Chemical Additions for Water Supply Systems

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sponsored by:

Disclaimer

Any reference to product or company names does not constitute endorsement by the Wisconsin State Laboratory of Hygiene, the University of Wisconsin, or the Department of Natural Resources.

Information offered here is only for PWS Chemical Addition Monitoring. These methods and QC suggestions are not acceptable for wastewater DMR compliance monitoring

Session Objectives

- Discuss safe handling of chemical additives in PWS systems
- Discuss tests used to monitor common chemical additives**:**
  - chlorine, fluoride, and phosphate
- Discuss interferences caused by chemical additives
- Selecting the proper fluoride measurement method
- Discuss & demonstrate SPADNS fluoride procedures
- Discuss and demonstrate the DPD chlorine test
- Discuss phosphate screening test
- Troubleshoot fluoride, chlorine and phosphate testing
- Review QA/QC requirements
- Discuss minimum record keeping and reporting requirements

WHERE should I test?

? Chlorine-
- Various points in system; especially dead-ends and low use areas
- Future requirements will mandate testing at points of entry
- Can use bacteria sampling points
- Indicate chlorine residuals on BactT sample form

? Fluoride-
- Various points in system but especially at ends of system.
- Can use bacteria sample sites, if well distributed.
- Indicate "operator test result" on lab form with monthly required "split sample"

? Phosphate-
- Ends of system-similar to chlorine testing.
- Should use a variety of sites to see how effective the addition is.

WHAT do I test for and HOW often?

Chlorine-
- must test for "free" chlorine residual at **least** twice each week
- ...and report it on DNR pumpage form.
- Many systems test daily.

Fluoride-
- Minimum daily for total fluoride, including weekends.
- Collecting samples on weekends and running tests on Monday is not acceptable.
- If weekend testing can't be done, fluoride addition must stop.
- Must report test results on "split" sample lab form and on monthly pumpage form.

Ortho-Phosphate-
- must test often enough to maintain control of the process...
- but at least twice per week is normally required.
- Many systems test daily

What do I have to report to DNR?

All chemical use must be reported on DNR pumpage forms. This includes

- daily well pumpage,
- daily chemicals added (*in pounds, gallons or inches*),
- daily chemical dosage (*from formula or nomograph*), and
- the required operator test results.

Must also report or send any "split" sample results to DNR if done through private lab.

Common Problems and Mistakes

- Improper test kits & improper procedures (zeroing the instrument, etc.)
- All testing done at one location—normally for convenience
- Use of outdated chemicals (powder packets) when running lab tests/use of old chemicals for the chemical addition at the well houses
- Not allowing sample to reach room temperature before testing
- Use of dirty glassware or dirty/dusty test kit
- Not allowing water to run long enough to get turbid-free water for testing
- "Total" chlorine test done instead of "free"

More Common Problems & Mistakes

- Operator does not list his/her own test result for fluoride or chlorine on lab form sent with sample
- Required daily testing (for fluoride) not done on weekends
- Inadequate mixing when water dilution is used
- Inadequate markings on mix tanks to determine accurate daily chemical use
- Falsifying results
- Adjusting feeders lower when chlorine odor complaints received

Sample Pumpage Report

		Gas Chlorine - 100%			Hydrofluocilic Acid 25%			AQUAMAG		
DATE	PUMPAGE IN 1,000 GAL.	CHEMICAL USED (lbs)	CALCULATED DOSE (PPM)	RESIDUAL TEST (PPM)	CHEMICAL USED (lbs)	CALCULATED DOSE (PPM)	RESIDUAL TEST (PPM)	CHEMICAL USED (lbs)	CALCULATED DOSE (PPM)	RESIDUAL TEST (PPM)
1	642	6.00	0.93		27.00	0.95	1.05	33.00	0.98	
2	844	6.00	0.71	0.51	35.50	0.95	1.20	40.00	0.90	0.98
3	748	6.00	0.80		31.50	0.96		40.00	1.02	
4	639	5.00	0.78		27.00	0.96	1.13	35.00	1.04	
5	424	5.00	1.18	0.50		0.00	1.21	20.00	0.90	0.86
6	807	6.00	0.74		33.00	0.93	1.03	43.00	1.02	
7	860	8.00	0.93	0.55	30.00	0.79	0.80	48.00	1.06	1.00
8	1151	12.00	1.04		49.00	0.97	1.02	66.00	1.09	
9	898	8.00	0.89	0.52	38.00	0.96	1.20	49.00	1.04	1.01
10	826	9.00	1.09		35.50	0.98	1.26	47.00	1.08	
11	928	9.00	0.97		39.50	0.97	1.19	52.00	1.07	
12	644	6.00	0.93	0.62	1.50	0.05	1.10	34.00	1.01	1.07
13	816	8.00	0.98		33.50	0.93	1.24	44.00	1.03	
14	865	9.00	1.04		37.00	0.97	1.15	50.00	1.10	
15	751	8.00	1.07		30.50	0.92	1.17	44.00	1.12	
16	778	7.00	0.90	0.45	32.00	0.93	1.19	45.00	1.10	
17	477	6.00	1.26		19.50	0.93	1.26	26.00	1.04	
18	941	6.00	0.64		38.50	0.93	1.27	53.00	1.07	0.31
19	633	3.00	0.47	0.74	26.00	0.93	1.40	36.00	1.08	
20	855	6.00	0.70		35.00	0.93	1.26	48.00	1.07	0.98
21	716	6.00	0.84	0.35	29.50	0.94	1.29	40.00	1.07	
22	754	6.00	0.80		31.50	0.95	1.18	42.00	1.06	
23	895	7.00	0.78		36.50	0.93	1.10	41.00	0.87	
24	627	5.00	0.80		25.50	0.92	1.08	46.00	1.40	
25	1025	7.00	0.68		42.00	0.93	1.16	56.00	1.04	1.44
26	606	5.00	0.83	0.47	23.50	0.88	0.96	34.00	1.07	
27	883	8.00	0.91		34.00	0.87	1.12	50.00	1.08	
28	1006	9.00	0.89	0.50	39.00	0.88	1.04	54.00	1.02	
29	725	7.00	0.97		27.50	0.86	1.13	42.00	1.10	
30	853	8.00	0.94	0.40	33.00	0.88	1.09	48.00	1.07	
31										
TOT.	23617	207.00	26.50	5.61	921.50	25.98	33.28	1306.00	31.63	7.65
AVG.	787.233	6.90	0.87681	0.51	31.78	0.92	1.1476	43.53	1.05	0.9563

Disinfection

Chlorine instrumentation /reagents provided by:
HACH
Orion
North Central Labs

Disinfection

Disinfection treatment methods include:

- chlorination,
- chlorine dioxide,
- chloramines,
- ozone, and
- ultraviolet (UV) light.

➔ Groundwater systems may require filtration if the water contains iron (Fe^{+2}) and manganese (Mn^{+2}).
➔ Insoluble oxides form when chlorine, chlorine dioxide, or ozone are added to these systems.
➔ Both ozonation and chlorination may cause flocculation of dissolved organics, thus increasing turbidity and necessitating filtration.

Disinfection cannot proceed until the oxidant demand has been destroyed. Thus, when testing it is critical to be able to distinguish between

- FAC (which disinfects), and
- ”Combined chlorine" (which offers limited disinfection power).

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 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.

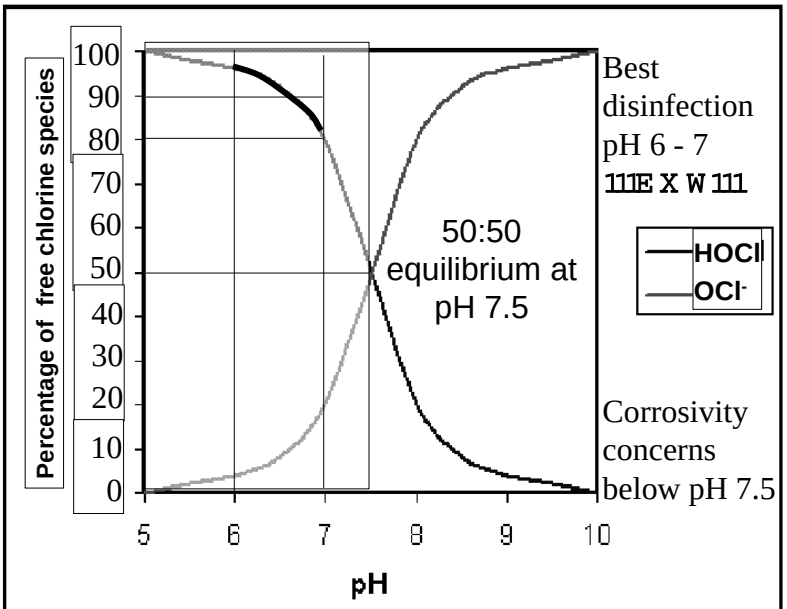
Hypochlorous acid is a weak acid and will disassociate according to:

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

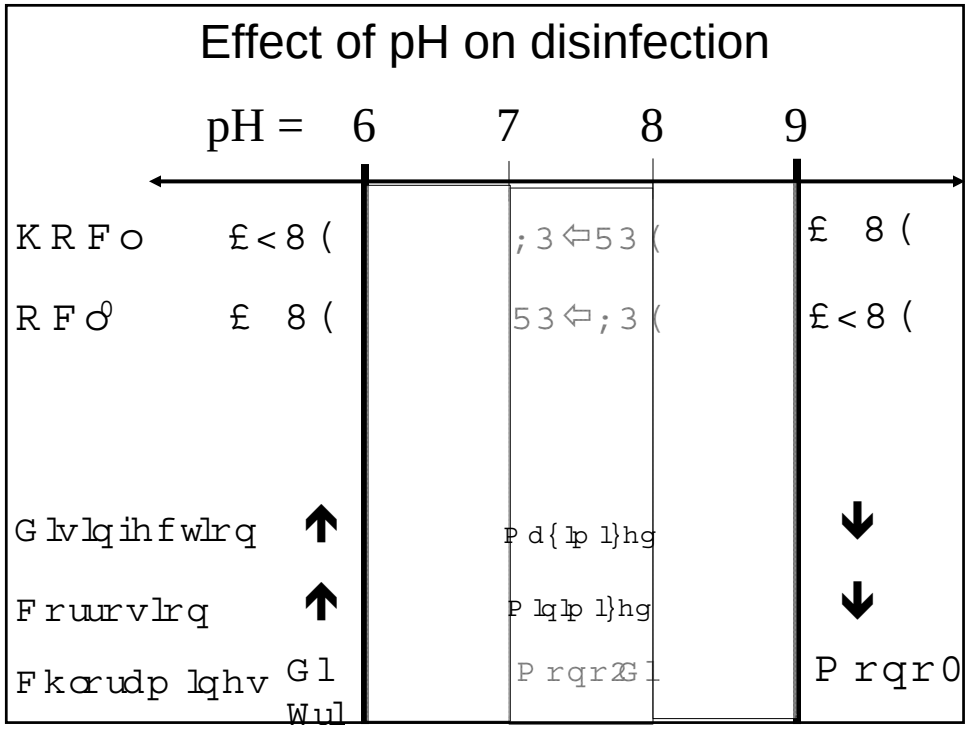
In waters with pH between 6.5-8.5, the reaction is incomplete and both species (HOCl and OCl –) will be present.

Hypochlorous acid 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)

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

Dichloramine: (stinkier)

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

Trichloramine: (stinkiest!)

$NHCl_2 + 3HOCl \downarrow NCl_3 + 3H_2O$ *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 fast is chloramine formation?

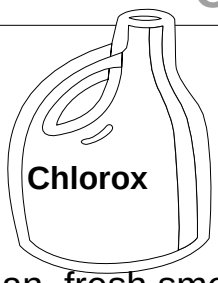
All of the free chlorine will be converted to monochloramine at pH 7 to 8 when the ratio of chlorine to ammonia is equimolar (**5:1 by weight**) or less. The rate of this reaction is extremely important, since it is pH-sensitive.

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!

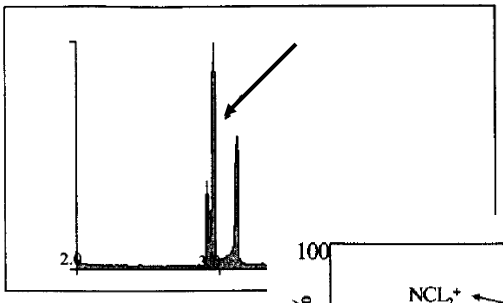


Clean, fresh smell
Slight chlorine odor

Pungent to acrid smell
Chloramine odor (Often 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



gure 3. Total ion chromatogram of

GC/MS analysis. Arrow indicates suspect peak

Mass spectral analysis confirms presence of chloramines

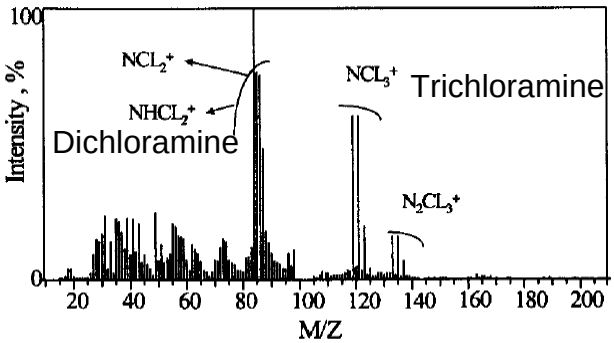
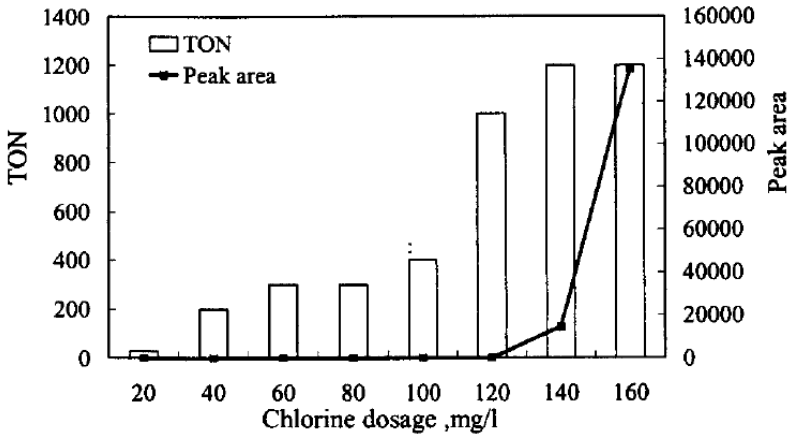


Figure 4. Electron impact mass spectra of suspected intense odor substances

Conclusive data



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

Parallel guidance from the spa industry

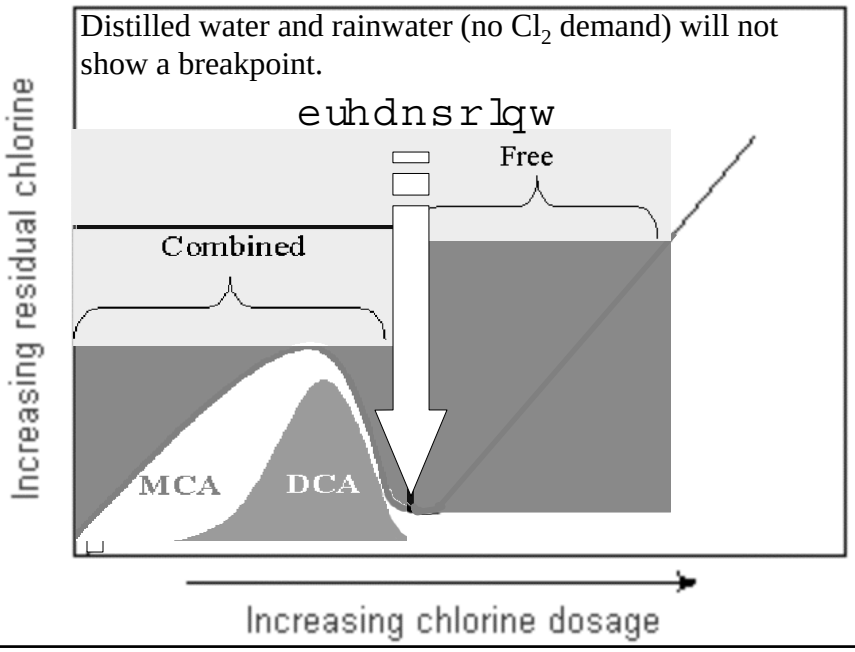
SPA WATER MAINTENANCE TROUBLESHOOTING GUIDE

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

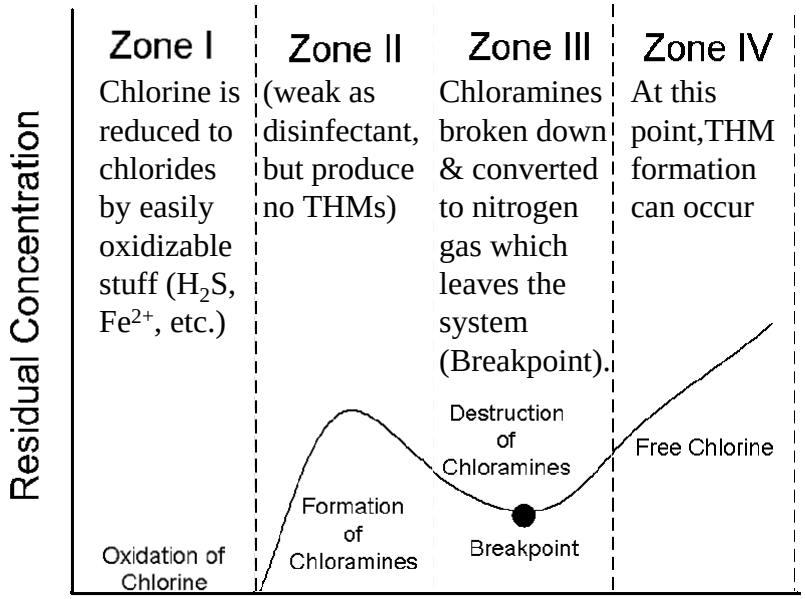
What we know so far...

- ✯ 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"



The "Breakpoint"

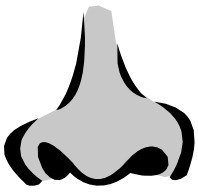


Breakpoint- why should we care?

