The Role of Chlorine in Dealing with Water Contamination

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Discussion Topics

- Dealing with unknowns— emergency chlorination
- The Power of Chlorine
- Understanding Disinfection: Basic Chlorine Chemistry
- The "Breakpoint" & How to get there
- Chlorine Testing- some concerns
- How much chlorine must be added?
- Can we overdo it?

How do you respond to a water-related emergency?

…people reportedly becoming ill

…suspicion is it might be the water

…it could be a bacterial illness

…it might be viral in nature

“Nooooo!”

is NOT an acceptable response

"The best defense is a good offense."

– *heavyweight champion Jack Dempsey*

Your ability to successfully respond to any potential situation starts here

…and your best offense starts with chlorine!

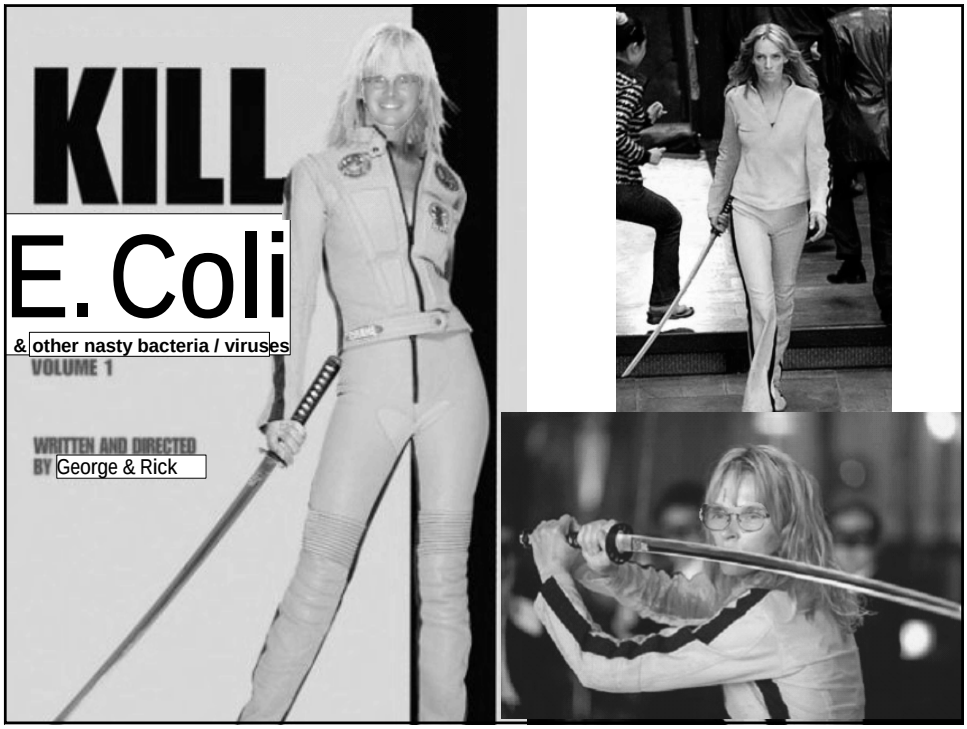
Emergency Response Plan

Suspected Chemical/Biological Attack on Water Supply

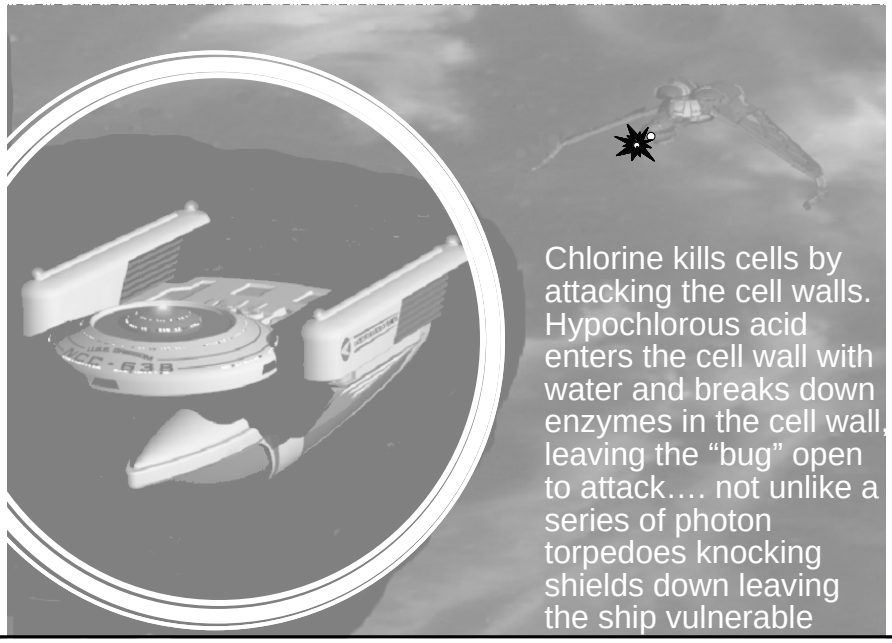
☑ Verify & maintain a chlorine residual of at least ~~0.5 ppm~~ 1.0 ppm throughout the distribution system

