The Secrets of Breakpoint Chlorination

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Disinfection vs. Chlorine Demand

Free Available Chlorine (FAC) is the major (disinfection agent)

"Demands" on chlorine

Instantaneous

If the water contains iron (Fe^{+2}) and manganese (Mn^{+2}), insoluble oxides are formed on introduction of chlorine

Longer Term

Organic matter- chlorine is consumed during the oxidation process

Intermediate

Reaction of chlorine with ammonia to form chloramines. This "combined chlorine" offers limited disinfection

BOTTOM LINE

Disinfection cannot proceed until the oxidant demand has been destroyed.

Chlorination

Chlorine gas rapidly hydrolyzes to hypochlorous acid according to:

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

Aqueous solutions of sodium or calcium hypochlorite hydrolyze too:

$$Ca(OCl)_2 + 2H_2O \rightarrow Ca^{2+} + 2HOCl + 2OH^-$$

$$NaOCl + H_2O \rightarrow Na^+ + HOCl + OH^-$$

Hypochlorous acid is a weak acid and will disassociate according to:

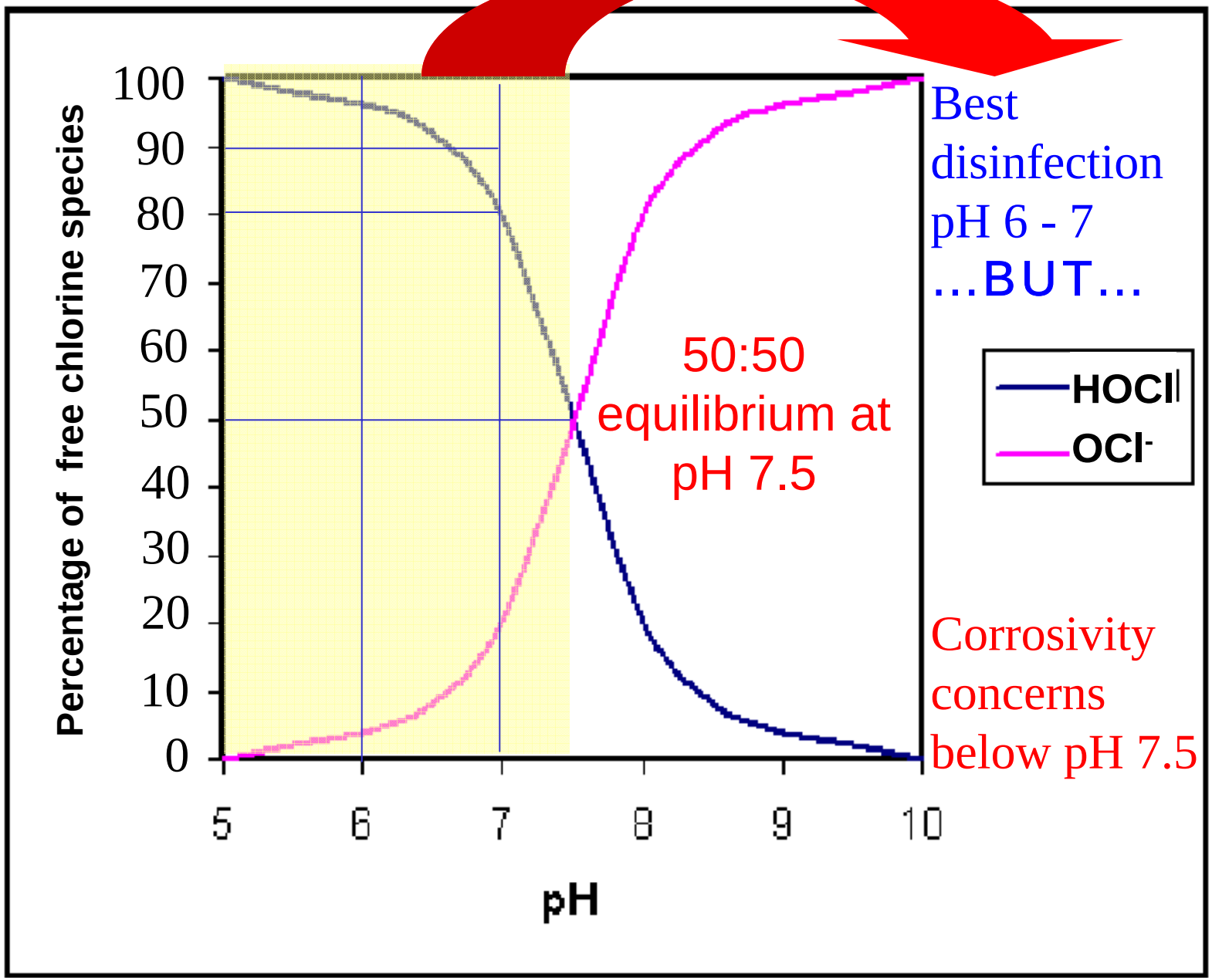
$$HOCl \Leftrightarrow H^+ + OCl -$$

The two chemical species formed by chlorine in water, hypochlorous acid (HOCl) and hypochlorite ion (OCl –), are commonly referred to as **"free" or "available"** chlorine.