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're 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**

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

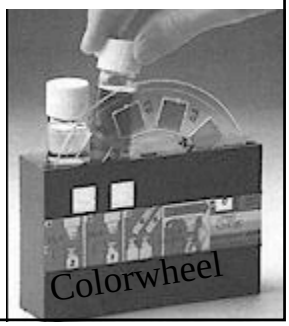
- Pretreat glass sample containers to remove any chlorine demand
  - *Soak in a dilute bleach solution for at least 1 hour*
  - *Dilute bleach solution =1 mL bleach to 1 liter of deionized water.*
  - *Rinse thoroughly with deionized or distilled water.*
- Common error in chlorine testing is obtaining 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.*

Chlorine Analysis options

DPD Method

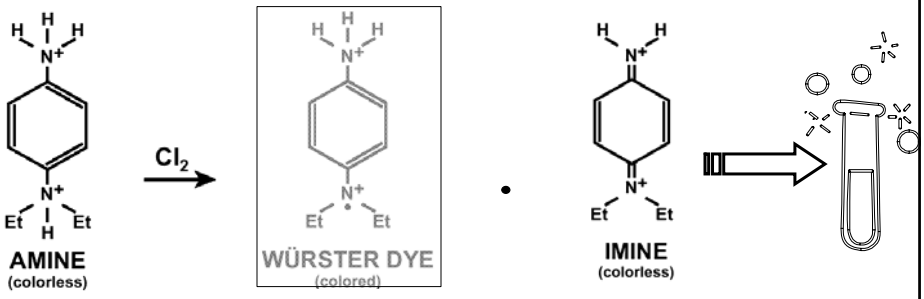
Linear Range = 0 to 1.4 ppm (very non-linear beyond 1.4)
Detection Limit: about 0.01 mg/L--under ideal conditions
Interferences: Many

~~**Electrode Method (ISE)**~~
~~Linear Range = 0.1 to 10 ppm~~
~~Interferences: Virtually none~~
~~*(using ISA buffer)*~~



The Chemistry of DPD

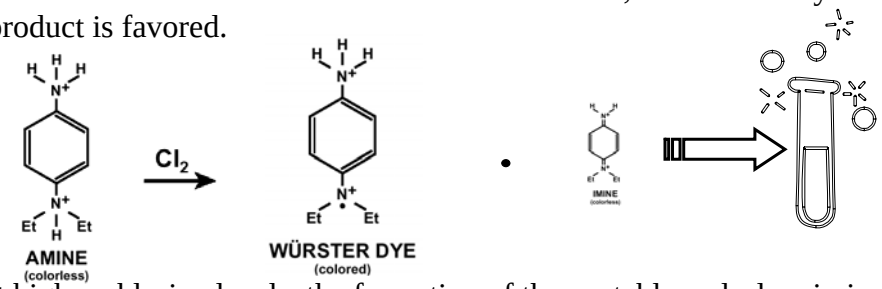
DPD



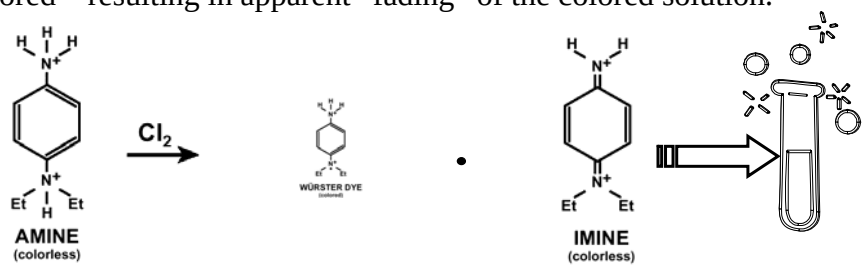
The proportion of colored to colorless product is related to the ratio of DPD indicator to oxidant (chlorine).

DPD Interferences - non-linearity

When DPD reacts with small amounts of chlorine, the Würster dye product is favored.



At higher chlorine levels, the formation of the unstable, colorless imine is favored—resulting in apparent "fading" of the colored solution.



Keep the DPD:chlorine ratio high to minimize fading of the resulting color

DPD Non-linearity

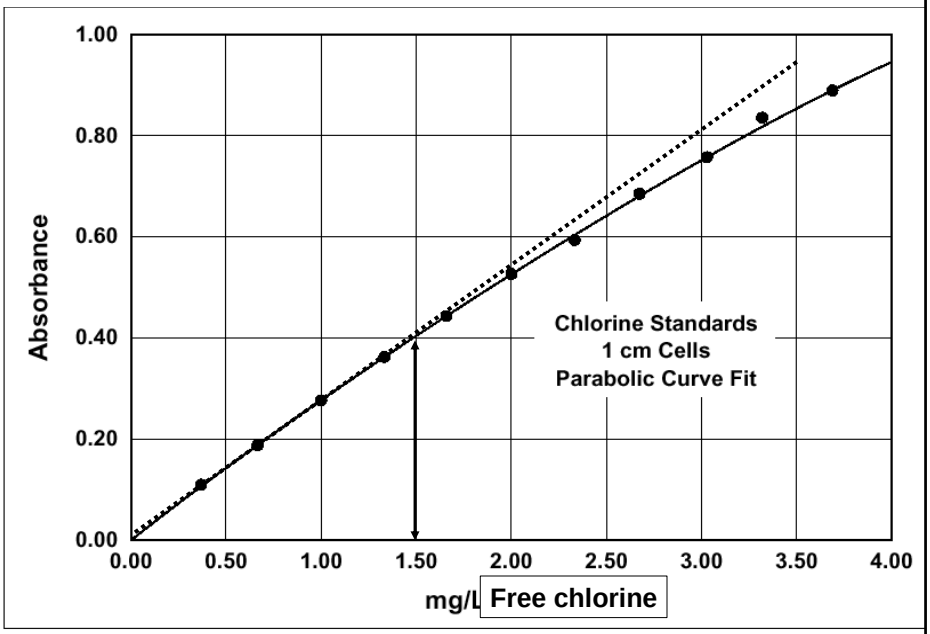


Figure 3.1: *Standard Methods* Calibration - DPD Colorimetric Method

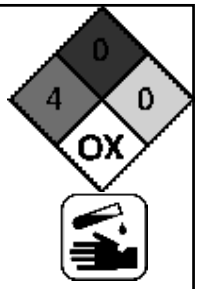
Key NR 811 requirements

NR 811.44 (3) RESIDUAL TESTING EQUIPMENT.

The equipment shall enable measurement of residuals

- to the nearest 0.1 mg/1 in the range below 0.5 mg/1 and
- to the nearest 0.2 mg/1 between 0.5 to 2.0 mg/1.

Chlorine Gas Safety Issues



1. Chlorine tanks should be stored indoors in a fire-resistant building.
2. Room must have an outwardly opening entrance door.
3. The chlorine room's entrance must be to the outside.
4. The chlorine room must have a door activated vent and light switch or external switches.
5. Gas chlorine room needs an observation window.
6. Chlorine cylinders shall be secured at all times.
7. The chlorinator and all tanks should be checked daily for leaks and a bottle of leak detector (ammonia) must be present. *A small amount of ammonium hydroxide (industrial strength ammonia or ammonium hydroxide) on a piece of cloth produces white vapor in the presence of chlorine.*
8. Scales must function properly.
9. Safety equipment A self-contained air supply gas mask must be available and in good condition.
10. Room shall be equipped with proper intake and exhaust ventilation.
11. Tanks and chlorinator must be kept in a separate room with a vent fan capable of complete air exchange in one to four minutes.

Chlorine Summary

- ☑ Disinfection approaches
- ☑ Chlorination basics
- ☑ Effect of pH on chlorination
- ☑ Chloramines
- ☑ Breakpoint Chlorination
- ☑ Analytical Techniques & Limitations
- ☑ Specific Regulatory Issues
- ☑ Quality Control
- ☑ Safety

Questions?

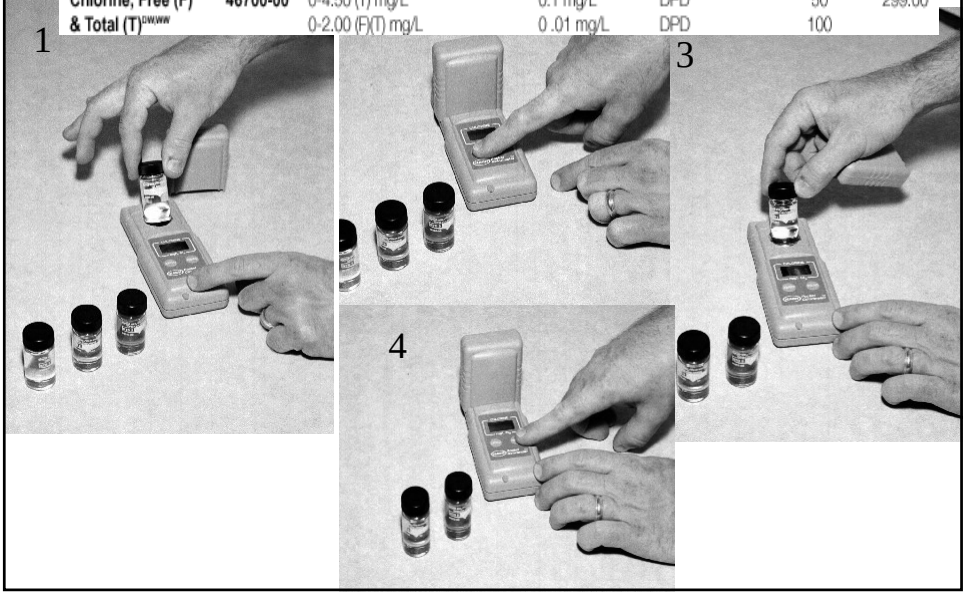
Measuring Free Chlorine with the Hach Pocket Colorimeter

Preliminary check of on-board calibration with secondary standards

1. Insert standard blank for kit, press zero. It should read 0.00.
2. Insert std #1, press read. Must be within kit specified tolerance
3. Insert std # 2 or 3, press read. Also must be within tolerance.
4. If results of all stds are acceptable, proceed with samples.
5. If not within tolerance, clean stds and colorimeter and re-check.
6. If still outside tolerance, consult manual. Re-calibration or servicing maybe necessary..

