The "Nuts & Bolts" of Chlorine Chemistry

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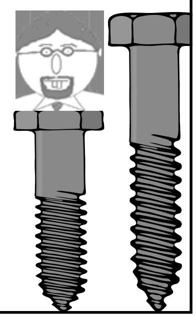
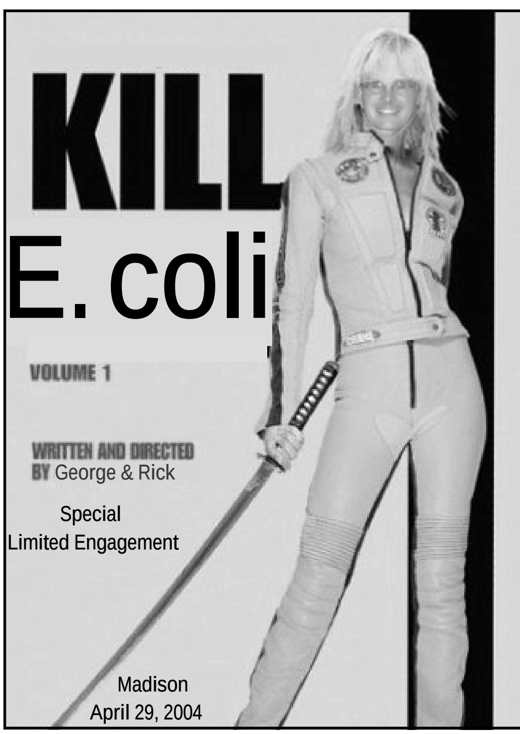




Any reference to product or company names does not constitute endorsement by the Wisconsin State Laboratory of Hygiene, the University of Wisconsin, or the Department of Natural Resources.

Disclaimer

Getting the Best Chlorine Residual Data

- Measurement of total residual chlorine (TRC) at levels low enough to meet wastewater discharge limits has been (historically) difficult at best.
- Methods approved for measurement of chlorine in wastewater are often technically demanding and time consuming.
- Commercial test kits are available to simplify these procedures. However, commercial test kits often gloss over the very important aspects of the testing, including calibration, spiking and other quality control (QC) processes.

Focus Points: WWTPs & Chlorine

- kill the bugs

  Disinfection
  (Chlorination)

- kill the bug killer

  De-Chlorination

- meet permit limits

The enemy: Primary target bugs

Coliform bacteria — Common soil & intestinal bacteria

⇩

Fecal Coliforms — Is the source warm-blooded animals?

⇩

Escherichia coli ("E. coli") — Clear indication of human sewage or animal waste.
Many "harmless" strains

⇩

E. coli O157:H7
- Very harmful strain
- 2-7% infected develop hemolytic uremic syndrome (HUS)
- 3-5% w/ HUS die

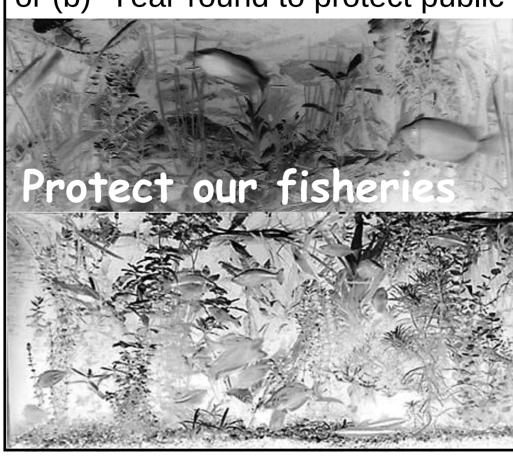
NR 210.06 Disinfection requirements

(1) Disinfection shall be required of dischargers subject to the provisions of this chapter ...

Disinfection shall be required:

(a) From May 1 through September 30 annually to protect recreational uses,

or (b) Year-round to protect public drinking water supplies.



NR 210.06 Disinfection requirements

(2) Where disinfection is required, the following effluent limitations shall apply:

(a) The **<u>geometric mean of the fecal coliform bacteria</u>** for effluent samples collected in a <u>period of 30 consecutive days</u> may <u>not exceed 400 CFU/100 ml</u>.

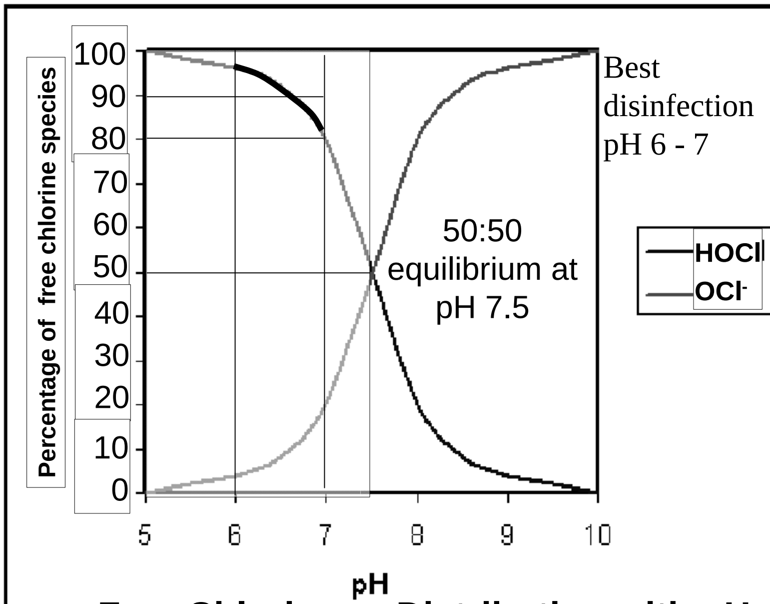
(b) When chlorine is used for disinfection, the **<u>daily maximum</u>** <u>TRC concentration may not exceed 0.1mg/l</u>.

In addition, when chlorine is used for disinfection, a dechlorination process shall be in operation for the period during which disinfection is required.

Note: The 0.1 mg/l total residual chlorine limit reflects best analytical technique for domestic wastewater effluents.

