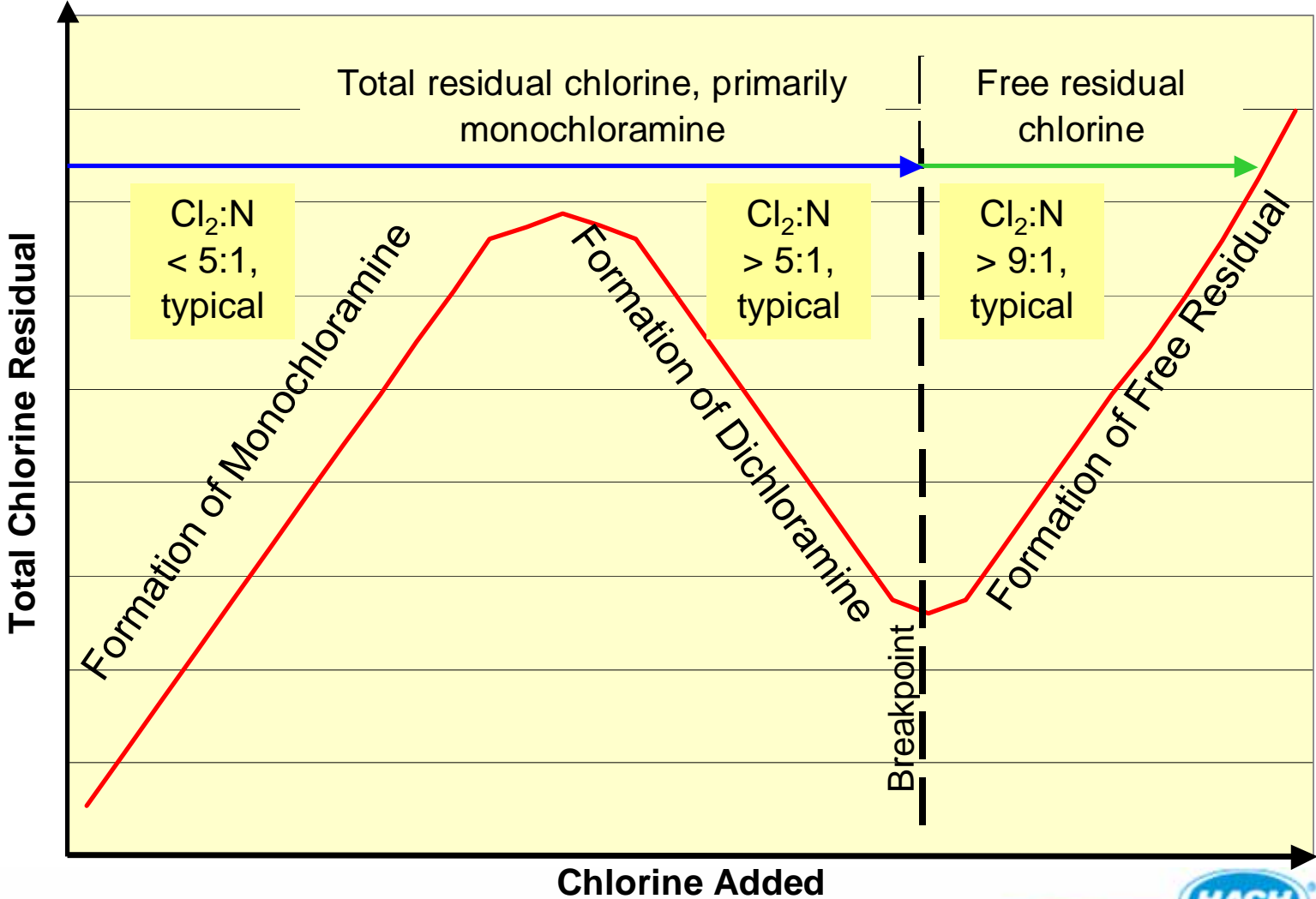


Understanding Chlorination and Chloramination Measurement

Marc-Philippe Camara
Regional Sales Manager

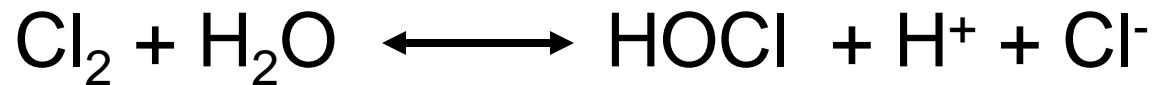


Takeaway

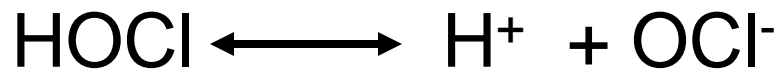


Reaction with Water