US Army recommends

Kill the bugs ⇨ Disinfection **(Chlorination)**



How does chlorine kill?



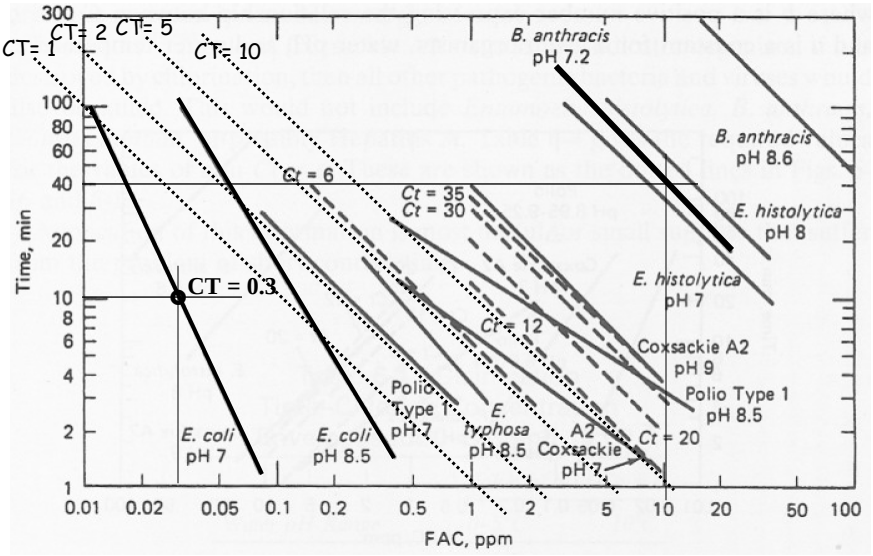
Chlorine kills cells by attacking the cell walls. Hypochlorous acid enters the cell wall with water and breaks down enzymes in the cell wall, leaving the “bug” open to attack…. not unlike a series of photon torpedoes knocking shields down leaving the ship vulnerable

How effective is chlorine?

- We need a measure to gauge the killing power
- The measure commonly used is the “CT” value for any particular agent
- “CT” stands for Concentration x Time
- Concentration is in ppm (parts per million)
- Time is in minutes
- A CT value of 10 could mean
  - Exposure to 10 ppm for 1.0 minute (10 x 1 = 10)
  - Exposure to 1.0 ppm for 10 minutes (1 x 10 = 10)
  - Exposure to 2.0 ppm for 5 minutes (2 x 5 = 10)
- **The lower the CT value, the more effective the killing agent is**

Reprinted from *Journal American Water Works Association* 54, 1379, Nov 1962.