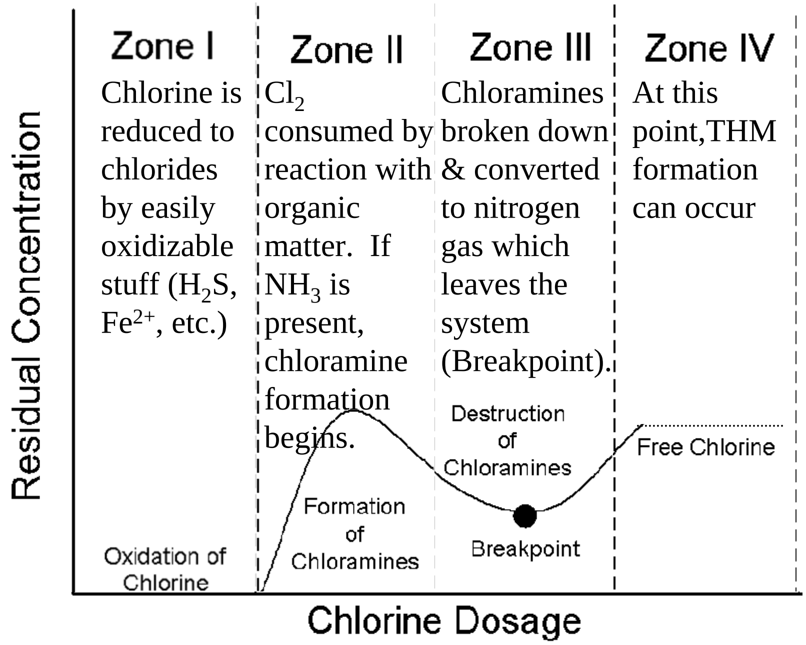
An effluent limitation for total residual chlorine based on best available technology for dechlorination of effluents was <u>determined to be below detection levels of currently available analytical techniques.</u>

Chlorination Basics



Free Chlorine --- Distribution with pH

Chlorination Basics



Chlorination Basics

- Determine your wastewater's chlorine demand
- Dose chlorine = Demand + "x"
- "x" typically about 1.0 ppm
- Shoot for a total residual target specified by basin engineer
- Check Chlorine level in contact chamber
- May want to test BOTH total and free Cl_2
- If you know that you have a **free** chlorine residual, you know you have adequate disinfection

Tips for Determining the Chlorine Demand and Dosing Rate

- Collect a sample of effluent prior to the chlorine contact chamber.
- Fill a series of beakers with sample and treat each with varying dosages of hypochlorite
- Mix the samples thoroughly and allow them to sit for the same length of time the effluent would be in the chlorine contact chamber.
- Keep the temperature of the solutions in the same range as the effluent
- After the desired contact time, test each solution for free and total residual chlorine, and pH.
- Use this information to determine the dosage that satisfies the demand and provides the desired residual chlorine level.
- Use the free & total residual chlorine levels and pH to assess the disinfection effectiveness
- Work with your engineer to adjust the chlorine and dechlorination feed rates based on the dosing tests.

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**

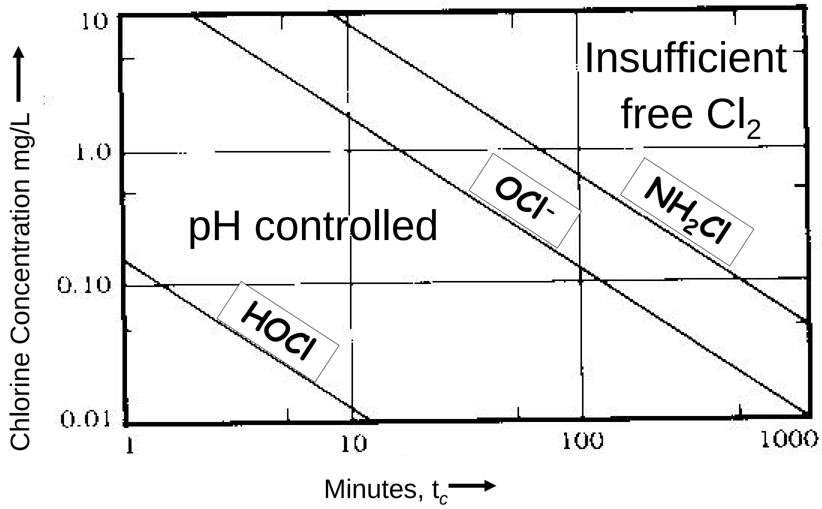
contact time

- 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

Each "log10 = 90% reduction; 4 log 10 = 99.99% reduction

Effectiveness of chlorine forms vs. E. coli

2-6 °C, 99% reduction



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

DE-Chlorination Basics

- Chlorine will dissipate passively
- Most use chemicals:

  sulfur dioxide (SO_2)
  sodium bisulfite ($NaHSO_3$)
  sodium sulfite (Na_2SO_3)

- Danger of chemicals is that they also pose a risk to aquatic life
- active agent is sulfite ion (SO_3^{-2})
- sulfite is an oxygen scavenger--lowers DO
- some chemicals introduce a BOD

Why is DE-chlorination So Important?

The Chlorine continuum (ppm)

0.2	0.1	0.037	0.015	0.012
Fish kill	Permit Limit	Permit Goal	LOD (ISE)	LOD (DPD)

