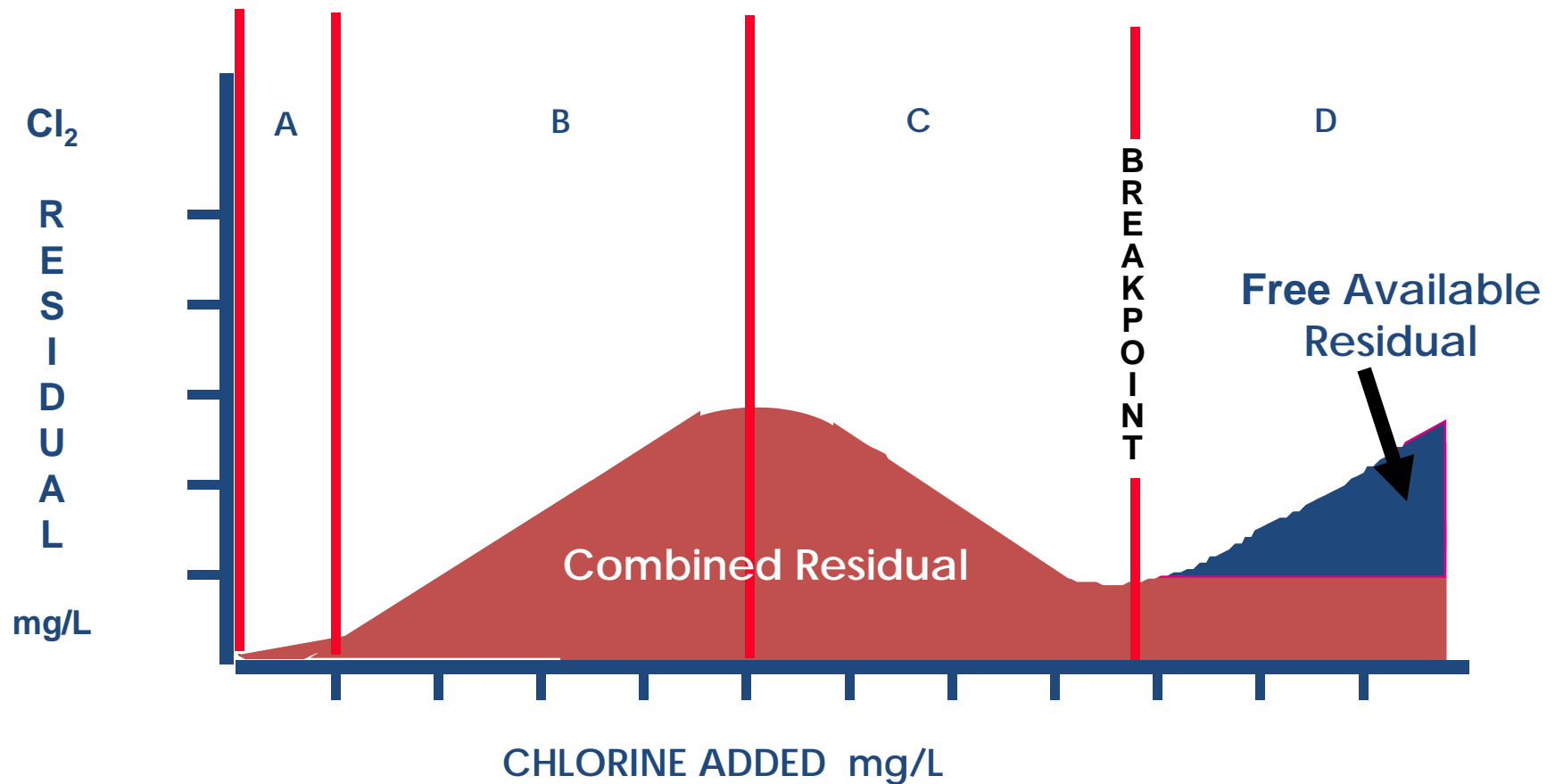
HOCl is a stronger disinfectant than OCl⁻