HACH chlorine DPD standardization

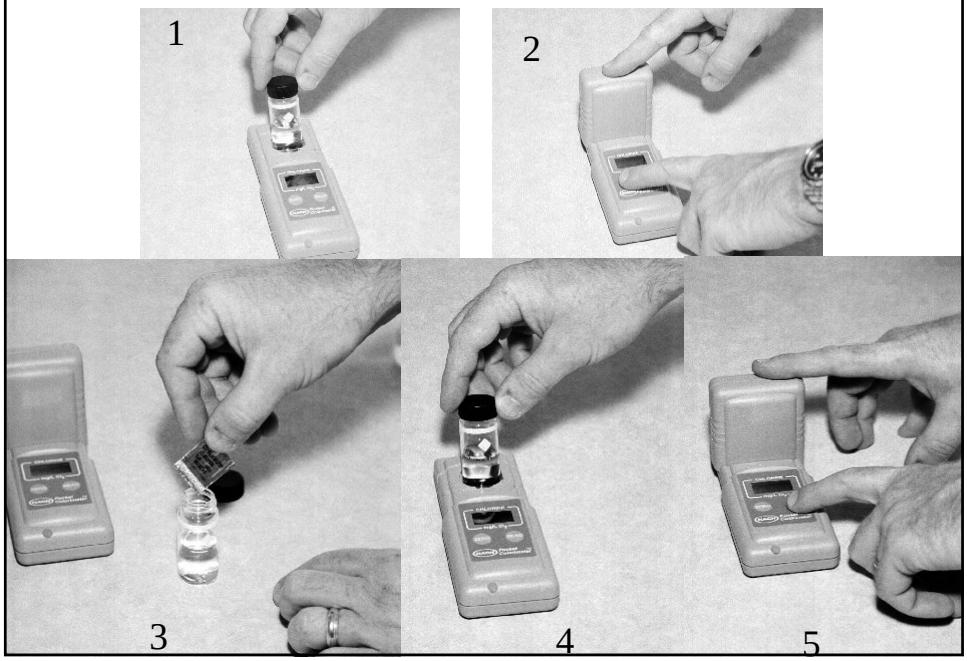
Description	Cat. No.	Range	Smallest Increment	Method	Approx. No. of Tests	Price
Chlorine, Free (F)[DW] & Total (T)[DW,WW]	46700-00	0-4.50 (T) mg/L	0.1 mg/L	DPD	50	299.00
		0-2.00 (F)(T) mg/L	0 .01 mg/L	DPD	100	



Free Chlorine with the Hach Pocket Colorimeter (Low Range Method)

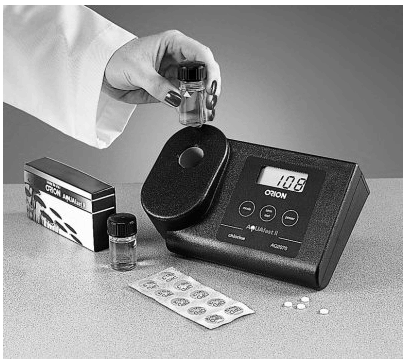
1. Fill a 10-mL cell to the line with deionized water (blank), cap.
2. Remove instrument cap.
3. Place the blank in the cell holder with the diamond mark facing you. Tightly cover the cell with the instrument cap (*flat side should face the back of the instrument).*
4. Press zero. *The instrument will turn on and eventually show 0.00.*
5. Remove the cell from cell holder.
6. Fill a cell to the 10-mL line with sample.
7. Add the contents of one DPD Free Chlorine Power Pillow to the sample cell. Cap and shake gently for 20 seconds. (*Total Chlorine Pillow for Total Chlorine*)
   Note: some powder will not dissolve but will not affect accuracy.
8. Within 1 minute after adding the DPD to the sample, place the prepared sample in the cell holder. (*3 minutes for Total Chlorine*)
9. Tightly cover the cell with instrument cap.
10. Press read. *The instrument will show --- followed by the results in mg/L free chlorine. If sample temporarily turns yellow after adding the DPD or flashes 2.20 (over-range), dilute a fresh sample with dionized water and repeat the test.*

HACH chlorine DPD sample analysis



Orion's Chlorine system

Instruments	Orion Cat. No.	Measurement Range	No. of Tests
Chlorine (free & total)	AQ2070	0.05 to 6.0 mg/L	50



Our Recommended QC Activities for the DPD Chlorine Method

- ✪ Use colorimeter-based methods like those available from Hach and Orion
- ↙ Use secondary standards (if available) to check calibration daily. (*e.g., Hach Secondary Standard Kit*). If secondary standards are unavailable, check calibration with at least one primary standard solution and a blank daily.
- ↙ Use primary standards at least monthly to verify secondary standards
- ✪ Make duplicate measurements of at least one sample weekly
- ✪ Test a matrix spike monthly using commercial standards.
- ✪ Always document testing, response of standards in a logbook or bench record , and any maintenance daily.
- ✪ Always clean-up spillage as it occurs.
- ✪ Thoroughly clean colorimeter monthly following manufacturer's recommendations.

Primary Standards	**Typically less stable materials or solutions used to verify secondary standards. ; a "double-check"**
Secondary Standards	**Stable materials used to check and verify instrument performance**

HACH Chlorine testing kit

Color Wheel Bias

Hach Color Wheel DPD Chlorine Test

Observed Free Chlorine Concenteration (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
Average	0.98	0.88	1.02
Range	0.8 - 1.1	0.75 - 1	0.9 - 1.2

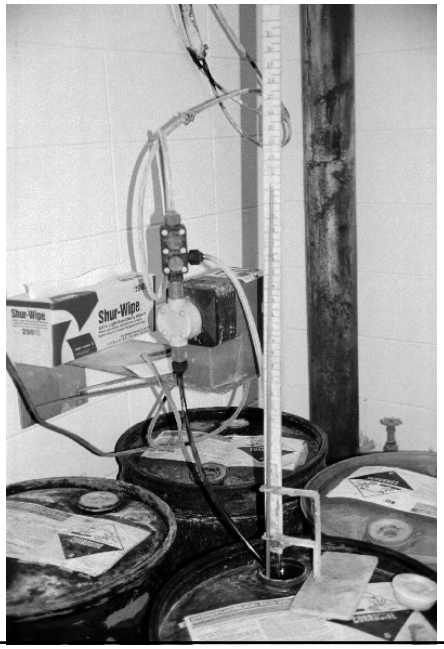
DPD Pocket Digital Colorimeter measurement: **0.71 ppm

Date: 10/16/00

Fluoride

Fluoride instrumentation/reagents provided by:
HACH
Orion

FLUORIDE & Fluoridation



FLUORIDE & Fluoridation

What is Fluoride?

... a common element in the earth's crust,
present in groundwater naturally from trace concentrations to **5 mg/l**

Sources

Food and drinking water are the main sources
Fluoride is frequently added to products such as toothpaste.

Fluoride and Tooth Decay

Fluoride increases tooth enamel resistance to acids that begin tooth decay
Levels of 0.7 - 1.2 mg/l in drinking water can reduce cavities by 40 - 5[illegible]%

Dental Fluorosis

Fluoride concentrations in drinking water higher than **2 mg/l**

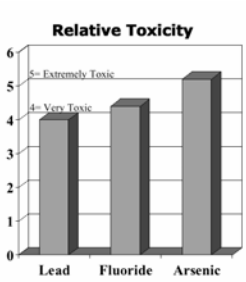
depends on concentration, amount consumed and supplemental ingestion

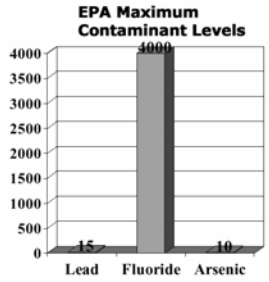
Mild forms of fluorosis: small white patches on the teeth.
Moderate forms: brown patches and minute pitting of enamel occur.
Severe forms: widespread deep brown/black stains and excessive pitting.
Above 4 mg/l can cause a rare, crippling disease called skeletal fluorosis.
Typically from exposure to levels of 10-20 mg/l over 10 to 20 years.