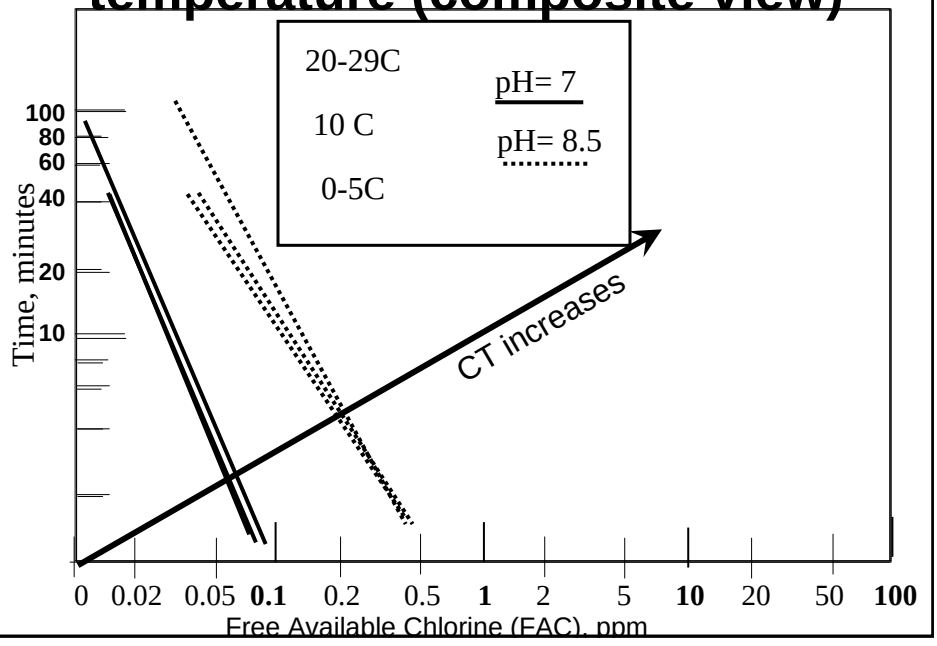
Chlorine effectiveness at 0-5° C (3 log)



CT values less than 1 for chlorine against E. coli show high effectiveness

Even a CT value of 400 means the resilient anthrax can be handled.

Chlorine effectiveness with temperature (composite view)



Effect of Cl_2 on E.coli

- Recent study on effect of chlorine on E. coli
- Tested 6 strains of O157:H7 at 4 Cl_2 levels
  - 0.25 mg/L
  - 0.5 mg/L
  - 1.0 mg/L
  - 2.0 mg/L

X **0 0.5 1 and 2 mins** contact time

- 5/6 isolates + E. coli control strain were highly susceptible to chlorine
- >7 log10 reduction of each of these strains by 0.25 mg/L free chlorine within 1 min (CT value = 0.25)

Each "log_{10}" = 90% reduction; 4 log_{10} = 99.99% reduction
SDWA requires 4 log reduction

Chlorine vs. Viruses, Giardia, "Crypto"

Summary of C.t values (mg/L. min)for 99% inactivation (2 log) at 5°C (Clark et al, 1993)

Organism	Disinfectant			
	Free chlorine, pH 6 to 7	Pre-formed chloramine, pH 8 to 9	Chlorine dioxide, pH 6 to 7	Ozone pH 6 to 7
E. *coli*	0.034-0.05	95-180	0.4-0.75	0.02
Polio virus 1	1.1-2.5	768-3740	0.2-6.7	0.1-0.2
Rotavirus	0.01-0.05	3806-6476	0.2-2.1	0.006-0.06
Bacteriophage f_2	0.08-0.18	-	-	-
G. *lamblia* cysts	47->150	-	-	0.5-0.6
G. *muris* cysts	30-630	-	7.2-18.5	1.8-2.0[a]
C. *parvum*	7200[b]	7200[c]	78[b]	5-10[c]

a Values for 99.9% inactivation at pH 6-9.
b 99% inactivation at pH 7 and 25°C.
c 90% inactivation at pH 7 and 25°C