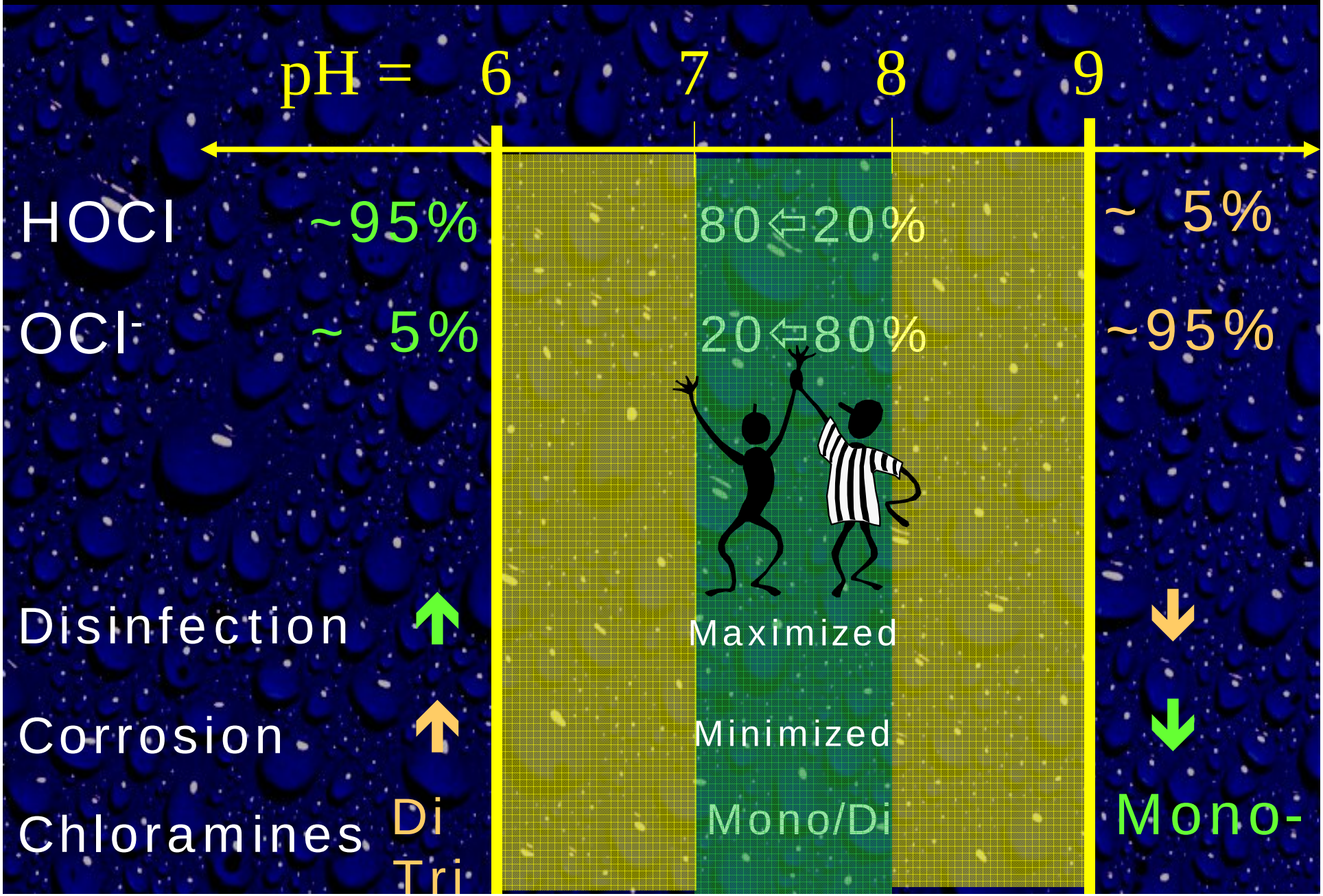
In waters with pH between 6.5-8.5, the reaction is incomplete and both species (HOCl and OCl –) will be present.

Hypochlorous acid is the more germicidal of the two.

Free Chlorine Distribution with pH



Effect of pH on disinfection



Combined Chlorine

What is it?