Fluoridation IS controversial

The Fluoride Risk
Evidence of a link to Cancer
Newsweek

"Water contains a number of substances that are undesirable, and fluorides are just one of them"
Dr. F. A. Bull, State Dental Director





"..public health officials have often suppressed legitimate scientific doubts in order to reassure the public."
- Oakland Tribune

"Effects of ingested fluoride is not within the purview of dentistry."
-California Board of Dental Examiners

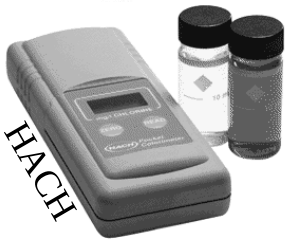
For example, if you have *cereal with milk and a Coke,* you have overdosed on fluoride. You have exceeded the American Dental Association's recommended daily dose

Fluoride Analysis options

QU ;44179 (7) TESTING EQUIPMENT.

- Equipment utilizing the SPADNS or electrode method is required.
- When also feeding phosphates, the electrode method is required.
- The Alizarin Visual method will be approved only in special cases where the owner can allocate the extra time needed for testing.

Pocket Colorimeter Analysis System



Electrode Method (ISE)
Linear Range = 0.1 to 10 ppm
Interferences: Virtually none (using ISA buffer)

SPADNS Method
Linear Range = 0 to 1.4 ppm (very non-linear > 1.4)
Interferences: Many

Parameter	Range	Smallest Increment	Method
Fluoride	0-2 mg/L	0.1 mg/L	*SPADNS

**greater sensitivity with bottled SPADNS reagent vs.AccuVac Ampule*

Interferences: ISE V. SPADNS

Substance	Method C (Electrode) Conc mg/L	Method C (Electrode) Type of Error*	Method D (SPADNS) Conc mg/L	Method D (SPADNS) Type of Error*
Aluminum (Al^{3+})	3.0	–	0.1†	–
Chlorine	5 000			Remove completely with arsenite
Color & turbidity				Remove or compensate for
Iron	200	–	10	–
Phosphate (PO_4^{3-})	50 000		16	+
Hexametaphosphate ([$NaPO_3$]) aka: Polyphosphate	50 000		1.0	+

Temperature Effects on Fluoride Results

Temperature Degrees Centigrade	True Fluoride mg/L	Measured fluoride SPADNS mg/L	Measured fluoride ISE mg/L
4 (39°F)	1.0	1.5	1.14*
10 (50°F)	1.0	1.5	1.27*
20 (69°F)	1.0	1.0	1.0
33 (91°F)	1.0	1.4	0.85*
50 (121°F)	1.0	0.8	0.77*

*** drifting problems**

Effect of Phosphate Additives on Fluoride Testing

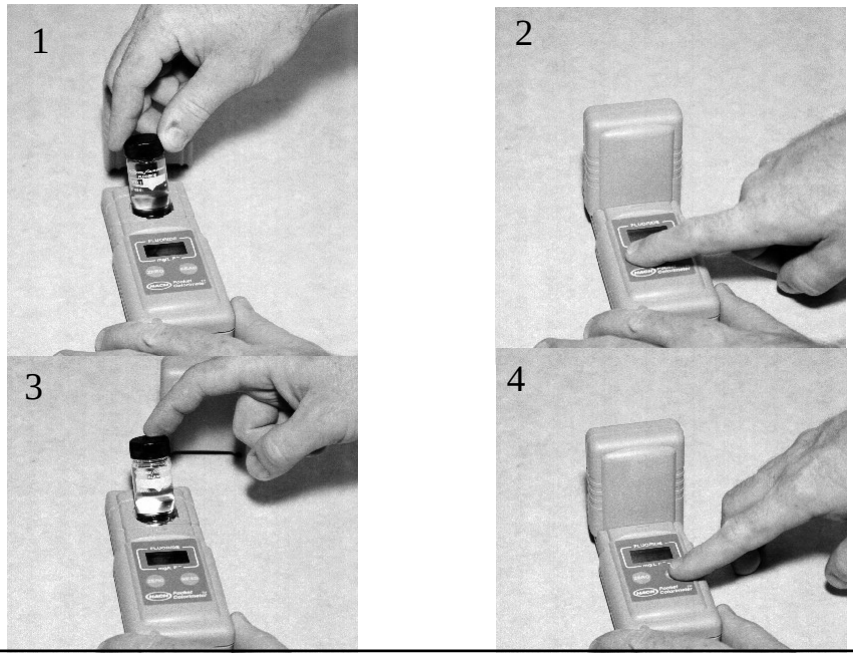
Ortho-phosphate	True F-	Measured F- with SPADNS	Measured F- with ISE
mg/L PO4	mg/L	mg/L	mg/L
0	1.00	1.00	1.01
0.5	1.00	1.30	1.01
1.0	1.00	1.55	1.02
1.5	1.00	1.65	1.00

Calibration of the SPADNS Fluoride Method and Hach Pocket Colorimeter

Preliminary check of on-board calibration with secondary standards

1. Insert std #1 in cell holder. Tightly cover instrument cap (*flat side should face back of the instrument*).
2. Press zero. *instrument will turn on, flash --- and eventually show 0.00*.
3. Remove std #1 from cell holder.
3. Insert blank from standards kit in cell holder and tightly cover instrument cap(*flat side should face back of the instrument*).
4. Press read. *The instrument will show the fluoride results in mg/L.*
4. Repeat steps 1-3 for remaining standards. *All results must be within the tolerances provided with the secondary standards kit*.
5. If results of all stds are acceptable, proceed with samples. If not within tolerance, clean stds and colorimeter and re-check. If still outside tolerance, consult manual. Re-calibration or e service may be required.

HACH Fluoride SPADNS QC checks



Measurement of Fluoride in Samples using the SPADNS Method and Hach Pocket Colorimeter

1. Fill an AccuVac** with (blank): Invert the vial and break the neck on the bottom of a beaker containing deionized water. *The correct amount will be drawn into AccuVac*.
2. Carefully cover broken end and invert at least 5-8 time to mix.
3. **<u>Repeat steps 1 and 2 for sample</u>**. Allow sample and blank to sit for 1 minute.
4. Place AccuVac with ***blank*** in cell holder and tightly cover with instrument cap (*flat side should face back of the instrument*).

⇨ Press zero. The instrument will turn on and eventually show 0.00.

⇨ Remove AccuVac from cell holder.

⇨ Place sample AccuVac in cell holder. Tightly cover with instrument cap.

⇨ Press read. *The instrument will show the fluoride results in mg/L.*

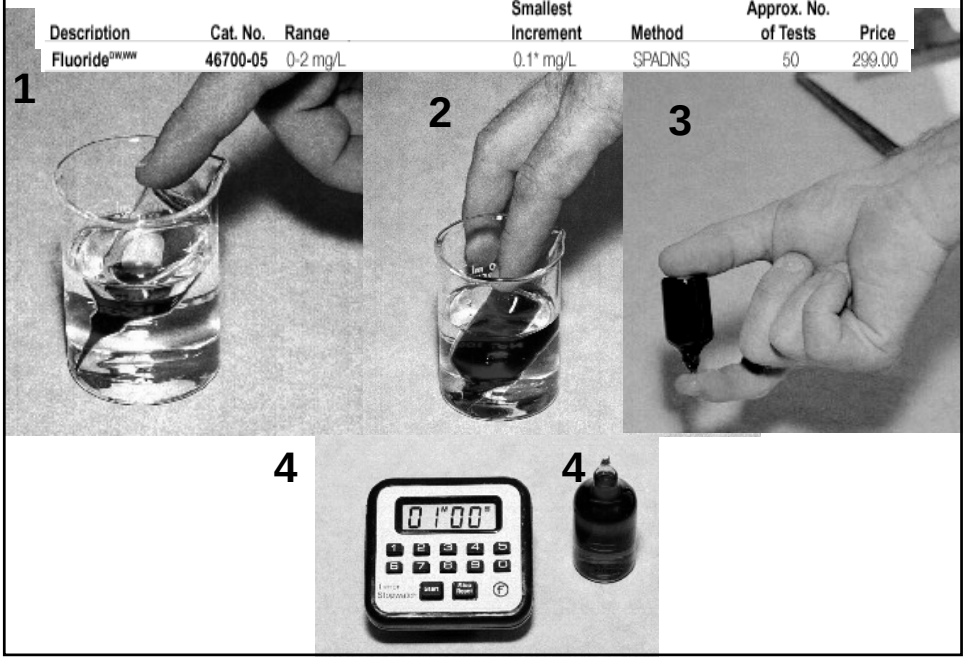
⇨ Repeat process for remaining samples.