Virus inactivation by Chlorine

CT VALUES FOR INACTIVATION OF VIRUSES BY FREE CHLORINE

	Log Inactivation					
	2		3		4	
	pH		pH		pH	
Temperature (°C)	6 to 9	10	6 to 9	10	6 to 9	10
0.5	6	45	9	66	12	90
5	4	30	6	44	8	60
10	3	22	4	33	6	45
15	2	15	3	22	4	30
20	1	11	2	16	3	22
25	1	7	1	11	2	15

4 Log = 99.99% kill

June 2003 PROCEDURE FOR DISINFECTION OF DRINKING WATER IN ONTARIO

Chlorine and anthrax

Anthrax Specifics

Worst case inhalation critical dose = 6000 spores

- Water containing 171 spores/L
- Drink 5 L/day x 7 days

Vegetative form:

≥ 99.6% killed with 5 ppm FAC/20 mins. contact time

Spore form:

Inactivated by water at 95°C for 25 mins.
Removed by filtration with pore size < 1 um
Destroyed readily with 5-10% chlorine bleach or formaldehyde

Environmental Health Perspectives Vol. 127: No. 12 December 1999

OK, chlorine works, but how? and why?: The chemistry of chlorine

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 to:

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

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

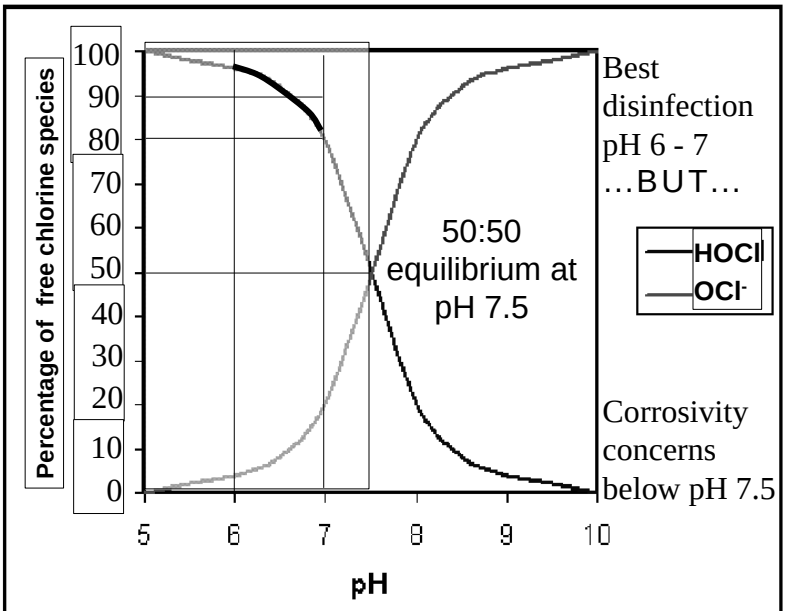
The two chemical species formed by chlorine in water, hypochlorous acid (HOCl) and hypochlorite ion (OCl –), are commonly referred to as **"free" or "available"** chlorine.

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

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

In waters with pH between 6.5-8.5, the reaction is incomplete and both species (HOCl and OCl –) will be present.
Hypochlorous acid (HOCl) is the more (20x) germicidal of the two.

Free Chlorine Distribution with pH



Reaction of chlorine/hypochlorite on addition to water

Gas chlorine

$Cl_2 + H_2O \rightarrow$

$HOCl + H^+ + Cl^-$

$\downarrow$

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

Free H^+ ions means pH is lowered

Hypochlorite

$Ca(OCl)_2 + 2H_2O \rightarrow$

$2HOCl + Ca^{++} + 2OH^-$

$\downarrow$

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

$NaOH \Rightarrow Na^+ + OH^-$

$NaOCl + H_2O \rightarrow$

$HOCl + Na^+ + OH^-$

$\downarrow$

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

$NaOH \Rightarrow Na^+ + OH^-$

NOTE: Sodium hydroxide (NaOH) is used as a stabilizing agent. On reaction with water, NaOH ionizes to Na^+ and OH^-, thereby adding to the available OH^- ions and further raising the pH.

Free OH^- ions means pH is raised

Lower pH → better disinfection (HOCl is predominant)

Effect of increasing bleach* concentration on pH of typical southwest WI well.