- Free chlorine that has combined with ammonia (NH_3)or other nitrogen-containing organic substances.
- Typically, chloramines are formed .

Where does NH_3, etc come from?

- Present in some source waters (e.g., surface water).
- Contamination; oxidation of organic matter
- Some systems (about 25% of U.S. water supplies) actually ADD ammonia.

Combined Chlorine

Why would you want to ADD ammonia?

- Chloramines still retain disinfect capability (~5% of FAC)
- Chloramines not powerful enough to form THMs.
- Last a lot longer in the mains than free chlorine,

Free chlorine + Combined chlorine = Total Chlorine Residual

Can measure "Total" Chlorine
Can measure "Free" Chlorine
Combined Chlorine can be determined by subtraction

Chloramine Formation

a) At pHs < 8, significant levels of HOCl are present

b) If NH_3 is present, HOCl will react to form one of 3 chloramines depending on pH, temperature, & reaction time.

Monochloramine: (stinky)

$2NH_3 + 2HOCl \rightarrow 2NH_2Cl + 2H_2O$ *pH 4.5 to 8*

Dichloramine: (stinkier)

$2NH_2Cl + 2HOCl \rightarrow 2NHCl_2 + 2H_2O$ *pH 4.5 to 8*

Trichloramine: (stinkiest!)

$NHCl_2 + 3HOCl \rightarrow NCl_3 + 3H_2O$ *pH < 4.5*

c) additional free chlorine + chloramine = H^+, H2O , and N_2 gas which will come out of solution.

Chloramines: effective vs. bacteria but NOT viruses.

How fast is chloramine formation?

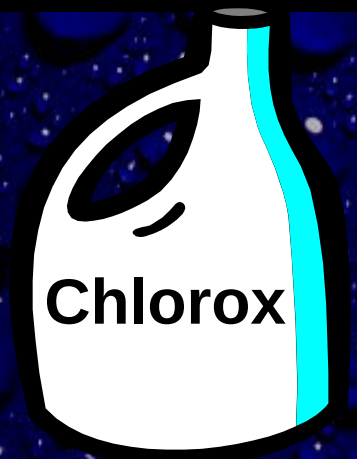
All of the free chlorine will be converted to monochloramine at pH 7 to 8 when the ratio of chlorine to ammonia is equimolar (**5:1 by weight**) or less. The rate of this reaction is extremely important, since it is pH-sensitive.

The following are calculated reaction rates for 99% conversion of free chlorine to monochloramine at 25°C with a molar ratio of 0.2 x 10-3 mol/l HOCl and 1.0 x 10-3 mol/l NH_3:

pH	2	4	7	8.3
Seconds	421	147	0.2	0.009

The reaction slows appreciably as the temperature drops. At 0°C, it takes nearly 5 minutes for 90% conversion at pH 7.

Ooooh…that smell!

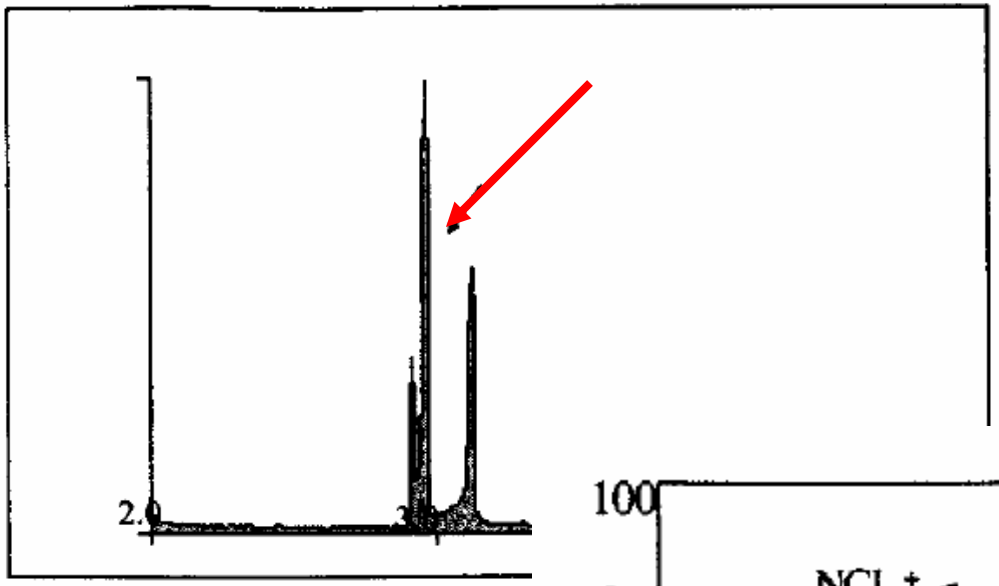


Clean, fresh smell
Slight chlorine odor

Pungent, acrid smell
Confused w/ strong
“chlorine” odor

It’s the difference that causes those burning eyes and skin rashes after using a pool or hot tub