**** Bulk SPADNS (2 mL/10 mL sample) may be substituted for AccuVacs**

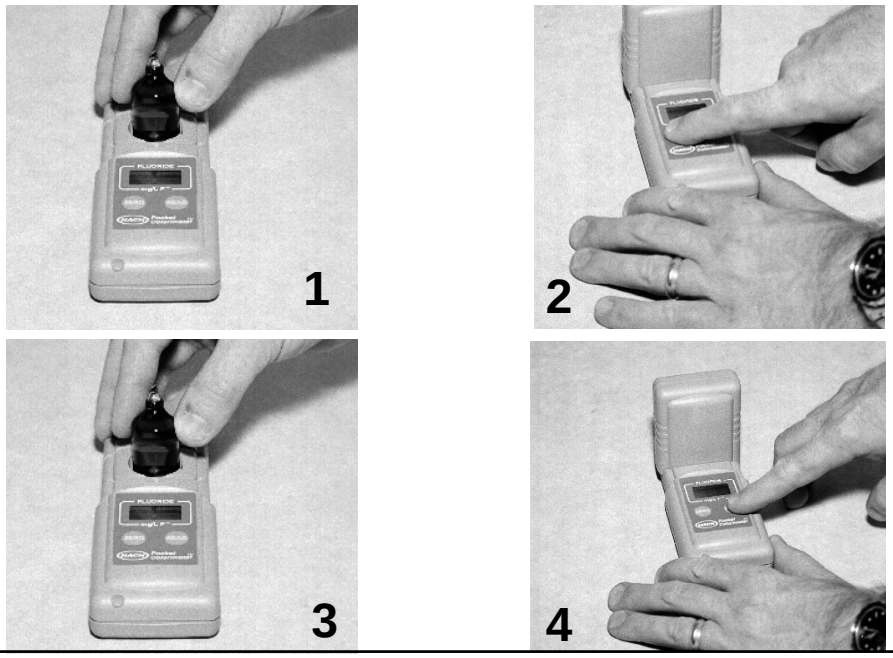
Note: the SPADNS method is inverse chemistry. The color decreases in intensity as the fluoride level increases.

HACH Fluoride SPADNS procedure

Description	Cat. No.	Range	Smallest Increment	Method	Approx. No. of Tests	Price
Fluoride[DW,WW]	46700-05	0-2 mg/L	0.1* mg/L	SPADNS	50	299.00



HACH Fluoride SPADNS procedure -2



Other Options for Making Fluoride Measurements with the SPADNS Method

- ☒ Orion Research offers a similar direct-reading, portable instrument that may be used with commercially prepared SPADNS solutions.
- ☒ Recommend using at least one standard solution and a blank to check the Orion or other direct reading instruments daily.
- ☒ Any colorimeter or spectrophotometer may be used for fluoride testing using the method outlined in Standard Methods for the Examination of Water and Wastewater, method 4500-F^-D.

Our Recommended QC Activities for the SPADNS Fluoride Method

- ↙ Use secondary standards (if available) to check calibration daily. (*e.g., Hach Secondary Standard Kit*). If secondary standards are unavailable, check calibration with at least one primary standard solution and a blank daily.
- ↙ Use primary standards at least monthly to verify secondary standards
- ↙ Make duplicate measurements of at least one sample weekly
- ↙ Test a matrix spike monthly using commercial standards.
- ↙ Always document testing and response of standards in a logbook or bench record daily.
- ↙ Always clean-up spillage as it occurs.
- ↙ Thoroughly clean colorimeter monthly following manufacturer's recommendations.
- ↙ Document all maintenance --including battery replacement-- in a logbook

Tips for Using the SPADNS Method

- Always warm samples to room temperature before testing (*see note*)
- Never collect the sample immediately down-stream of the fluoride injector.
- Never collect the sample in a bottle containing sodium thiosulfate, a de-chlorinating agent.
  Thiosulfate will cause erroneous results.
- Never sample immediately down-stream of the chlorine injector.
  Chlorine will cause a negative interference.
- Always use the ISE method if phosphate blends are added to the water system.
  Phosphate will cause a positive interference.

Note: ***Samples must be within 2°C of manufacturers calibration conditions. Failure to do so will result in erroneous results.***

HACH Fluoride SPADNS equipment

ISE Procedures

CDC Recommendations for Fluoridation, 1995

1. **Operators should use the ion electrode method of fluoride** analysis because chemicals (e.g., alum) used in a surface water plant will cause fluctuating interferences in the colorimetric method (SPADNS) of fluoride analysis .

2**. A magnetic stirrer must be used** in conjunction with the ion electrode method of fluoride analysis.

3. **The colorimetric method (SPADNS) of fluoride analysis can be used where no interference occurs or where the interferences are consistent** (e.g., from iron, chloride, phosphate, sulfate, or color). The final fluoride test result can be adjusted for these interferences. State laboratory personnel, the state Water Supply engineer, and the water plant operator should reconcile the interferences and make the appropriate adjustment.

Other pertinent NR 809 Fluoride reqs.

NR 809.705(1)(a) ... maintain the fluoride concentration within the range of 1.0 to 1.5 mg/L (***goa is 1.1 in WI***)... for optimum dental benefits.

(b) The monitoring program shall include:

1. ...**results of daily fluoride tests...**
2. **One sample per month** ... **submitted to the SLH**

(c) **[it] shall be a portion of a split sample**

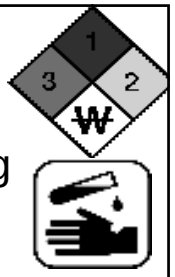
The **fluoride concentration obtained by the operator shall be noted** on the data sheet prior to submission to the state laboratory.

General Safety Issues - Fluoridation

Exposure to fluoride chemicals

- Wet or dry chemicals on the skin ↖ thoroughly wash the contaminated skin area immediately.
- Clothing contaminated with a wet chemical ↖ remove the wet contaminated clothing immediately.
- Clothing contaminated with dry chemicals ↖ change work clothing daily no later than the close of the work day

Safety Issues - Fluosilicic Acid



Fluosilicic acid

a. The operator should wear the following PPE:
   - Gauntlet neoprene gloves with cuffs, which should be a minimum length of 12 inches (30.5 cm);
   - Full face shield and splash-proof safety goggles; and
   - Heavy-duty, acid-proof neoprene apron or acid-proof clothing/shoes.

b. A safety shower and an eye wash station must be available and easily accessible.

Fluoride Summary

- ☑ Fluoridation & fluorosis
- ☑ SPADNS procedure
- ☑ Ion-selective electrode procedure
- ☑ Interferences
- ☑ Demonstrate method options
- ☑ Review regulatory requirements
- ☑ Review Quality Control options
- ☑ Safety

Questions?

Phosphate

Phosphate instrumentation/reagents provided by:
HACH
Orion

PHOSPHATE
(corrosion & sequestration)

Orthophosphate:
Used for corrosion control.

Zinc: A catalyst which aids in corrosion control when used with phosphates.

Polyphosphate:
Used to sequester iron and manganese

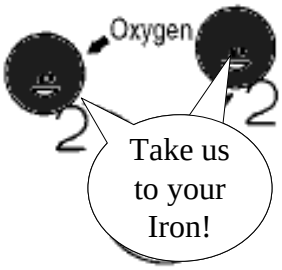
Why sequester?

Iron and Manganese Problems

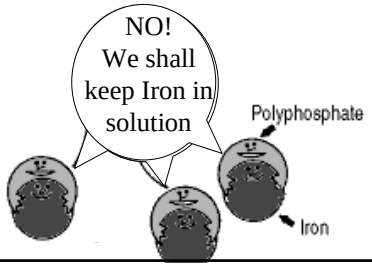
Effects on Household Water

- Neither iron nor manganese in water present a health hazard.
- Aesthetically, however, they may cause taste, staining and accumulation problems.
- Iron will cause reddish-brown staining of laundry, porcelain, dishes, utensils, and even glassware.
- Manganese acts in a similar way but causes a brownish-black stain. Soaps and detergents do not remove these stains, and the use of chlorine bleach can actually intensify the stains.
- For most individuals 0.3 parts per million (ppm) of iron and 0.05 ppm of manganese is objectionable.

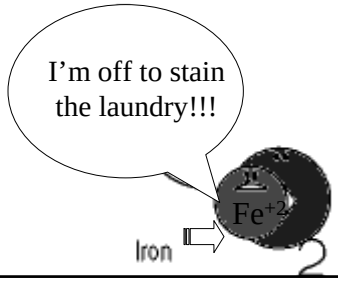
Sequestration



Polyphosphates out-compete oxygen for the iron



Oxygen + iron = iron oxides = red stains



The Objective

What are we trying to do here?

1. Produce a blue color equivalent to the amount of PO_4^{-3} present

PO_4^{-3}

$(NH_4)_2Mo_2O_7 + C_8H_4K_2O_{12}Sb_2 + PO_4^{-3} \longrightarrow H_3PMo_{12}O_{40}$

$H_3PMo_{12}O_{40} + C_6H_8O_6 \longrightarrow$ Molybdenum blue

Phosphate Interferences

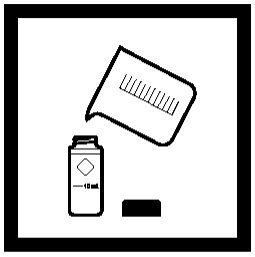
Contamination!

- Wash glassware well, using a non-phosphate detergent
- THROW OUT your Alconox (~8.7% phosphorus)
- Rinse with dilute (1%) hydrochloric acid
- Even new glassware needs to be washed
- DO NOT touch inside glassware with bare hands!
- DO NOT smoke anywhere near testing or glassware storage
- Segregate glassware for phosphorus (*but still rotate glassware*)

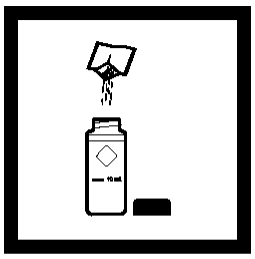
Method 8048

PHOSPHORUS, Reactive (0 to 3.00 mg/L PO_4^{3-})

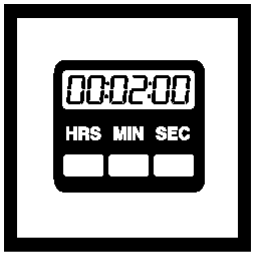
Description	Cat. No.	Range	Smallest Increment	Method	Approx. No. of Tests	Price
Phosphate[MW]	46700-06	0-3.00 mg/L	0.01 mg/L	PhosVer® 3	100	299.00



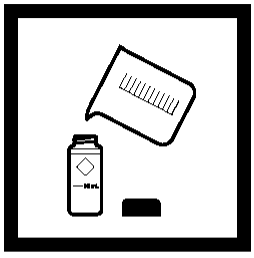
1. Fill a 10-mL cell to the 10-mL line with sample.