Total vs Free Chlorine

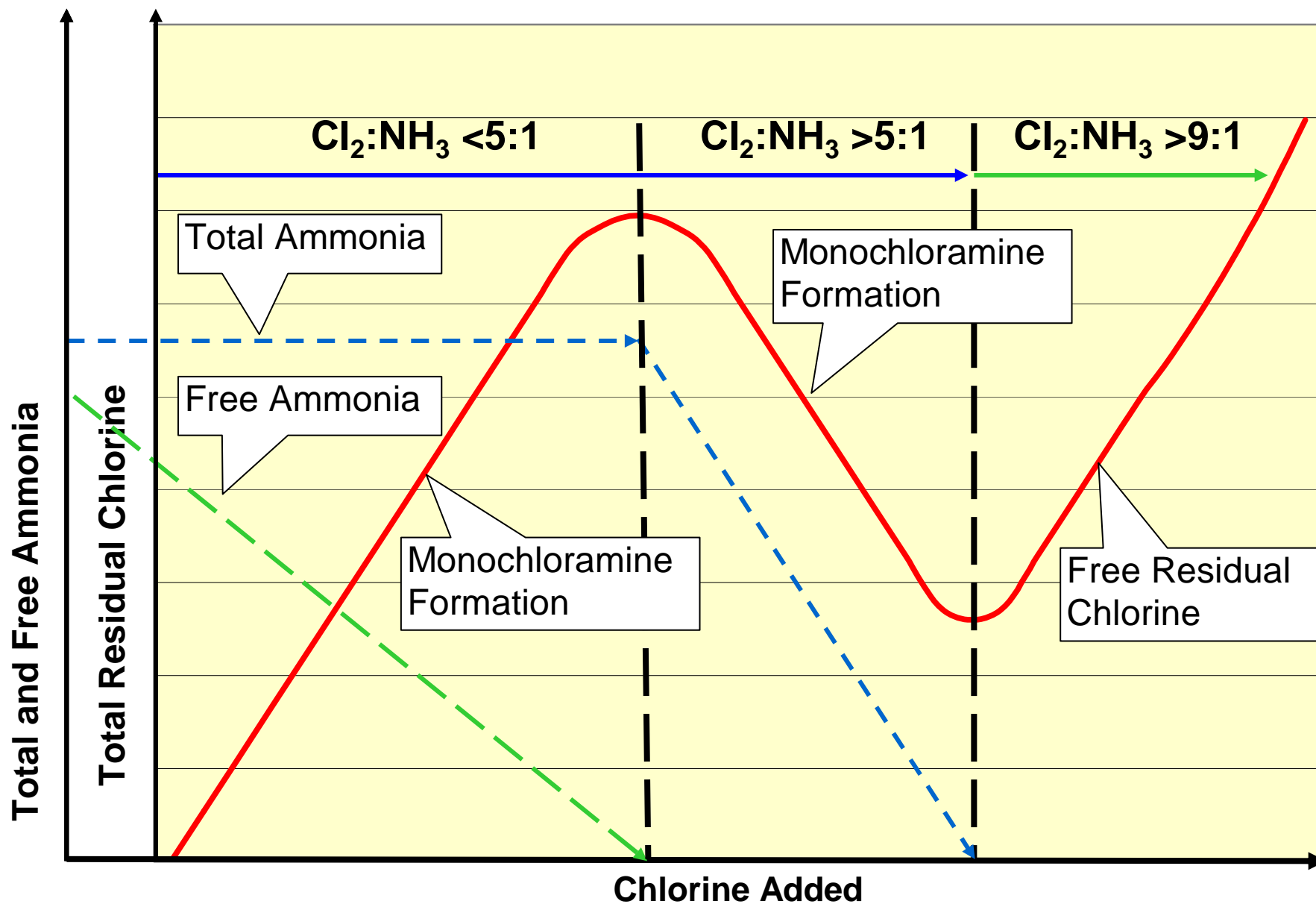
- Free Chlorine = $\text{HOCl} + \text{OCl}^-$
- Free Chlorine + Ammonia = Chloramines
(Combined Chlorine)
- Free Chlorine + Chloramines = Total Chlorine
- Free chlorine in drinking water is between 0.2 – 2.0 mg/L