<-------------- Fish stressed ------------->

MATERIAL SAFETY DATA SHEET

SECTION 1. PRODUCT IDENTIFICATION

PRODUCT NAME: Chlorine

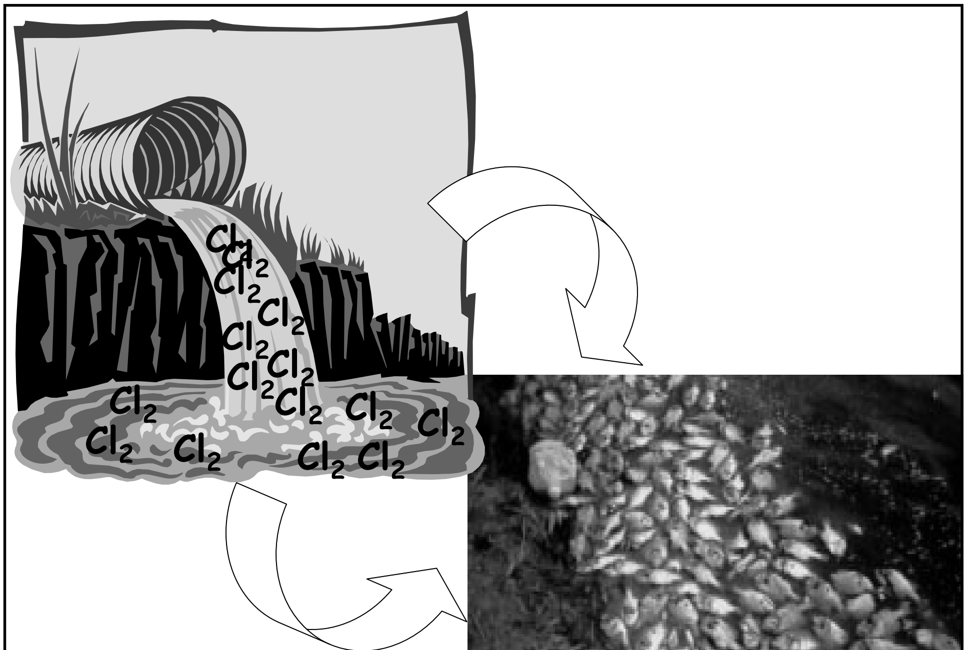
CHEMICAL NAME: Chlorine **FORMULA:** Cl_2

SECTION 12. ECOLOGICAL INFORMATION

AQUATIC TOXICITY: The following aquatic toxicity data are available for Chlorine:

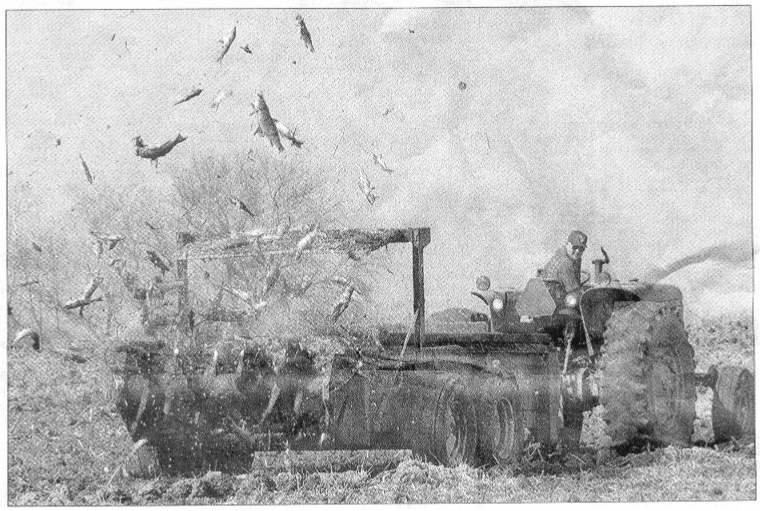
LC_{50} Bluegill: 0.44 mg/l (96 hours)
LC_{50} Yellow perch: 0.88 mg/l (1 hour)
LC_{50} Channel catfish (fingerling): 0.07 mg/l (96 hours)
LC_{50} Daphnia magna: 0.017 mg/l (46 hours)

To prevent stress, concentrations as low as 0.003 ppm may be required.
Water with adequate water circulation will be free of chlorine in $\leq$ 24 hours.



Deleterious effects

…which leads to something like this



Deleterious Effects II

Chlorination Balancing Act De-Chlorination

INSUFFICIENT | EXCESSIVE

Dangerous pathogens discharged
Beaches unsafe
permit violation

Cl_2
CHLORINATION

Cl_2 toxic to aquatic life
More toxics (THMs) produced
Requires more dechlorination
higher costs
permit violation

INSUFFICIENT | EXCESSIVE

Cl_2 toxic to aquatic life
fish kills
More toxics (THMs) produced
permit violation

$\cancel{Cl_2}$
DE-CHLORINATION

SO_3 scavenges O_2, drops DO
potential fish kills
higher costs
potential enforcement

What Other States Are Doing

Wisconsin:

- current permit limits set at 0.037 mg/L total residual chlorine (TRC)
- Accept 0.100 mg/L as an LOD

North Carolina:

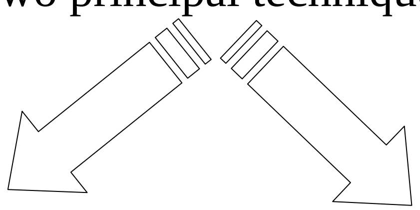
- current chlorine standards are 0.017 mg/L total residual chlorine (TRC) for trout waters
- 0.017 mg/L TRC as an action level for non-trout waters.

Pennsylvania:

- current permit limits set at 0.011 mg/L total residual chlorine (TRC)

Chlorine Analysis Options

Two principal techniques



Ion Selective Electrode (ISE)

DPD Colorimetric

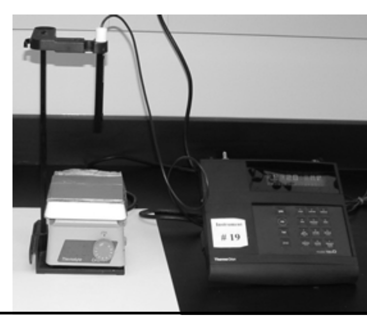
ISE

Key Equipment needed for ISE




- Electronic or mechanical, variable volume pipettors in the 100 to 1000 µL range

- Orion model 97-70 residual chlorine electrode
- pH/ISE meter
- Magnetic stir plate
- Magnetic stir bar