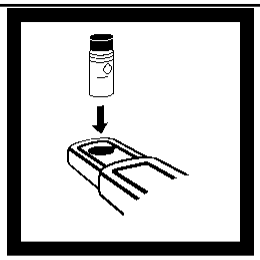


2. Add the contents of one PhosVer 3 Powder Pillow to the cell (the

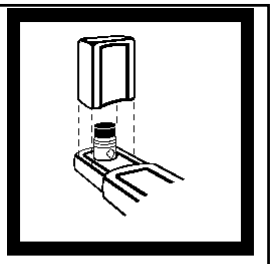


3. Wait at least 2 minutes (but no more than 10 minutes) for full color

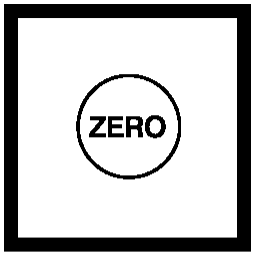




5. Place the blank into

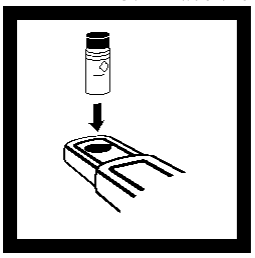


6. Tightly cover the

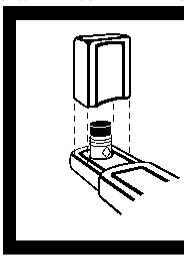


7. Press: **ZERO**

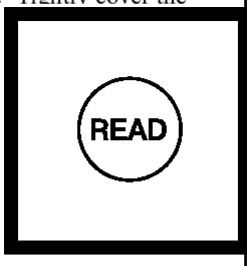
The instrument will turn on, and the display will show - - -, followed by **0.00**.



8. Place the prepared sample into the cell holde



9. Tightly cover t sample cell with th



10. Press: **READ**

The instrument will sho - - -, followed by the resu in mg/L phosphate (as PO_4^{3-}).

To convert reading from	To	Multiply by
mg/L PO_4^{3-}	mg/L P_2O_5	0.747
mg/L PO_4^{3-}	mg/L P	0.326

Phosphate 1 HR Auto-Test™ 0-80 ppm

Test Procedure

1. Fill the sample cup to the 25 mL mark with the sample (**fig. 1**).
2. Place the Auto-Test cuvette in the sample cup. Snap the tip by pressing the cuvette against the side of the cup. The cuvette will fill, leaving a small bubble to facilitate mixing (**fig. 2**).

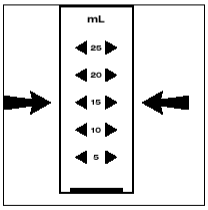


Figure 1

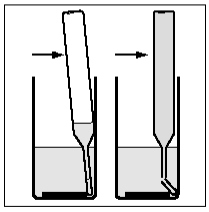


Figure 2

3. Mix the contents of the cuvette by inverting it several times, allowing the bubble to travel from end to end each time. Wipe all liquid from the exterior of the cuvette.
4. Insert cuvette into AQ4000. Align the ▼ on the Auto-Test cuvette with the ◆ on the adapter to obtain a continuous beeping and view ******* across the display. If ******* and beeping is not observed, rotate cuvette right or left to initiate the measurement.
5. Immediately cover the cuvette with the cuvette cover.
6. The AQ4000 will be begin a 5 minute countdown. After the countdown is completed, the AQ4000 will automatically proceed to the measure mode.
7. Record the concentration reading from the AQ4000 display as either mg/L or ppm PO_4 or log measurement into the data logger by pressing the

The Phosphate 1 HR Auto-Test method employs the vanadomolybdophosphoric acid chemistry.[1,2]

Test N' Tube instructions

- ☑ Add 5.0 mL sample to a "Reactive Phosphorus" Test n' Tube Vial
- ☑ Zero on this sample
- ☑ Add one PhosVer 3 Powder Pillow (does NOT fully dissolve)
- ☑ Cap; shake 10-15 secs.
- ☑ Time for 2 minutes
- ☑ Put vial into instrument and read*

** Read samples between 2 and 8 mins. after PhosVer 3 addition*

Test N' Tube interferences

Metals (a number of them) -	But at levels you would not routinely encounter in wastewater
Arsenates -	At any level. But these should be quite rare
Color/ High Turbidity -	Inconsistent results. Acid in powder pillow may dissolve some of the suspended particles. Also, variable desorption of orthophosphate from the particles
Highly buffered samples or pH extremes -	May exceed buffering capacity of the reagents and require pretreatment.

Relevant NR 811 Sequestration reqs

NR 811.51 Sequestration. (1) SEQUESTRATION BY POLYPHOSPHATES.

- suitable only for low levels of iron and manganese,
- Where phosphate treatment is used, chlorine residuals shall be maintained in the system.
- In addition:
  - (a) Polyphosphates may not be applied ahead of iron and manganese removal
  - (d) Stock phosphate solution shall be kept covered and disinfected [with a] 10 mg/1 free chlorine residual.
  - (e) total phosphate applied may not exceed 10 mg/l as PO_4
  - (f) ***appropriate phosphate testing equipment*** shall be provided.

Phosphate Addition for Sequestering

➔Feed prior to chlorination.
➔Should not be used with:
- combined iron and manganese over 1.0 mg/l
- and/or manganese over 0.3 mg/l.

➔Approx. feed rate: 2 mg/l of phosphate per mg/l of combined Fe/Mn.
➔Much higher (*as high as 8:1*) if
- pH is over 7.8, or if
- there is pre-oxidation of the iron or manganese.

➔Will vary considerably for a specific product.

Problems:
May be aggressive to AC pipe or cement linings, (*reacts w/calcium*).
This ↓ the effective calcium level, ⇨ more corrosive to plumbing.
Corrosion is worse if sulfates, chloride, or dissolved oxygen is high.
Nutrient for bacteria and algae. Can cause algae blooms ….

Phosphate Summary

☑ Sequestration: Fe, Mn

☑ Phosphate procedures

☑ Demonstrate Test n' Tube

☑ NR 811 requirements

☑ Safety

Questions?

*Other Colorimeter Kits Available for Chlorine, Fluoride and Phosphate**

Hanna Instruments

Orbeco-Hellige

Images courtesy of NCL of Wisconsin, Inc

Where can I purchase standards for Chlorine, Fluoride, Phosphate and pH

- Most scientific specialty companies
- NCL
- Hach Chemical Company
- Fisher
- VWR-Scientific Products
- Orion Research
- USA Bluebook
- Many others

Treatment Chemical Stability

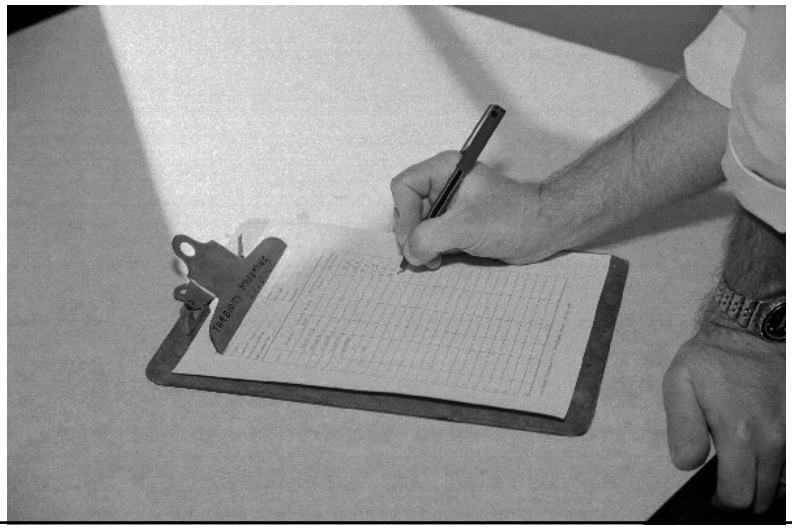
Chemical	Open	Unopened
Hypochlorite	--------	3 mo.
Hypochlorite, diluted	1 mo.	--------
note: loses about 30% effectiveness when diluted 50%		
Fluosicilic Acid	12 mo.	12 mo.
Phosphate blend	12 mo.	12 mo.
note: discard if any growth develops		
Caustic Soda	12 mo.	12 mo.

Lab Chemical Reagent Stability

	Chemical	Open	Unopened
sK	Buffer solutions	3 mo.	12 mos.
	NOTE: pour off into small container; replace weekly		
Fkorulqh	DPD- Powder or pills	12 mo.	12 mo.
	Secondary gel standards	12 mo.	12 mo.
	Primary standards (ampuls)	12 mo.	12 mo.
	Primary standards (permanganate)	6 mo.	6 mo.
Iorulgh	SPADNs- Powder or pills	12 mo.	12 mo.
	SPADNs- solution	6 mo.	6 mo
	Secondary gel standards	12 mo.	12 mo.
	Primary standards	6 mo.	6 mo.
Skrvskdwh	Color reagent- Powder	12 mo.	12 mo.
	Combined color reagent solution	6 hr.	**6 hr.**
	Primary standards (store at4 °C)	6 mo.	6 mo.