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

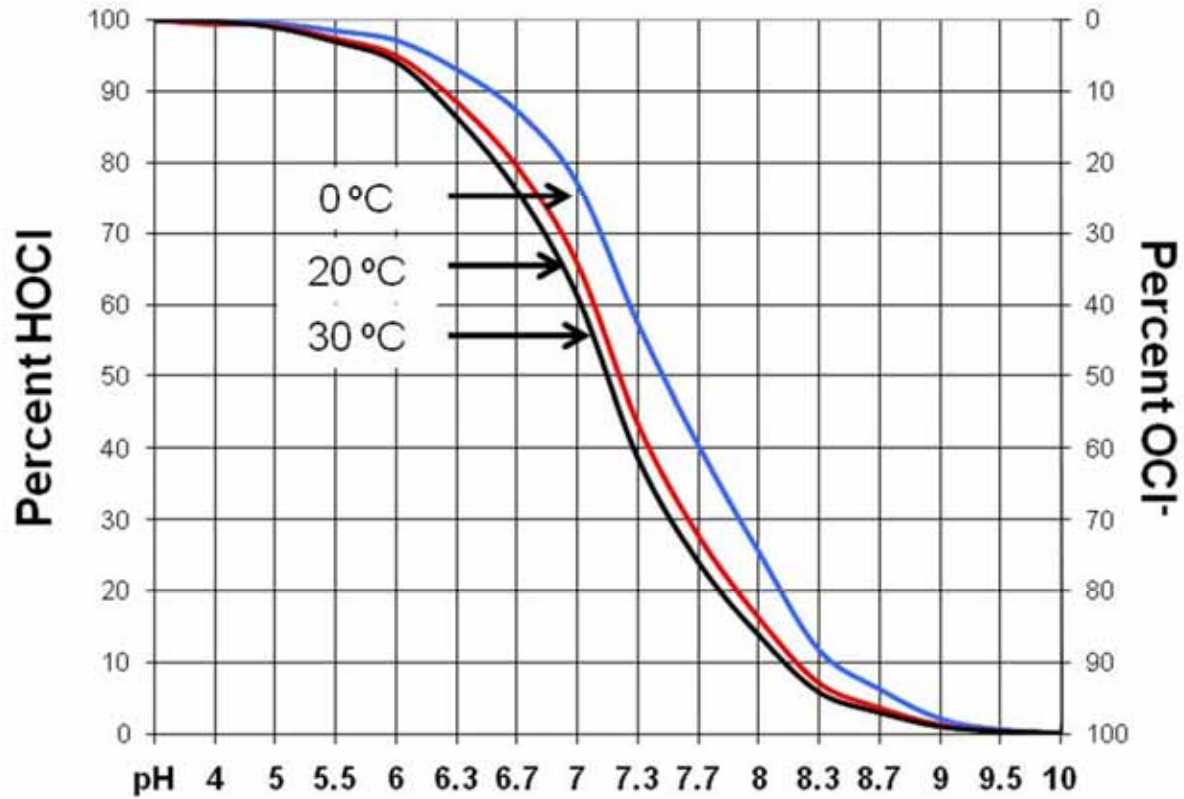


- Reaction is reversible. Above pH 4, reaction is to the right
- HOCl dissociates to the hydrogen ion and hypochlorite ion (OCl^-) varying with temperature and pH