Work done to identify the source of odor



GC/MS analysis. Arrow indicates suspect peak

gure 3. Total ion chromatogram of

Mass spectral analysis confirms presence of chloramines

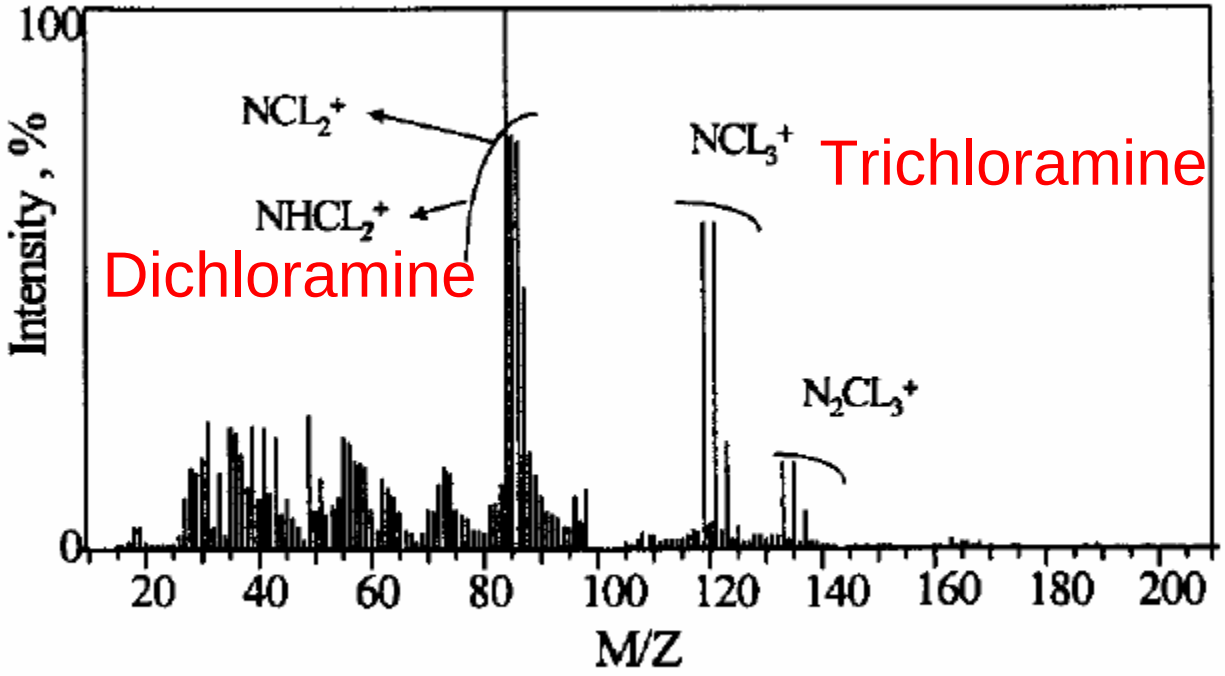
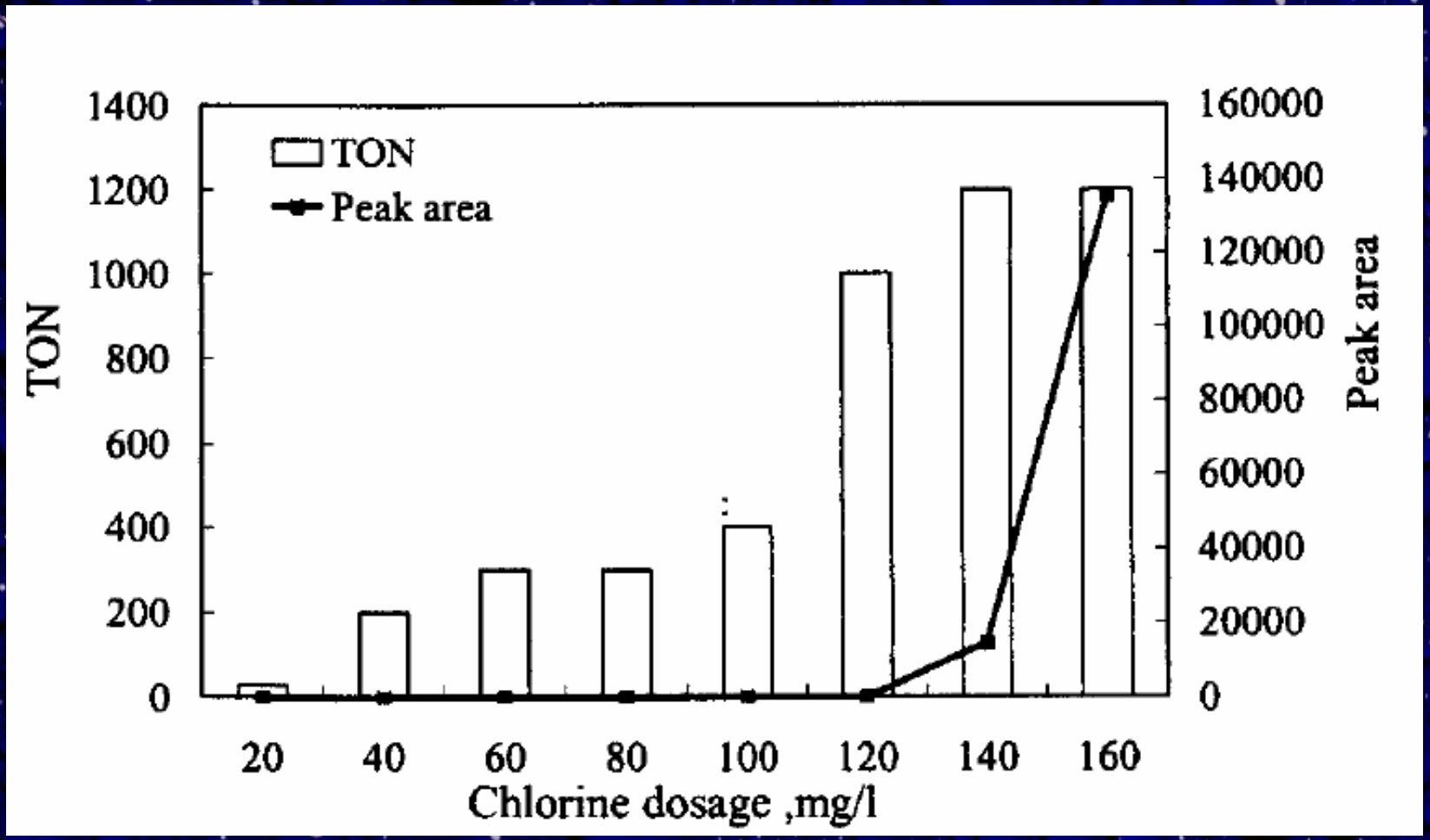