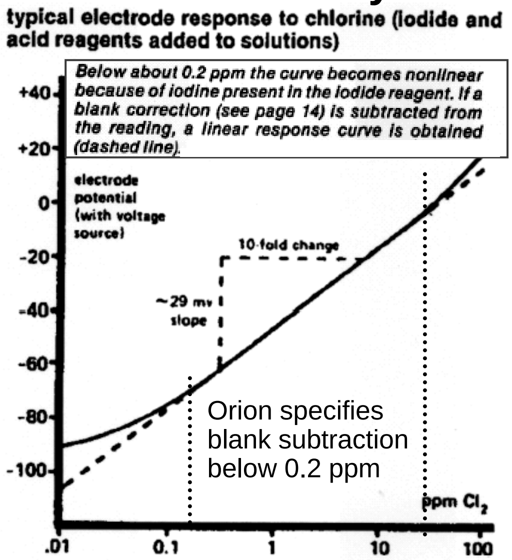
Class A automated

Ion Selective Electrode (ISE) Theory

- Based on iodometric measurement of chlorine
- Iodide (I^-)and acid (H^+) are added to the sample
- Iodide reacts with chlorine to form iodine
- The iodine concentration is equal to the chlorine concentration
- The ISE contains a platinum sensing element and iodine sensing reference element
- The platinum element develops a potential that depends on the relative amount of iodine and iodide in solution.
- The iodine-sensing element develops a potential that depends on the iodide level in solution
- The meter measures the difference between these potentials (the iodine concentration)
- Iodine concentration = total residual chlorine concentration
- Differences from ammonia:
  - A. Slope is positive
  - B. mV per decade of concentration is 29.0, not 58

Problems with the ISE method

1. Non-linearity



From: Orion Research. 1983. Instruction Manual

2. Temperature change <u>is also a problem</u>

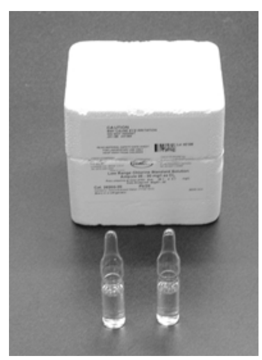
Calibration curve shifts about 0.2 mV per degree C difference between standards and samples

Reagents & Stds needed for ISE

Required

- Residual chlorine standard (***iodate*** *equivalent to chlorine*)
- Iodide reagent
- Acid reagent

Recommended



- Primary chlorine standard (***additional QC check***)

How is iodate equivalent to chlorine?

Chlorine produces iodine in a 1:1 molar ratio

$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$ *1st H^+ =1st equivalent*

$HOCl \Leftrightarrow H^+ + OCl^-$ *2nd H^+ = 2nd equivalent*

$ClO^- + 2\,H^+ + 2\,I^- \rightarrow I_2 + Cl^- + H_2O$

Iodate produces iodine in a 1:3 molar ratio

$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$

There are 2 H^+ equivalents per mole Cl_2; 1 per mole KIO_3

Std Methods: 0.1002 g KIO_3/L = 0.00281 equivalent Cl_2/L
1 ml = 100 mg as Cl_2

$$\frac{0.1002\ \cancel{g\ KIO_3}}{L} \times \frac{1\ \cancel{mole}}{214\ \cancel{g\ KIO_3}} \times \frac{3\ \cancel{moles\ I_2}}{1\ \cancel{moles\ I_2}} \times \frac{2\ \text{equivalents}\ Cl_2}{\cancel{mole}}$$

$$= 0.0028093\ \frac{\text{equivalents}}{L} = 0.00281\ N \text{ as } Cl_2$$

Standards of ISE Method

- The ISE may be calibrated using either a chlorine standard or potassium iodate standard solution.
- The iodate solution is less costly and more stable than chlorine standards.
- Iodate solution produces a reaction equivalent to chlorine in the ISE method.
- The iodate solution is recommended.
- Primary chlorine standards are available in single use vials as an additional QC check.

Suggested Way to Prepare Working Chlorine Standards

Chlorine Conc. (mg/L)	mL of 100 ppm iodate solution diluted to 100 mL
0.10	0.100
0.20*	0.200
0.50	0.500
0.70	0.700
1.00	1.000
2.0*	2.0

*Used for slope check

Standardizing the ISE

1. Add a magnetic stir bar to a 150 mL beaker

2. Pour off 100 ppm chlorine or iodate (*chlorine equivalent*) standard into a dispo-beaker

3. Fit a clean disposable tip onto a 1000 µL pipettor.

4. Pipet standard into 150 mL beaker, starting with the lowest concentration.

ISE Sample Analysis Procedure

5. Pour off acid and iodide reagent into dispo-beakers.

7. Add **1 mL of iodide reagent** to the beaker.

6. Add **1 mL of acid reagent** to the beaker containing the standard

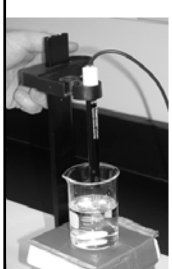
8. Swirl beaker to mix

9. Allow solution to sit and **react for 2 minutes**

ISE Sample Analysis Procedure

10. Add 100 mL of distilled water to beaker.

12. Insert electrode into solution and turn off magnetic stirrer, set meter to the mV mode.

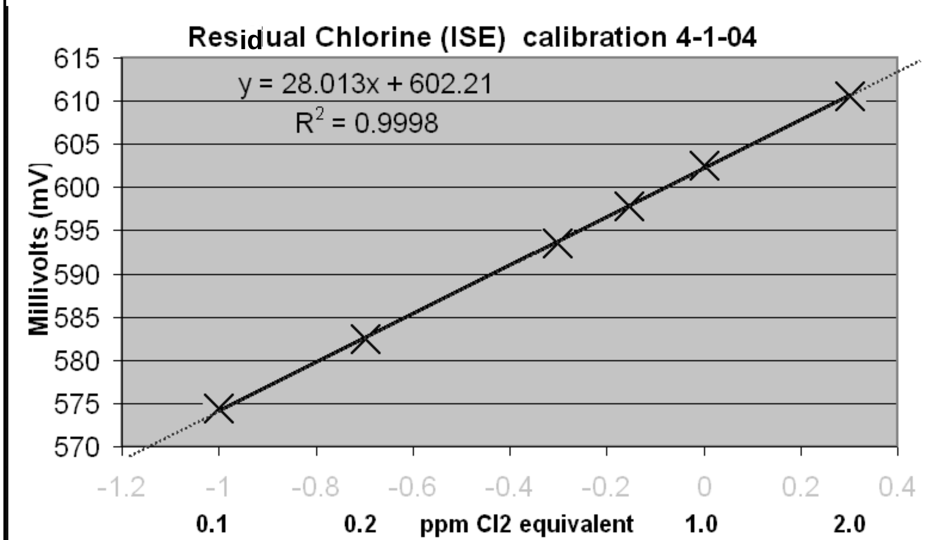


11. Place beaker on magnetic stirrer and allow solution to mix about 20-30 seconds.

13. Allow meter to stabilize. Be patient, it may take 5 or more minutes to stabilize. Record mV readings on bench sheet.

14. Repeat steps 3-13 to measure the remaining standards.

ISE Calibration Example



Calculating std curve

- Plug observed mV readings and chlorine concentration of standards into the spreadsheet.
  - *Remember that, like ammonia, you need to use the LOG of concentration when generating a regression.*
- Calculate a standard curve and record the equation of the line and correlation coefficient (r) on the bench sheet.
- The "r" value must be 0.995 or greater.
- DO NOT proceed with sample measurements unless the slope and "r" requirements are met.