HOCl vs. OCl⁻

Percent HOCl vs OCl⁻



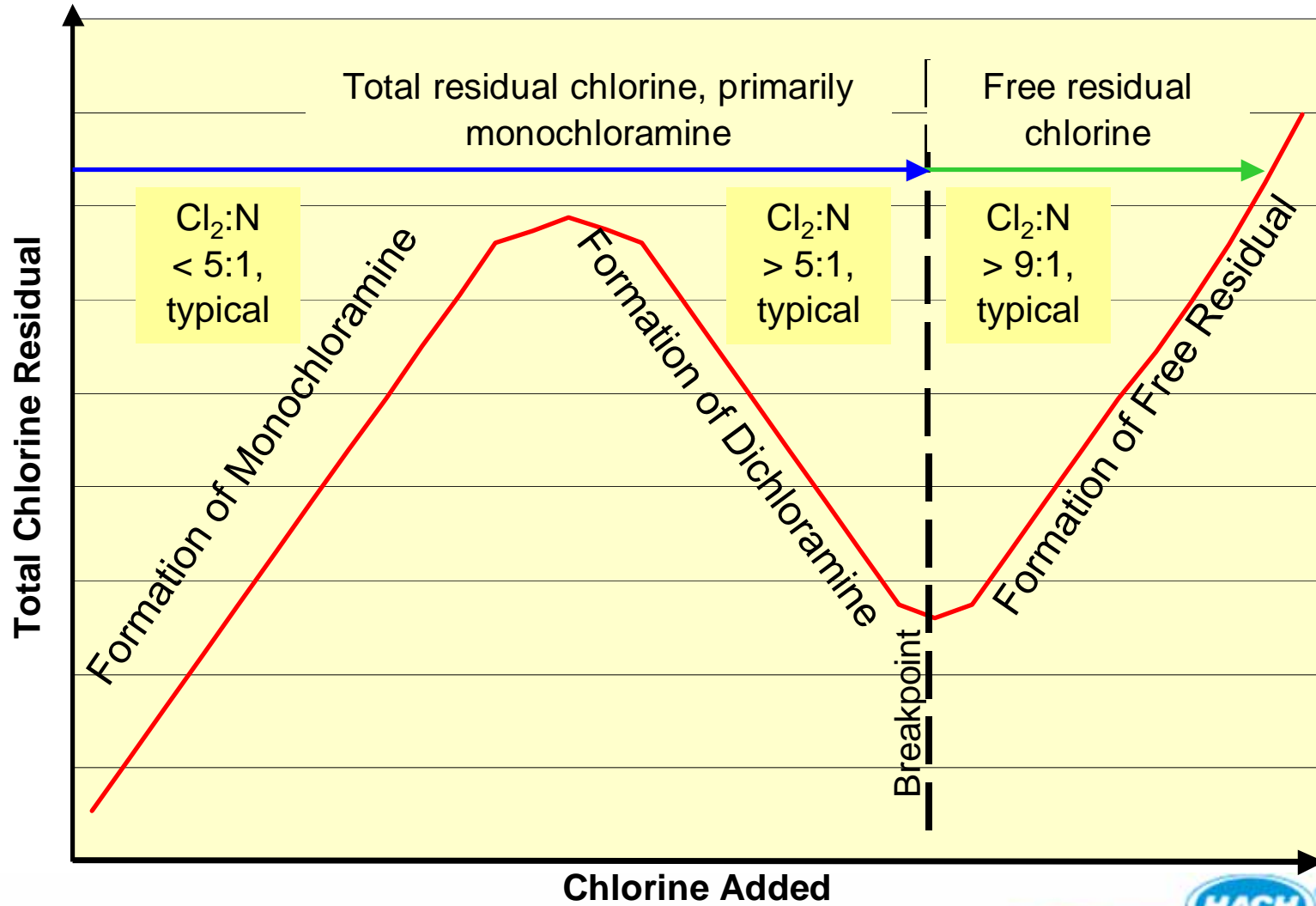
Free Available Chlorine

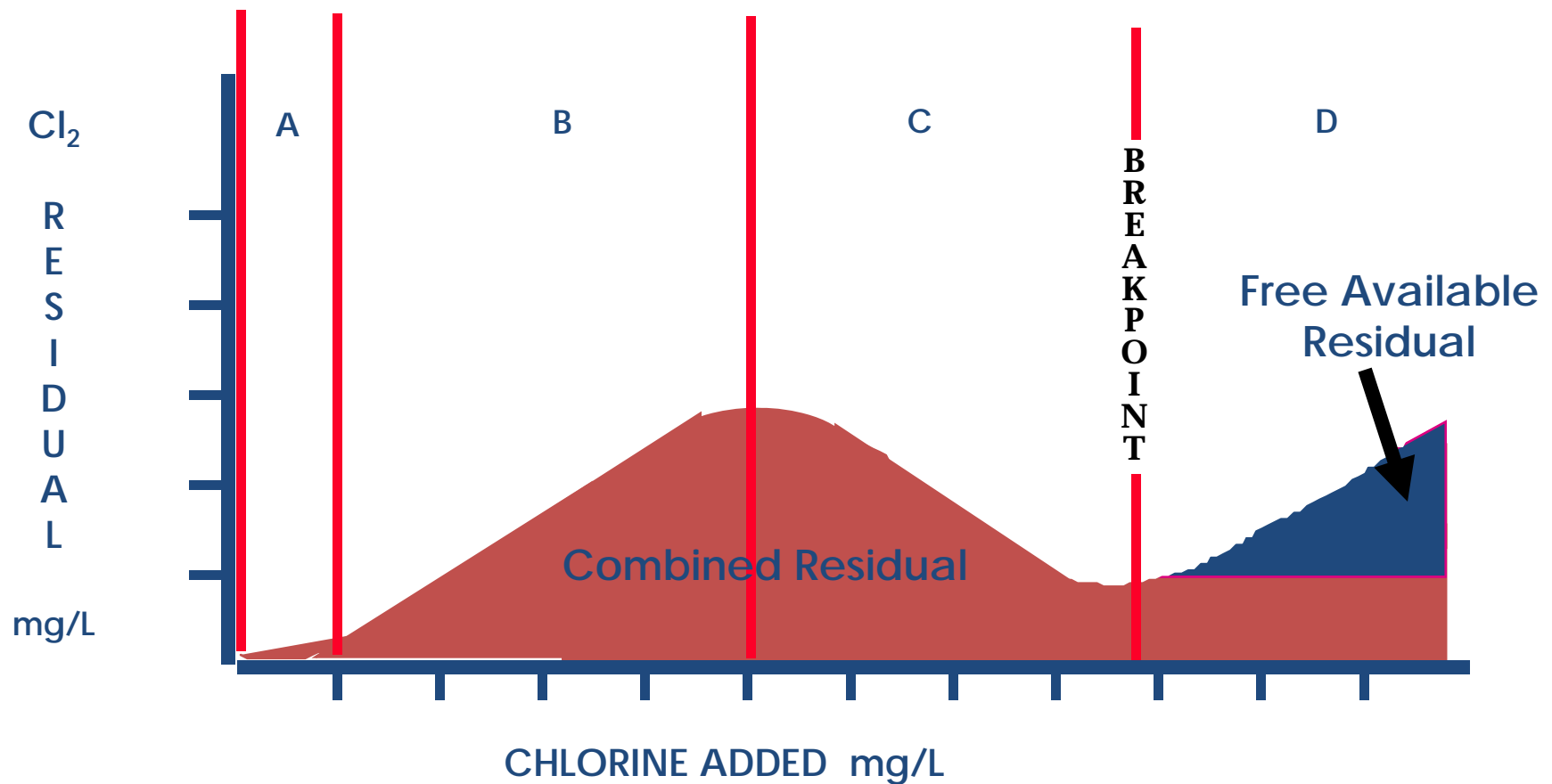
- Chlorine existing in water as hypochlorous acid (HOCl) or the hypochlorite ion (OCl⁻) is defined as free available chlorine

Combined Chlorine - Chloramination

- Chlorine (HOCl and OCl^-) reacts with ammonia to form chloramines, commonly referred to as 'combined chlorine'
- The predominate species are monochloramine and dichloramine. A small fraction is trichloramine or nitrogen trichloride
- Some Chloroorganics will also be part of your Combined Chlorine measurement

Breakpoint Curve





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

Breakpoint Curve Considerations

- Shape of the curve is dependent upon
 - amount of ammonia and other chlorine demand substances in the water
 - temperature
 - pH
 - contact time
- Most effective disinfection, least taste and odor occurs with free residual chlorine
- Free chlorine may lead to formation of DBP