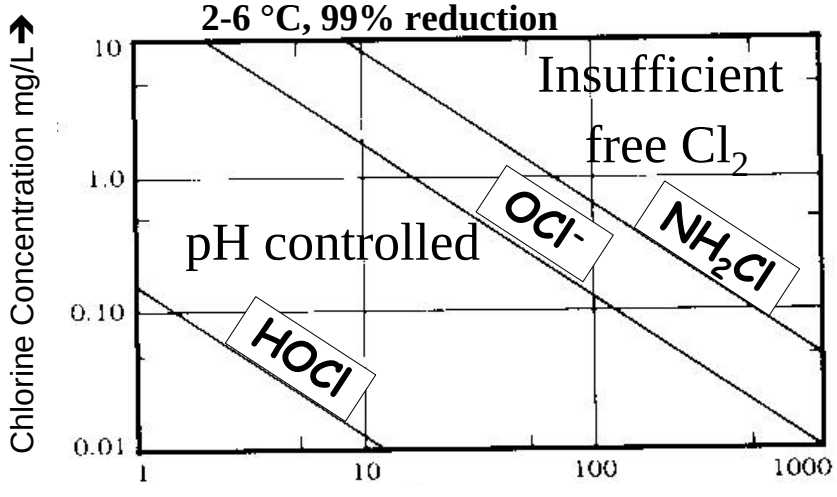
Free Cl_2 ppm	pH	% HOCl	% OCl-
100	**7.83**	**30%**	**70%**
200	8.33	10%	90%
500	8.73	5%	95%
1000	9.24	3%	97%
2000	9.57	2%	98%

Use of household bleach:
= ↑ pH,
= ↑ OCl-, ↓ HOCl
= ↑↓ effectiveness of FAC
Chlorine gas is the best option

Data from State Laboratory of Hygiene
*Household bleach = 5.25% available chlorine

Effectiveness of chlorine forms vs. E. coli

From: Reynolds & Richards, 1996. Unit Processes in Environmental Engineering.



Hypochlorous acid >> Hypochlorite >> Chloramines

Chlorine Disinfection: other concerns

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

Intermediate

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

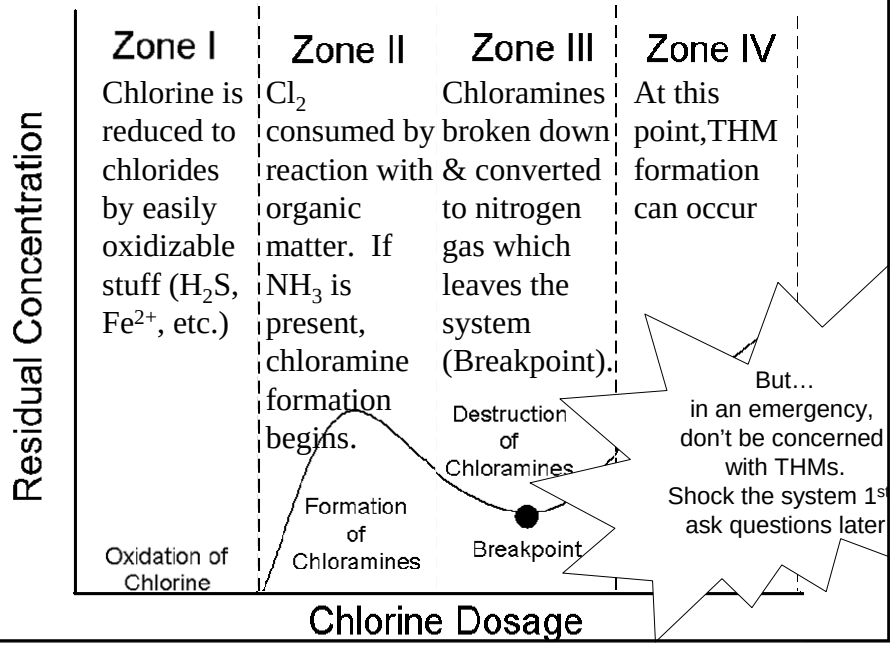
Longer Term

- Organic matter- chlorine is consumed during the oxidation process

BOTTOM LINE

Disinfection cannot proceed until the oxidant demand has been destroyed.