Slope Check and Other Considerations

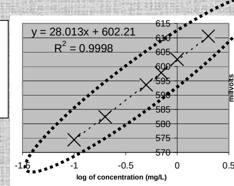
- Check the slope by finding the difference between the 2.0 and 0.20 mg/L (one decade) chlorine standards. (e.g., 610.5 – 581.9 = 28.6 mV).
- The slope must be in the 26-30 mV/decade range
- The manufacturer states the ISE is only linear from 0.2 to 20 mg/L. Consequently, the 26-30 mV/decade specification is only valid above 0.2 mg/L.
- The observed mV readings increase with increasing concentrations of chlorine.

NOTE: The opposite is true for most other ISE applications (such as ammonia).

Evaluate the Calibration Data

Total Residual Chlorine by ISE

Sample Location **(specific)** **Sample Type** **(Grab, composite)**
Raw ____________________ ______________________
Final ____________________ ______________________
If composite: ____ Flow proportional ____Time proportional
Sample Date/Time: ___________ Collected by: ______________



		Criteria	
Correlation (r)=	0.99988	$\geq$ (0.995)	ok
Slope=	28.01	26 to 30 mV	ok
Intercept=	602.21		
LOD=	**0.015**		

------Control Limits-------

Influent Replicate	18.1	% RPD		enter "%RPD"
Effluent Replicate	0.04	Range		or "Range"
Influent Spike	75%	to	125%	
Effluent Spike	80%	to	120%	

Sample	Sample mLs	Sample + DI mLs	DF	mV	Cl_2 mg/L	True Value Notes	Quality Control	
Standard 1	50	50	1	**574.4**	**0.10**	**0.1**	**101.7%**	ok
Standard 2	50	50	1	**582.4**	**0.20**	**0.20**	**98.2%**	ok
Standard 3	50	50	1	**593.6**	**0.49**	**0.5**	**98.6%**	ok
Standard 4	50	50	1	**597.8**	**0.70**	**0.70**	**99.5%**	ok
Standard 5	50	50	1	**602.5**	**1.02**	**1.0**	**102.4%**	ok
Standard 6	50	50	1	**610.6**	**1.99**	**2.0**	**99.7%**	ok
Blank	50	50	1	532.3	0.003	Criteria: <LOD	pass	

Look for points that don't "fit".

Check slope & intercept

<u>"Back-calculate" stds</u>
$\pm$ 5% for high std
$\pm$10% for mid stds
$\pm$30% for low std

Measuring Chlorine in Samples using the ISE

1. Add a magnetic stir bar to a 150 mL beaker

3. Insert a clean disposable tip a 1000 µL pipettor.

2. Pipet 100 mL of sample into a clean 150 mL beaker.

4. Add 1 mL of iodide reagent to the beaker.

Measuring Chlorine in Samples using the ISE

5. Add 1 mL of acid reagent to the beaker containing the standard

7. Insert electrode into solution and turn off magnetic stirrer, set meter to the mV mode.

8. Allow solution to sit and react for 2 minutes

6. Place beaker on magnetic stirrer and allow solution to mix about 20-30 seconds.

9. Allow meter to stabilize. Be patient, it may take 5 or more minutes to stabilize. Record mV readings on bench sheet.

10. Repeat steps 3-9 to measure the remaining samples.

Record all appropriate information on the benchsheet

REMEMBER:

Sample	Sample mLs	Sample + DI mLs	DF	mV	Cl_2 mg/L
Standard 1	50	50	1	**574.4**	**0.10**
Standard 2	50	50	1	**582.4**	**0.20**
Standard 3	50	50	1	**593.6**	**0.49**
Standard 4	50	50	1	**597.8**	**0.70**
Standard 5	50	50	1	**602.5**	**1.02**
Standard 6	50	50	1	**610.6**	**1.99**
Blank	50	50	1	532.3	0.003
Known Standard	50	50	1	563.1	0.040
Effluent 4/1/02	50	50	1	567.5	0.058
Effluent Replicate	50	50	1	569.2	0.066
Effluent Spike	50	50	1	574.3	0.101

Additional Recommended Quality Control Check

- Test a single use, primary chlorine standard such as those available from Hach and NCL.
- Each vial contains chlorine
- Standards are available in the 25-30 mg/L and 50-75 mg/L range.

- Break open the glass vial and pipet a portion into a 150 mL beaker.
- Add distilled water to bring the volume to 100 mL.
- Test just like a real sample.

Total Residual Chlorine by ISE

Sample Location (specific) **Sample Type (Grab, composite)**

Raw ____________________ ______________________

Final ____________________ ______________________

If composite: ____ Flow proportional ____Time proportional

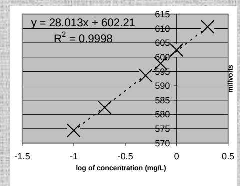
Sample Date/Time: ___________ Collected by: _____________

Stock Standard mg/L ______ Lot # ______ Expiration _______

Working Std mg/L ______ Lot # ______ Expiration _______

Spike Standard mg/L ______ Lot # ______ Expiration _______

Correlation (r)=	0.99988	≥ (0.995)	ok
Slope=	28.01	26 to 30 mV	ok
Intercept=	602.21		
LOD=	**0.015**		



------Control Limits-------

Influent Replicate	18.1	% RPD		◂ enter "%RPD"
Effluent Replicate	0.04	Range		◂ or "Range"
Influent Spike	75%	to	125%	
Effluent Spike	80%	to	120%	