Figure 4. Electron impact mass spectra of suspected intense odor substances

Conclusive data



Relationship between odor and peak area of suspected odor-causing peak (compound)

Parallel guidance from the spa industry

SPA WATER MAINTENANCE TROUBLESHOOTING GUIDE

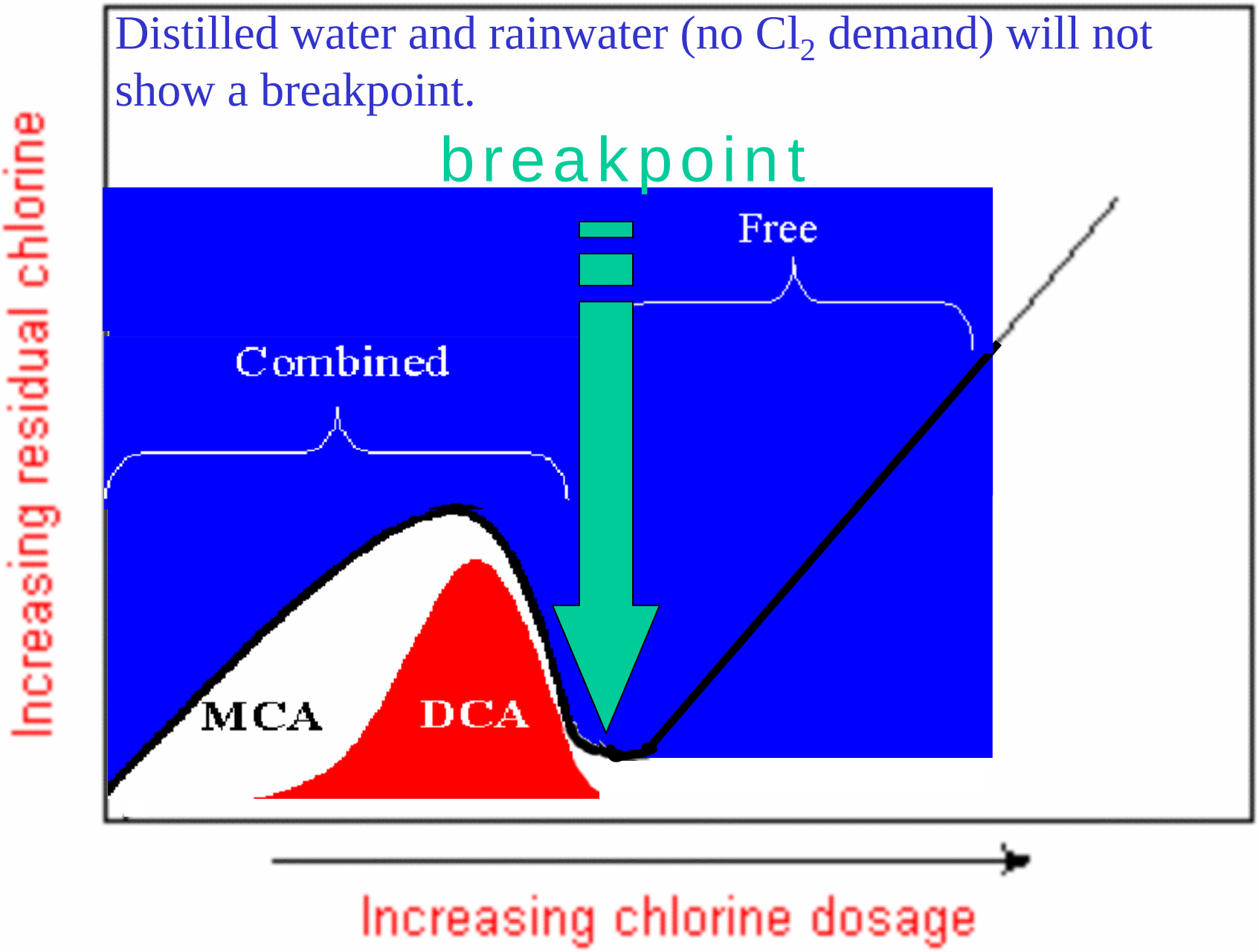
Problem	Probable Causes	Solutions
Chlorine Odor	• Chloramine level too high • Low pH	• Shock spa with sanitizer • Adjust pH to recommended range
Eye Irritation	• Low pH • Low sanitizer level	• Adjust pH • Shock spa with sanitizer and maintain sanitizer level
Skin Irritation / Rash	• Unsanitary water • Free chlorine level above 5 ppm	• Shock spa with sanitizer and maintain sanitizer level • Allow free chlorine level to drop below 5 ppm before spa use

What we know so far...