Chloramination

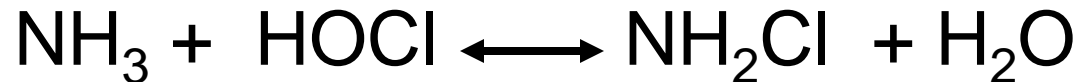
- Chloramination: Purposeful use of chlorine and ammonia to form monochloramine.
 - Minimizes formation of chlorinated organics
 - Ammonia to chlorine Ratio is controlled to favor formation of monochloramine, typically 5:1 $\text{Cl}_2:\text{N}$
- Total residual chlorine test: All free and combined chlorine species

Chloramines

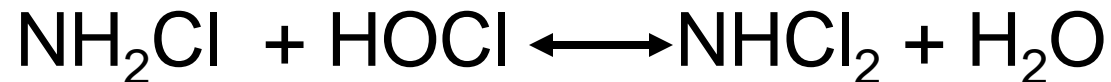
- Less effective disinfection than free chlorine. HOCl is 25X more effective biocide
- Chloramines require longer contact time and/or greater concentration than free chlorine.
- Possible taste and odor (dichloramine)
- More stable than free chlorine (long distribution systems)
- Generally do not produce DBP (NH₂Cl may form DBP, but are not as hazardous)