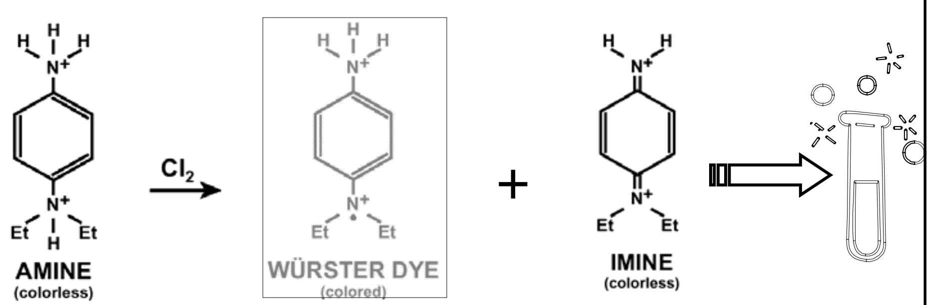
Sample	Sample mLs	Sample + DI mLs	DF	mV	Cl_2 mg/L	True Value / Notes	Quality Control	
Standard 1	50	50	1	**574.4**	**0.10**	**0.1**	**101.7%**	ok
Standard 2	50	50	1	**582.4**	**0.20**	**0.20**	**98.2%**	ok
Standard 3	50	50	1	**593.6**	**0.49**	**0.5**	**98.6%**	ok
Standard 4	50	50	1	**597.8**	**0.70**	**0.70**	**99.5%**	ok
Standard 5	50	50	1	**602.5**	**1.02**	**1.0**	**102.4%**	ok
Standard 6	50	50	1	**610.6**	**1.99**	**2.0**	**99.7%**	ok
Blank	50	50	1	532.3	0.003	Criteria: <LOD	pass	
Known Standard	50	50	1	563.1	0.040	**0.037** Criteria: 90-110%	**108.6%** pass	
Effluent 4/1/02	50	50	1	567.5	0.058		**Range**	
Effluent Replicate	50	50	1	569.2	0.066		**0.009** pass	
Effluent Spike	50	50	1	574.3	0.101		**116.9%** pass	

50	mLs	Sample Volume used
50.0185	mLs	Total volume sample + spike
100	mg/L	Concentration of spike solution
0.0185	mLs	Volume of spike solution added

S A M P L E B E N C H S H E E T

The Chemistry of DPD

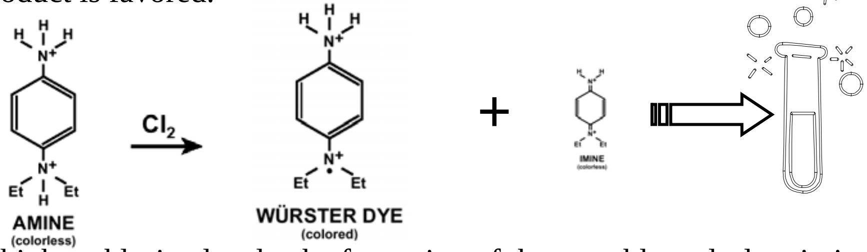
DPD



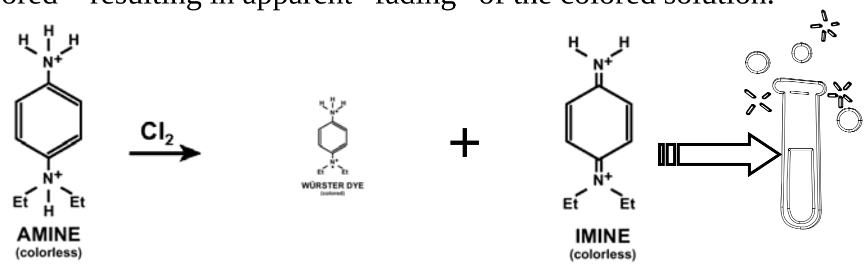
The proportion of colored to colorless product is related to the ratio of DPD indicator to oxidant (chlorine).

DPD Interferences - non-linearity

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



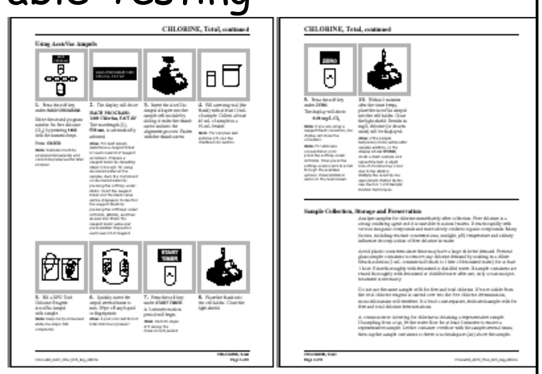
At higher chlorine levels, the formation of the unstable, colorless imine is favored—resulting in apparent "fading" of the colored solution.



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

Commercial Method + QA/QC =
Acceptable Testing

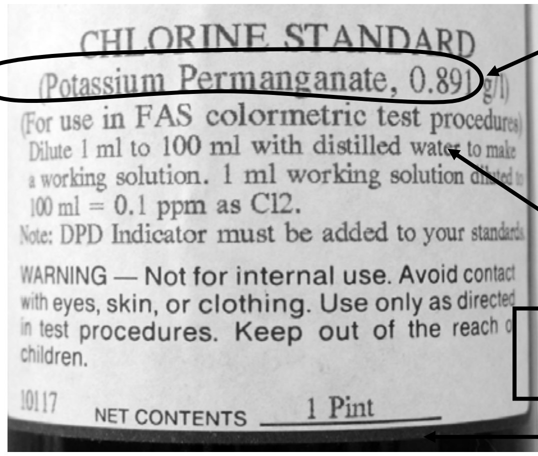
- The exclusive use of generic instructions is not acceptable.
  - No true calibration
  - No QC
  - No spikes/dupes
- These instructions are useful for quick checks and summary only



Generic Instruction
These instructions are simplistic. Alone, they are insufficient for proper testing.

- Using a commercial method does not exempt you from the QA and QC established in the original EPA/Std. Methods.