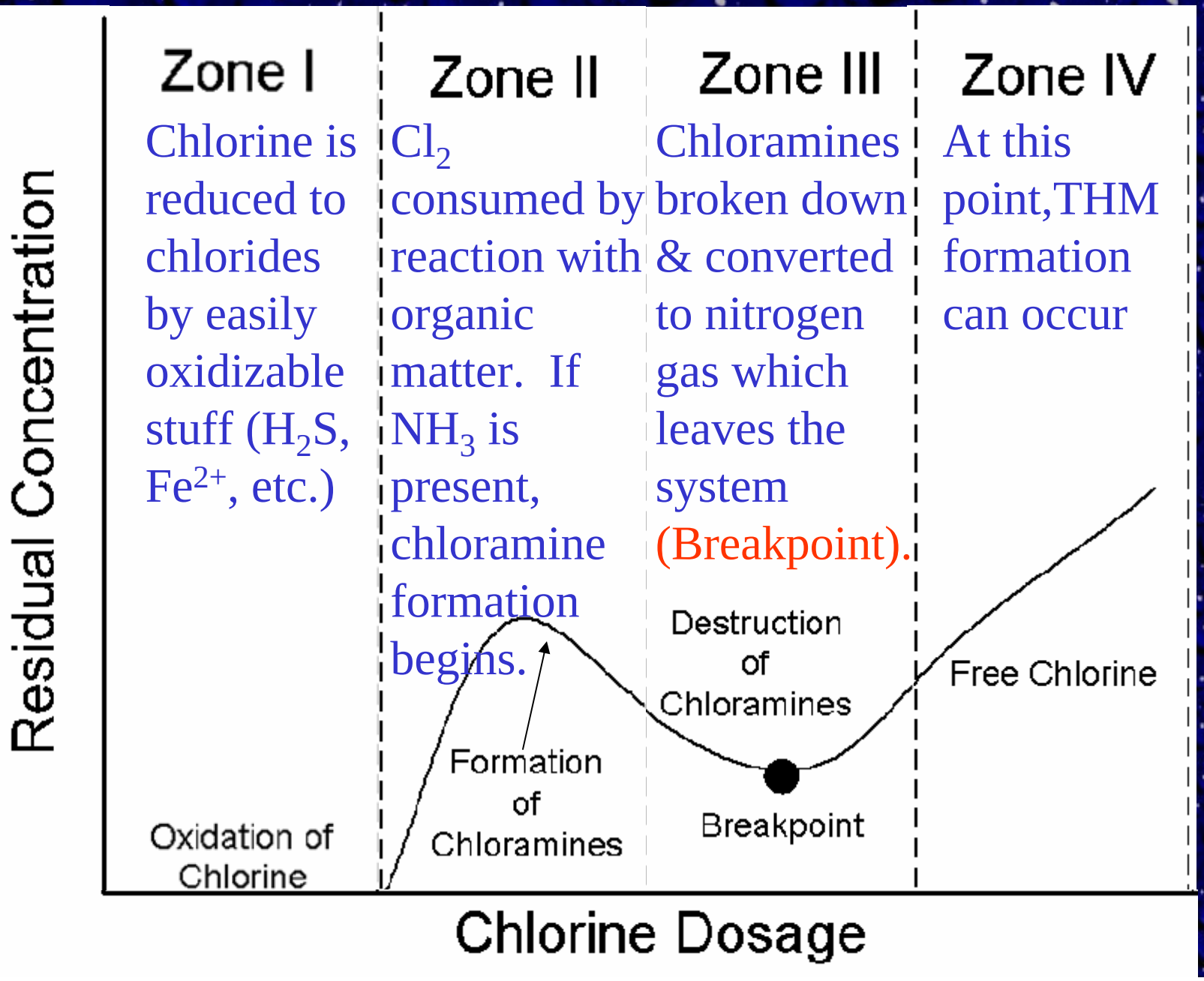
- ✯ Chlorine is consumed by organic matter, bound up by iron and manganese, and COMBINES with ammonia
- ✯ pH is a critical factor in determining chlorine's disinfection ability and corrosivity of the water
- ✯ Combined chlorine still has a residual
- ✯ Combined chlorine is not as good a disinfectant as FAC
- ✯ Free residual + combined residual = Total residual
- ✯ Total residual - free residual = combined residual
- ✯ Chlorine odor is good; chloramine odor is bad
- ✯ Reports of chlorine odor generally mean the chlorinator should be bumped UP…not down

The "Breakpoint"

Distilled water and rainwater (no Cl_2 demand) will not show a breakpoint.



The "Breakpoint"…another look



Breakpoint- why should we care?

The importance of break-point chlorination lies in the control of:

taste,

odor,

Complaints of "chlorine" odor and "burning eyes" from pools/ spas that people usually attribute to <u>over</u>-chlorination is actually due to chloramines! (i.e. UNDER-chlorination)

and increased germicidal efficiency.

The killing power of chlorine on the right side of the break point is 25 times higher than that of the left side

Getting to Breakpoint

Total chlorine residual =
free available chlorine + combined available chlorine.

Total residual should not be significantly > free residual
(i.e. a total 1.0 mg/l and a free 0.2 mg/l).
When this occurs, indications are that breakpoint chlorination has not been met and additional chlorine should be applied

Free residual test should ideally be = or slightly < total chlorine residual
(i.e. a free 0.8 mg/l and a total 1.0 mg/l).
These test results indicate that breakpoint chlorination

Therefore, testing for TOTAL chlorine
in addition to FREE chlorine can help!!

Ensuring you are at Breakpoint

- Measure Free and Total chlorine
- Bump up chlorinator to increase chlorine dose a certain known amount
- On the following day, re-test Free and Total chlorine.
- If Total increases but Free does not, you are NOT at breakpoint.
- Repeat process until both Total and Free chlorine increase similarly upon adjustment

Can you have too much chlorine?

Chlorine is a health concern at certain levels of exposure.

Drinking water containing chlorine well in excess of drinking water standards could cause irritating effects to eyes and nose.

Some people who drink water containing chlorine well in excess of standards could experience stomach discomfort.

Drinking water standards for chlorine protect against the risk of these adverse effects.

Little or no risk with drinking water that meets the USEPA MRDL and should be considered safe with respect to chlorine.

Final Stage 1 D/DBP Rule MRDL: **4.0 mg/L**

Compliance is based on an annual average.

Breakpoint Troubles at Endpoints

CAUSE:

Most likely... sedimentation in dead-end lines

SOLUTIONS:

- Flush dead lines frequently
  (*may require weekly flush--especially during summer months*)
- "Poly-pig" mains to remove sludge

Questions?