Chlorination & Breakpoint



What are chloramines? How do they affect disinfection?

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^+, H_2O , and N_2 gas which will come out of solution.

Chloramines: effective vs. bacteria but NOT viruses.

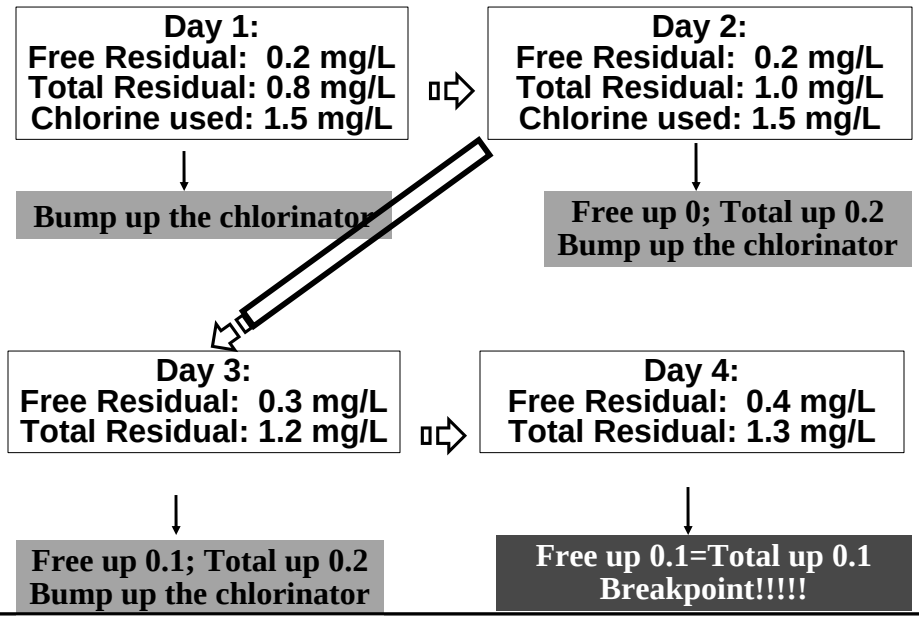
How do I know if I have "free" chlorine (FAC) needed for best disinfection?

- To have free available chlorine for disinfection you must be past the "breakpoint"
- Before the breakpoint, chlorine is used up by inorganics (oxidizing Fe, Mn to chloride) and organics (chloramine formation) in the system
- Beyond breakpoint, every ppm of chlorine added to the system is measured as FREE chlorine
- "Shock" chlorination is another rapid way to ensure the presence of significant FAC.

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**

Breakpoint Flowchart



Why Breakpoint Chlorination?

- **Recommended deterrent to bioterrorism**
  - 2 of the DNR's "16 recommendations" for reducing risk relate to chlorination
  - Many biotoxins can be inactivated by proper disinfection with "free" chlorine.
- **Public protection**
  - Remember the Walkerton, Ontario outbreak (May 2000) of E. coli O157:H7
- **Liability protection for your water utility.**
  - illnesses… loss of life➔ attorneys… litigation…

How much chlorine do I need

- There is general agreement that "shock" chlorination should be performed using 50 to 200 ppm of chlorine.
- Contact time should ensure at least 8-12 hours at a concentration of at least 10 ppm
- If you test the water throughout the system after 8 -12 hrs and chlorine levels have dropped below 10 ppm, REPEAT
- This raises two important questions:
  - 1. How much bleach does it take to establish a 200 ppm concentration throughout my well/system
  - 2. How can I accurately test my chlorine level at these types of concentrations

Shock Chlorination – Large Systems

- Determine flow rate (ex. 5.0 gpm)
- Target chlorine concentration= 100 ppm
- Gallons of bleach needed =

$$\frac{5\ \frac{\text{gallons}}{\text{minute}} \times 100\ \text{ppm}\ Cl_2\ \text{goal} \times 1440\ \frac{\text{minutes}}{\text{day}}}{52{,}500\ \text{ppm (conc. of household bleach)}} = 13.7\ \text{gallons}$$

For 100 ppm: simply multiply flow (in gpm) by 2.743

- Determine metered pump output (ex. 24 gpd)
- 13.7 gallons divided by 24 gallons per day = 0.57 or 57%.
- Set metering pump at 57% speed.