Chloramines

- Less effective disinfection than free chlorine.
HOCl is 25X more effective biocide
- Chloramines require longer contact time and/or greater concentration than free chlorine.
- Possible taste and odor (dichloramine)
- More stable than free chlorine (long distribution systems)



- A. Chlorine destroyed by residual compounds
- B. Formation of chloramines and chloro-organics
- C. Chloro-organics and chloramines destroyed
- D. Free available residual formed. Some chloro-organics remain



How to Test?

Colorimetric Methods – Lab or Field Use



- Chlorine – DPD
- Chloramination – MonoChlor F
- **SL1000 Chem Key**

Handheld PCH Pocket Colorimeter

Free and Total Chlorine



- DPD method
- USEPA approved/accepted for drinking water
- Two Ranges:
 - LR - 0.02 to 2.00 mg/L
 - HR - 0.1 to 8.0 mg/L as Cl₂
- Reagents included:
(100 tests each, low range, or 50 tests each, high range)
- Unit now available to calibrate/check **amperometric** chlorine analyzers

Test Kits

	Comparators	Test Strips
Chlorine	X	X
Monochloramine	N/A	N/A

Avoid use of color comparators for regulatory reporting due to subjective errors



Measurement Hints

- Sampling
 - Analyze immediately after sample collection
 - Fresh representative sample, water to flow at least 3-5 min
 - Allow enough contact time
 - Rinse, Rinse and Rinse
 - Avoid plastic containers
 - If off site measurement, leave no headspace in sample bottle, chill at 4 °C and analyze as quick as possible

The analysis is only as good as the sample

Measurement Hints

- Testing
 - Dedicate different sample cells for Free and Total
 - Rinse, Rinse and Rinse
 - Both Free and Total test are similar, but reagent and reaction time are not
 - Free requires about 30 sec, read within a minute
 - Total requires about 3 min., read within 4-5 minutes
 - If sample turns yellow or colorless, dilute sample and multiply result by dilution factor.

Common Interferences

- Other oxidants: ClO_2 , O_3 , Br_2 , H_2O_2 , I_2 , KMnO_4
 - Disinfection by-products, I.e. chlorite and chlorate
 - Particulate contamination – turbidity
 - Organic N-Cl (organic chloramines in wastewater)
- Monochloramine on free chlorine DPD test
 - Buffer capacity (high alkalinity or acidity)
 - Sample color
 - Mn^{+3} to Mn^{+7} & Cr^{+7}

Why is my chlorine analysis not accurate?

- Free chlorine interference with manganese and/or monochloramine DPD test
- Free chlorine value will often read higher than total chlorine value
- Solutions:
 - Test with Hach method 10241 to define level of interference using PC2, DR900, etc.
 - Test for Total or Free Ammonia

Compensating for Manganese Interference

- Split sample. Analyze first portion as usual
- Subtract result of second portion from first portion

- Second Portion:
 - Adjust pH w/1N sulfuric acid
 - Add drops of 30 g/L potassium iodide; wait one minute
 - Add drops of 5 g/L sodium arsenite
 - Add DPD and complete test

Sample Size	5 ml	10 ml	25 ml
H₂SO₄, 1N	Adjust to pH 6-7	Adjust to pH 6-7	Adjust to pH 6-7
Potassium Iodide, 30 g/l	2 drops	2 drops	3 drops
Sodium Arsenite, 5 g/l	2 drops	2 drops	3 drops



Local resources

- Department of Environment and Conservation
- Local test kits provider

Hach help

- Atlantic Purification Systems Ltd.
- rebecca@aps.ns.ca; carly@aps.ns.ca
- Hach Technical Support Line: 800 665 7635