Preparing Potassium Permanganate - Chlorine Equivalent Standard

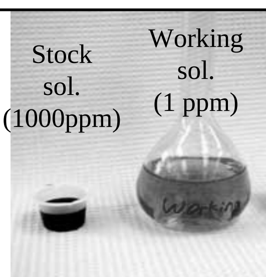


Standard is of correct concentration and labeled appropriately

1000 ppm Cl_2

Dark bottle prevents degradation due to light

Preparing Calibration Standards



Prepare working standard by diluting 1 mL of 1000 ppm to 1L with DI water. Must use pipettor & 1L volumetric flask.

Working Solution 1 ppm	Final Volume	Final Concentration
3.00 ml	100 ml	0.03 ppm
5.00 ml	100 ml	0.05 ppm
10.00 ml	100 ml	0.10 ppm
15.00 ml	100 ml	0.15 ppm
20.00 ml	100 ml	0.20 ppm
25.00 ml	100 ml	0.25 ppm

DNR LOD goal 0.037ppm

DNR req'd LOD 0.100 ppm

Preparing Calibration Standards with a Variable Volume Pipettor

Working Solution 10 ppm	Final Volume	Final Concentration
0.30 ml*	100 ml	0.03 ppm
0.5 ml*	100 ml	0.05 ppm DNR LOD goal 0.037ppm
1.0 ml*	100 ml	0.10 ppm DNR req'd LOD 0.100 ppm
1.5 ml**	100 ml	0.15 ppm
2.0 ml **	100 ml	0.20 ppm
2.5 ml **	100 ml	0.25 ppm

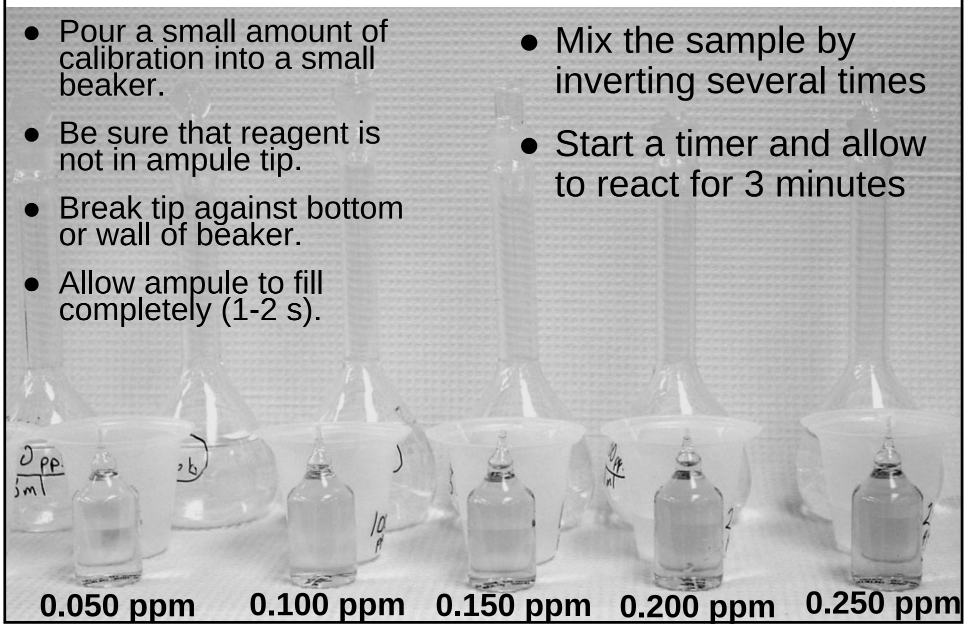
* Use a 0.1-1 mL variable volume pipettor
** Use a 0.5-5 or 1-10 mL variable volume pipettor

Approaches for Color Development

- Commercially available DPD ampules
- Dry powder "pillows"
- Commercially available DPD Solutions *(per Standard Methods)*

Developing Color w/ vacuum ampules

- Pour a small amount of calibration into a small beaker.
- Be sure that reagent is not in ampule tip.
- Break tip against bottom or wall of beaker.
- Allow ampule to fill completely (1-2 s).
- Mix the sample by inverting several times
- Start a timer and allow to react for 3 minutes



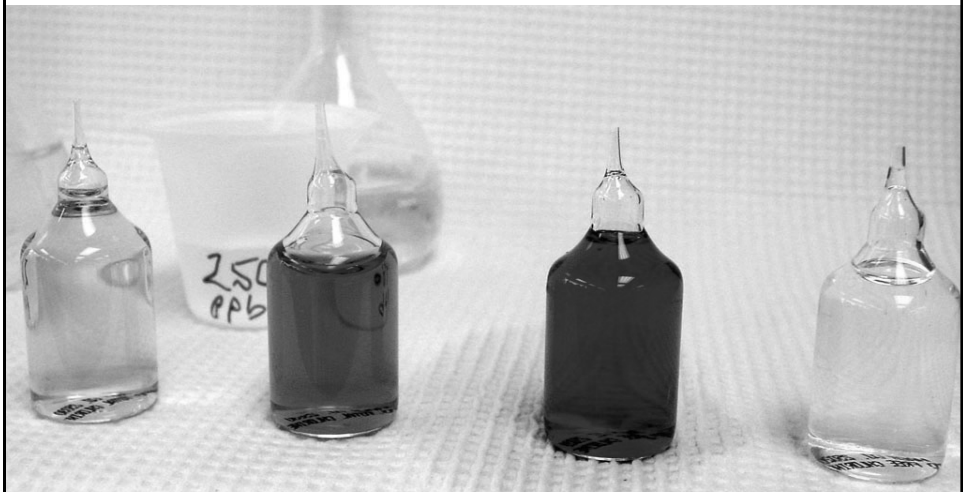
How to Break an Ampule

- Reagent in tip of ampule
- likely to be separated with broken tip increasing chance for low bias.

Ampule is handled carefully to avoid reagent falling into tip.

- Beaker and ampule are tipped to the side.
- Reagent is more likely to stay in the ampule and not fall into tip.