Shock Chlorination – Well Systems

- Determine well casing diameter (ex. 4")
- What's the water depth (well depth – water level)
  (100 foot well depth water at 28 feet; depth =100-28 = 72 ft).
- Multiply the water depth in feet (from above) by the appropriate factor in column C from the table
  - Ex. 72 feet x 0.652 (4" well casing) = 46.9 gallons
- Add in any other volume in system (e.g.,water heaters, piping)
- Multiply total system volume in gallons by 2.4 to determine # of ounces of bleach which must be added to achieve a 100 ppm concentration.

Diameter of well Inches	Area feet²	gal/ft
A	B	C
2"	0.022	0.163
4"	0.087	0.652
6"	0.196	1.47
8"	0.349	2.61
10"	0.545	4.08
12"	0.785	5.88
18"	1.766	13.22
24"	3.140	23.50
30"	4.906	36.72
36"	7.065	52.87

$$C_1 \times V_1 = C_2 \times V_2$$

100 ppm Desired Cl_2 level X system volume = 52,500 ppm conc. Of bleach X volume of bleach

$$\frac{C_1 \times V_1}{C_2} = V_2 \qquad \frac{100 \times V_1}{52{,}500} = V_2$$

$$\frac{\text{System Volume}}{525} = V_{\text{olume of chlorine bleach needed}}$$

Testing Concerns

- 1. Do NOT use colorwheels or color comparators. Use a portable colorimeter and obtain a quality result.
- 2. The DPD method is known to be non-linear at levels above about 1 ppm. To test systems containing chlorine at the levels we've discussed, you'll need to dilute the sample to the point below 1 ppm

Color Wheel Bias

Hach Color Wheel DPD Chlorine Test

Observed Free Chlorine Concentration (ppm) **

Person	*Lab*	*Window Light*	*Outside*
George	0.8	0.9	0.95
Graham	0.9	0.9	1
Tony	1.05	0.95	1.05
Chris	1.1	0.8	1
Joanie	1	0.75	0.9
Doug	1	1	1.2
Range	0.8 - 1.1	0.75 - 1	0.9 - 1.2

True value **0.7** ppm

DPD Pocket Digital Colorimeter: **0.71

DPD Non-linearity

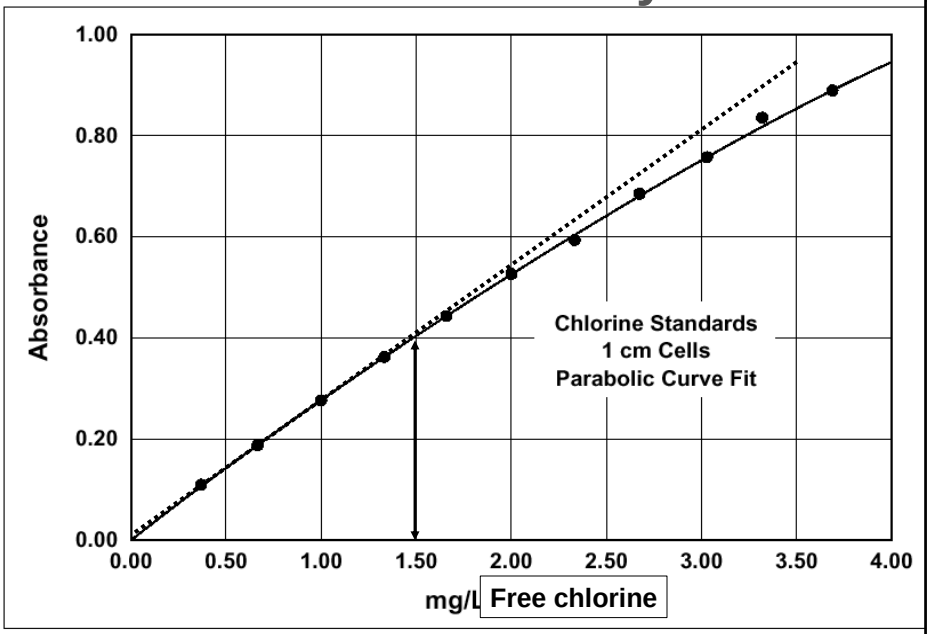
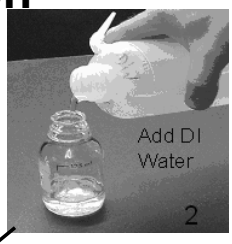