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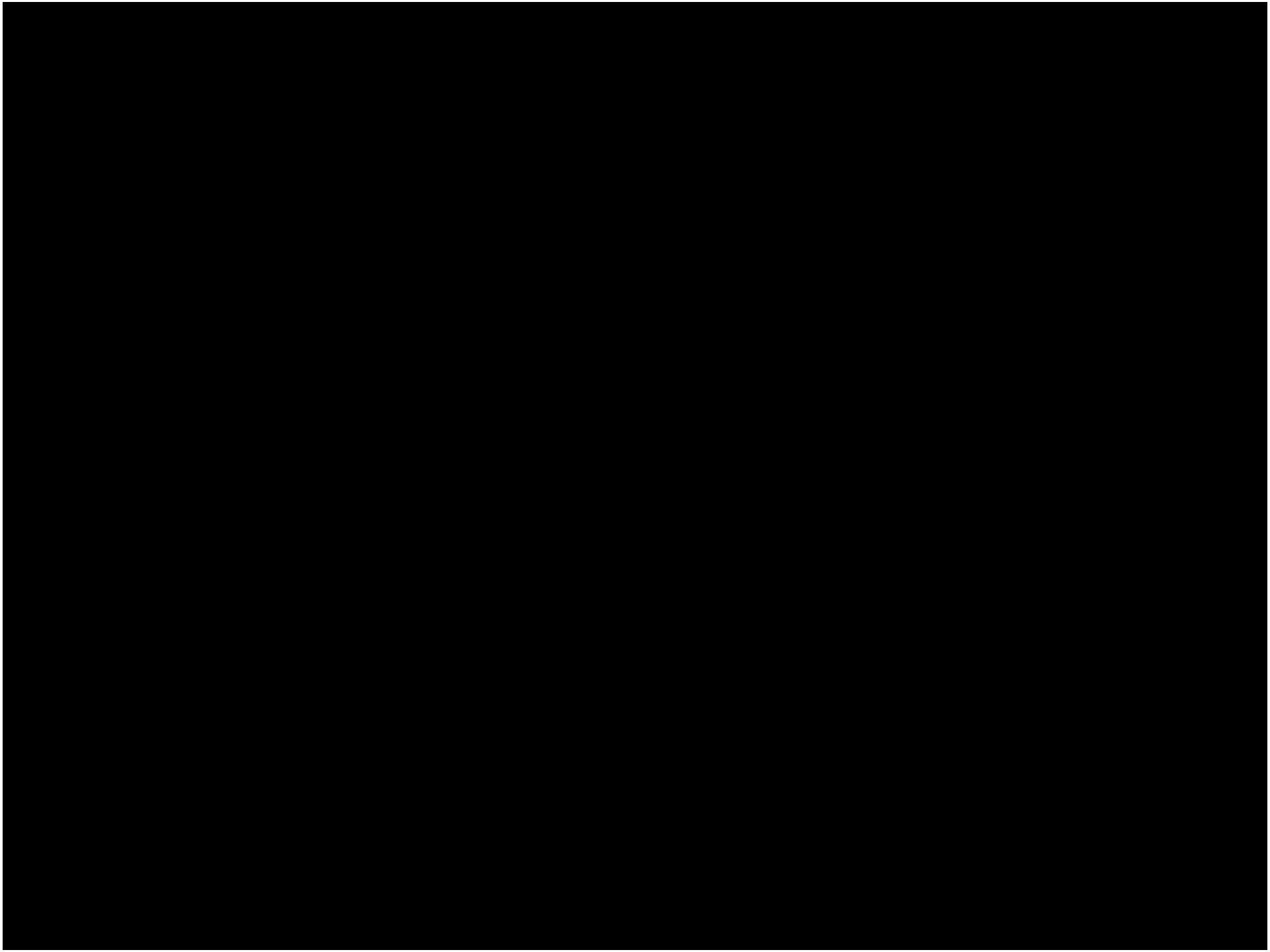

Chlorine Sampling Issues

- Analyze samples for chlorine immediately after collection.
- Free chlorine is a strong oxidizing agent; unstable in natural waters.
- It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds.
- Factors including reactant concentrations,sunlight, pH, and temperature influence decomposition of free chlorine in water.
- Avoid plastic containers → may have a large chlorine demand.
- Don't use a SLH BacT bottle

Chlorine Sampling Issues

- Pretreat glass sample containers to remove any chlorine demand
  - *Soak in a dilute bleach solution for at least 1 hour*
  - *Dilute bleach solution =1 mL bleach to 1 liter of deionized water.*
  - *Rinse thoroughly with deionized or distilled water.*
- Common error in chlorine testing is obtaining an unrepresentative sample.
  - *If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample.*
  - *Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample.*