Chloramine Formation

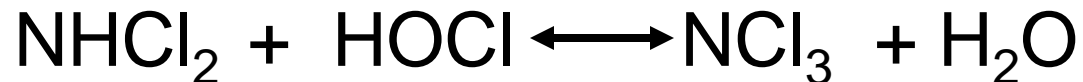
- Monochloramine - NH_2Cl



- Dichloramine - NHCl_2



- Trichloramine (Nitrogen Trichloride) - NCl_3

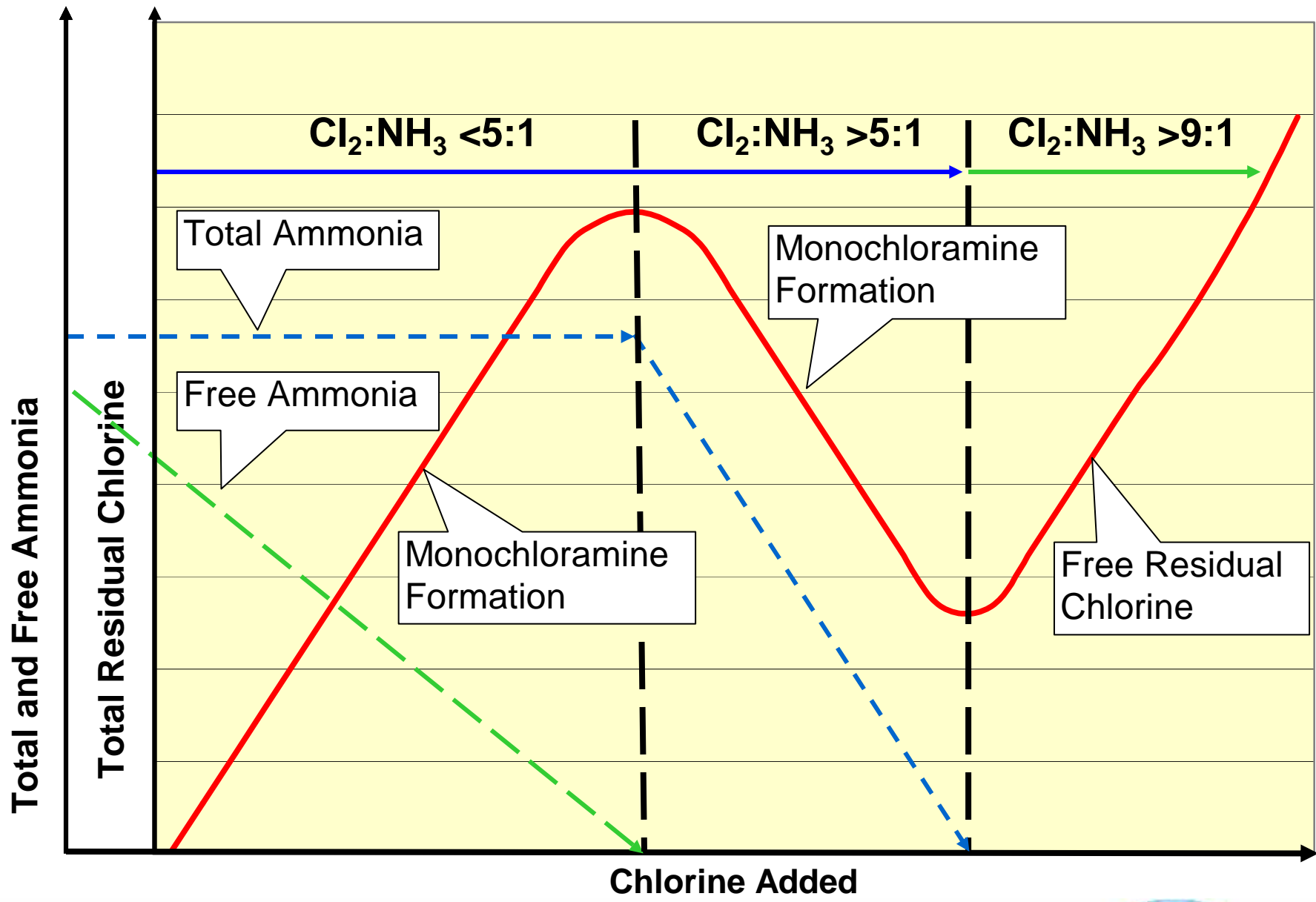


- Chloramines are not as effective disinfectants as free chlorine

Definition of Unreacted Ammonia

- Ammonia in solution as
 - NH_3 Free ammonia gas dissolved in water or;
 - NH_4^+ The ammonium ion

Ratio depends on pH



Myths, Misunderstandings and Oddities

- ❖ Total Residual Chlorine – Free Residual Chlorine = Chloramines
- ❖ If free residual chlorine is “X”% of total, you’re beyond breakpoint
- ❖ Total residual chlorine > Free Residual Chlorine

How to Test?

Colorimetric Methods – Lab or Field Use



- Chlorine – DPD
- Chloramination – MonoChlor F

Test Kits



	Compara-tors	Test Strips
Chlorine	X	X
MonoChloramine	NA	NA



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

Handheld PC2 Pocket Colorimeter – Free and Total Chlorine



- DPD method
- Code 587000
- 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 analysers

Measurement Hints

- Sampling
 - Analyze immediately after sample collection
 - Fresh representative sample, water to flow at least 3-5 min.
 - Allow enough contact time between chlorine feed and sample, sample further down and at the end of distribution line
 - 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
 - Note if you see a change 1 min after the test
 - 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
- Monochloramine on free chlorine DPD test
- Buffer capacity (high alkalinity or acidity)
- Sample color
- Mn^{+3} to Mn^{+7}
- Cr^{+7}
- Organic N-Cl (organic chloramines in wastewater)

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:
 - 30 sec reaction time on DPD free chlorine test
 - Test with Hach method 10241 to define level of interference using PC2, DR900, etc.
 - Test for Total or Free Ammonia

Test for Free Chlorine in chloraminated water

- Overcomes interference for Free Chlorine by chloramines
- Used for breakpoint chlorination, chloramination and distribution system monitoring
- Test not approved for reporting, but useful for troubleshooting.
- Can be used in Spectros or PC2 Pocket Colorimeters
- Range:
 - 0.04 – 5 mg/L Free Chlorine as Cl₂
- Hach Lab Method 10241, Requires:
 - Freechlor F Reagent Solution, 50 ml SCDB (code 2964926)
 - Monochlor F Reagent Pillows, 100/pkg (code 2802229)

Compensating for Manganese Interference

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

Sample Size	5 ml	10 ml	25 ml
H ₂ SO ₄ , 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

Question ?

- Need more help?
 - Local resources:
 - Department of Environment and Conservation
 - Local test kits provider
 - Hach help
 - Local Hach Distributor
 - techhelp@hach.com
 - Hach Technical Support Line: 800 665 7635