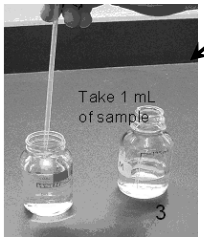
Figure 3.1: *Standard Methods* Calibration - DPD Colorimetric Method

What's the best way to dilute samples?
100-fold dilution

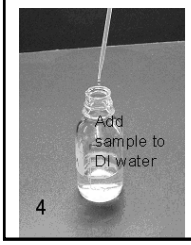
1. Add a small amount of reagent water to the bottle



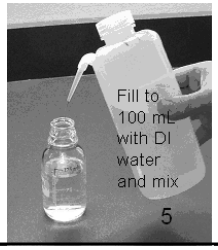
Supplies:
Reagent water,
1 mL pipette,
bottle with
calibrated 100 mL
mark



2. Add 1.0 mL of sample to the bottle



3. Dilute to the 100 mL mark with reagent water



Can you have too much chlorine?

Chlorine is a health concern at certain levels of exposure. Drinking water containing chlorine in excess of standards:

- *potential for irritating effects to eyes and nasal passages.*
- *potential for stomach discomfort.*

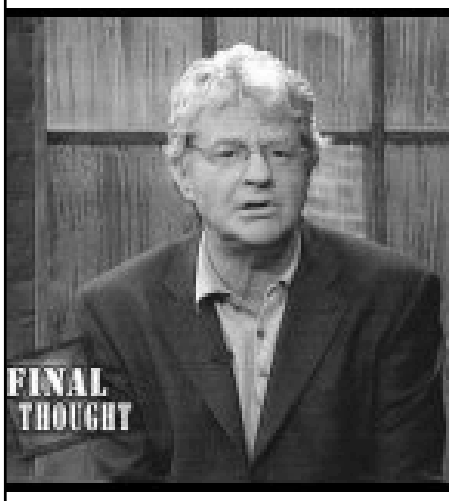
Disinfection ByProducts Rule (FR 12/16/98)
Maximum Residual Disinfection Level (MRDL): **4.0 mg/L**
Compliance is based on an annual average.

(this allows the residual to be substantially increased on a short term basis such as would be required to deal with a known or suspected act of chemical/ bio-terrorism)

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

Final Thoughts

The best defense in the event your water supply system security is compromised is to...



- …practice breakpoint chlorination <u>at all times</u>
- …test for and maintain a FAC residual of 0.5 ppm <u>throughout</u> the system
- …remember that disinfection is based on "CT" …
  Concentration (ppm)
  × Contact Time (minutes)
- …shock chlorination is best technique, gas chlorine works best

Chlorine Summary

- ☑ In an emergency, consult your ERP & chlorina
- ☑ Chlorine works!
- ☑ …even at low levels and brief contact
- ☑ Gas chlorine= low pH = best disinfection
- ☑ Hypochlorite raises pH, lowers effectivity
- ☑ The "Breakpoint" & Disinfection power
- ☑ Getting to Breakpoint
- ☑ Chlorine Testing- some concerns
- ☑ How much chlorine must be added?
- ☑ Can we overdo it?

Questions?

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