Documentation

Document!!!



General Documentation Tips for Reagents and Standards.

- Date and initial all reagents and standards when received.
- Replace reagents and standards before they expire
- Discard standards or reagents if growth develops or they become discolored.
- Store reagents and standards away from direct sunlight.
- Only refrigerate materials if recommended by the manufacturer.
- Keep a logbook to document lot numbers and expiration dates of standards. Reference lot numbers on your bench/testing records.

General Documentation

- Date, time, analyst doing the testing
- Method used/method reference number
- Response of standards, duplicates, monthly spikes, etc.
- Simple logbook format (for standards and maintenance)
- Keep it simple and easy so you will use them

Why Keep a Logbook?

- Records support the validity of your testing
- Helps troubleshoot problems.
- Good preventative maintenance tool particularly when there is more than one operator.
- Adds credibility to your results and ability to operate system.
- It will impress the City Administrators/Board Members and instill greater public confidence.
- Allows better control of water treatment chemicals which improves effectiveness and can reduce cost.
- Better yet…keeps those pesky DNR Engineers off your back!!

Analysis Logs - suggestions

pH Logbook

Maagville, WI PWS ID#: 99704818. Well #1

			Sampling		Low CAL	High CAL	Check Buffer		
Date	*Time*	*Collector*	*Location*	*Sample*	*BUFFER pH*	*BUFFER pH*	*True pH*	*Meas. pH*	*Comments and/or Corrective Action*

Chlorine Logbook

Maagville, WI PWS ID#: 99704818. Well #1

			Sampling	Analysis	Sample	Check Standard		
Date	*Time*	*Collector*	*Location*	*(F)ree or (T)otal*	*Cl_2 ppm*	*True Cl_2*	*Meas. Cl_2*	*Comments and/or Corrective Action*
						0.5 ppm		

Recommended concentration for check standard is 0.5 ppm

Analysis Logs - suggestions

Fluoride Logbook

Maagville, WI PWS ID#: 99704818. Well #1

				Fluoride Results, ppm			
			Sampling		0.60 ppm Std	1.40 ppm Std.	
Date	Time	Collector	Location	Sample	± 0.2 ppm	± 0.2 ppm	Comments and/or Corrective Action

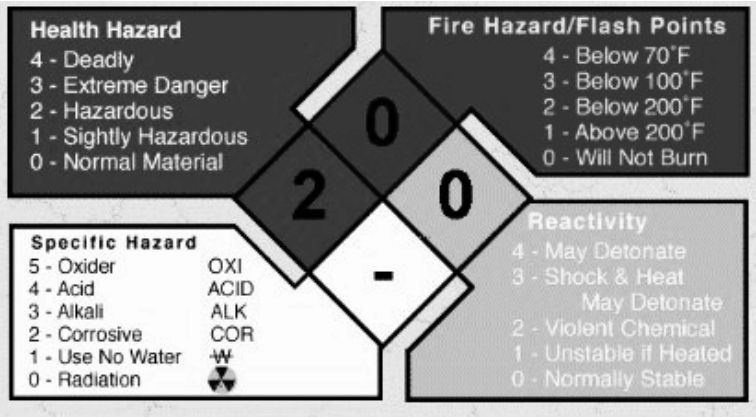
Ortho-phosphate Logbook

Maagville, WI PWS ID#: 99704818. Well #1

			Sampling	Sample	Check Standard		
Date	Time	Collector	Location	PO_4 ppm	True PO4	Meas. PO4	Comments and/or Corrective Action
					1.0 ppm		
Recommended concentration for check standard is 1.0 ppm							

NFPA Code Explanations

blue red



white yellow

General Safety Issues

- Never use the same volumetricware to mix hypochlorite and fluoride soultions. *These will react violently to produce chlorine gas. Can result in serious injury--even death.*
- Read labels carefully! (*F- tube in OCl- tank*)
- Make personal protective equipment (PPE) readily available.
- All facilities: have an eyewash and safety shower available.
- Maintain a file of MSDS information--ring binder or posted.
- All operators must read and understand MSDS information
- Have a phone available; conspicuously post emergency numbers.
- Clearly label all volumetric equipment.
- Have spill containment and treatment supplies available.
- Train all personnel in spill management.

“Grand-fathered” facilities

What if your facility does not meet current code specifications?

- Add a self-contained ventilation device over HF and chlorine supplies.
- Add portable eyewash and hand shower where faucets are available.
- *If faucets not available, add a SELF-CONTAINED EYEWASH STATION.*
- *Create a portable supply kit.*

Safety Equipment

Minimum recommended safety considerations

- Goggles and safety shield
- gloves
- sleeves
- respirator (*required if using chlorine gas*)
- sink-based eyewash with showerhead
- or…portable eyewash station

Spill Control supplies

- Containment materials
- soda ash for HF
- materials for caustics

Minimum safety equipment needs

Eyewash station

Soda Ash

Spill Control

Spill response pack

Acid Cleanup kit

Drench Hoses

Fisherbrand Drench Hoses
With squeeze valves

Single, spray-type outlet head delivers a soft, wide spray to user's eyes, face or body. Self-regulating flow control ensures soft flow regardless of water pressure. Internal filter removes particles and debris from water. Head is protected against dust and dirt by a flip-top dust cover where water flow automatically swings cover off outlet head.

Chrome-plated forged brass squeeze valve is activated by a stainless-steel lever handle. Valve closes when handle is released.

Drench hose is 8 ft. (2.4m) reinforced PVC. Maximum working pressure: 300psi. Recommended pressure: 80psi.

Eyewash/Drench Hose Units

The spray head assembly can be left in place for use as a fixed eyewash or the head assembly can be removed for use as a drench hose. Ideal for areas where space-saving designs are required.

Dual spray-type outlet head delivers a soft, wide spray to user's face or body. Self-regulating flow control ensures soft flow regardless of water pressure, and internal filter removes particles and debris from water. Head is protected against dust and dirt by a flip-top dust cover which swings off automatically when the water flow starts.

Cost: less than $300

Chrome-plated forged brass squeeze valves are activated by a stainless-steel lever handle. Valves have locking clip that engages when handle is pressed, providing hands-free operation. Valves stay open until locking clip is released.

Drench hose is 8 ft. (2.4m) reinforced PVC. 300psi maximum working pressure; maximum recommended pressure is 80psi. Available for deck or wall mounting. Deck mount model has chrome-plated brass flange with handle locator guide to ensure that spray heads and handle face forward. Wall mount model comes with epoxy-coated bracket with spring clips to ensure that spray heads and handle face forward.

Tips for Mixing Chemicals

(diluting fluoride, caustic or hypochlorite solutions)

- Always label all chemicals with NFPA approved label including concentration of solution.
- Double check containers before mixing
- Wear chemical resistant gloves, face shield or safety goggles, coated apron and coated sleeves.
- Always mix chemicals in a well ventilated area.

Do what you oughta….always add acid TO water

- Use the ***A&W rule***: add acid or base to water. Never add water to acid or base-it can react violently, super-heat, produce excess fumes, splash and cause instantaneous chemical burns.

Tips for Mixing Chemicals

(diluting fluoride, caustic or hypochlorite solutions)

- If making large dilutions that require gallons of chemical, use graduated pails (available from most safety and scientific specialty companies).
- Always mix diluted solutions carefully with a large plastic paddle between additions and at the end.
- Clean-up all spills, rinse buckets, graduated cylinders and paddles after Use. Store in a clean, dry area.

What if there is a chemical spill???

- Follow your Emergency Response Plan
  - •should have provisions to deal with evacuation and spill containment.
- If hydrofluosilicic acid is mixed with hypochlorite solution, leave the building immediately (*chlorine gas will be given off-this is a dangerous gas which can kill*)
- If acid or base alone is spilled, try to minimize the spread with spill booms, apply appropriate neutralizer; leave the area!!!!
  - •Soda ash & sand work well for acids
  - •Commercial base neutralizer for caustic solutions
- Caution: Dangerous fumes can be given off if large amounts of caustic or acid are spilled and neutralizer is applied. Always have Emergency Response Team deal with large spills (greater than a quart of material).
- Always wear personal safety equipment when cleaning up spills (chemical resistant gloves (Nitrile is good), coated aprons coated sleeves, etc. *These materials can be purchased in a spill clean-up kit ($100-200)*

Do I need a self-contained breathing device (SCBA)??

* If you use chlorine gas you must have a NIOSH approved SCBA available-this should be part of your Emergency Response Plan.
* If you have SCBA, you must comply with the OSHA Respirator Protection Rules.
  These rules require yearly training, fit testing, physical evaluation, etc.
* If you don't have a plan in place, contact Wisconsin Rural Water or your DNR Water Supply Engineer for assistance.
* Consult www.osha.std if you would like more information about personal protection in the work place.

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For More Information

State Lab web site:
http://www.slh.wisc.edu/outreach/
LabCert web site":
http://www.dnr.state.wi.us/org/es/science/lc/