DPD Color Levels



About 0.100 mg/L chlorine sample - light magenta

"Strong" chlorine sample - deep magenta

"Overshot" chlorine sample - reddish brown

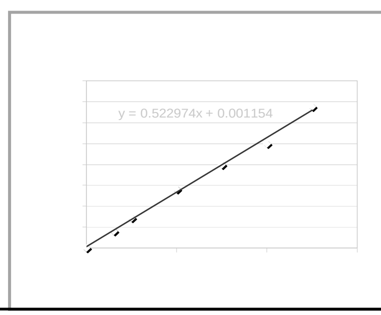
Destroyed DPD - colorless (very high chlorine level)

Making a Calibration Curve: Record Data

- Record the absorbance of each calibration standard
- This data is used when calculating a calibration curve.

Sample	True Value Notes	Absorbance
Calibration Blank	0.0	0.000
Standard 1	0.03	0.016
Standard 2	0.05	0.029
Standard 3	0.10	0.056
Standard 4	0.15	0.080
Standard 5	0.20	0.100
Standard 6	0.25	0.135

Use a calculator, Excel, or "on-board" software that comes with most spectrophotometers.
In Excel, you can use the CORREL formula.



R = 0.998079

Total Residual Chlorine (DPD) Benchsheet

Sample Location **(specific)** **Sample Type** **(grab, composite)**

Raw ________________ ________________________

Final ________________ ________________________

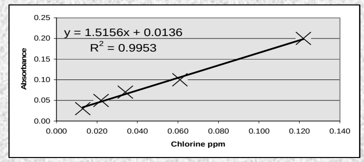
If composite: ____ Flow proportional ____Time proportional

Sample Date/Time: ________ **Collected by:** ____________

Stock Standard mg/L ____ Lot # _____ Expires _______

Working Standard mg/L ____ Lot # _____ Expires _______

Spike Standard mg/L ____ Lot # _____ Expires _______



------Control Limits-------							
Influent Replicate		%RPD		Correlation (r)=	0.99584	'r' acceptable	$\geq$ 0.995
Effluent Replicate	8.24	%RPD		Slope=	1.57375		
Influent Spike		to		Intercept=	0.00890	acceptable	< LOD
Effluent Spike	84.6%	to	123.4%	LOD=	0.015		

Criteria

Sample	Sample mLs	Sample + DI mLs	DF	Absorbance	Instrument Cl_2 mg/L	Cl_2 mg/L	True Value Notes	Quality Control
Calibration Blank	50	50	1	0.000	0.01		0.0	
Standard 1	50	50	1	0.013	0.03	RF= 0.433	0.03	97.9%
Standard 2	50	50	1	0.022	0.04	RF= 0.440	0.05	87.0%
Standard 3	50	50	1	0.034	0.06	RF= 0.486	0.07	89.2%
Standard 4	50	50	1	0.061	0.10	RF= 0.610	0.10	104.9%
Standard 5	50	50	1	0.122	0.20	RF= 0.610	0.20	100.5%
Standard 6						RF=		
Standard 7								
Method Blank	50	50	1	0.003	0.014	0.014	Criteria: <LOD	pass
Known Standard	50	50	1	0.06	0.103	0.103	0.1 Criteria: 90-110%	103.3% pass
Effluent x/x/04	50	50	1	0.047	0.083	0.083		%RPD
Effluent Replicate	50	50	1	0.051	0.089	0.089		7.318 pass
Effluent Spike	50	50	1	0.109	0.180	0.180		121.0% pass

10 mLs	Sample Volume used in the Spiked sample	
10.031 mLs	Total volume sample + spike	
26.1 mg/L	Concentration of spike solution	
0.031 mLs	Volume of spike solution added	0.0806599541421593 ug/mL

SAMPLE BENCHSHEET

Analyzing a Sample

- When analyzing a sample record both absorbances (without DPD and with DPD) on the data sheet.
- Subtract the without DPD absorbance from the with DPD absorbance to get the adjusted absorbance.
- This adjusted absorbance corrects for any natural absorbance of the sample due to color or turbidity.
- Handle blank & sample +DPD the same! (Timing)

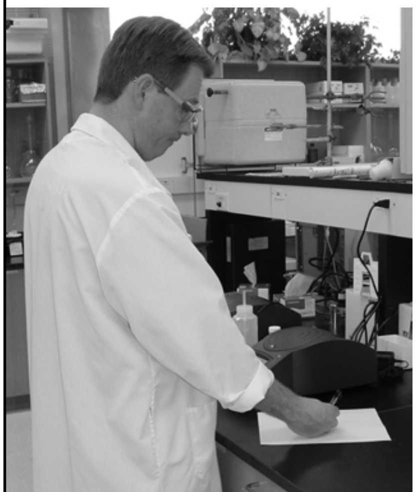
Example

Sample no.	no DPD	with DPD	Adj. Abs.
Outfall no. 1	0.01	0.032	0.022
Outfall no. 2	0.012	0.048	0.036

Use this value to calculate the sample concentration

WITH DPD - without DPD = Adjusted Absorbance

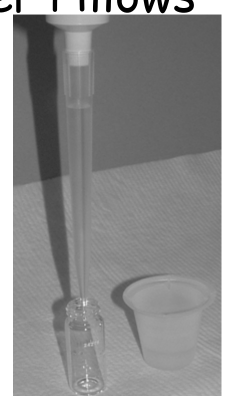
Don't forget the paperwork!

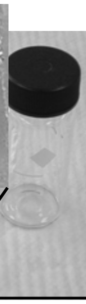


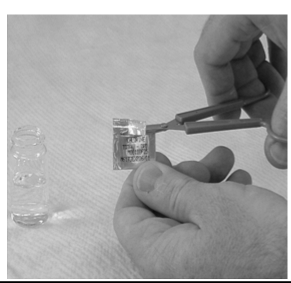
Sample	Sample mLs	Sample + DI mLs	DF	Absorbance	Instrument Cl_2 mg/L	Cl_2 mg/L
Calibration Blank	50	50	1	**0.000**	*0.01*	
Standard 1	50	50	1	**0.013**	*0.03*	*RF= 0.433*
Standard 2	50	50	1	**0.022**	*0.04*	*RF= 0.440*
Standard 3	50	50	1	**0.034**	*0.06*	*RF= 0.486*
Standard 4	50	50	1	**0.061**	*0.10*	*RF= 0.610*
Standard 5	50	50	1	**0.122**	*0.20*	*RF= 0.610*
Standard 6						*RF=*
Standard 7						
Method Blank	50	50	1	0.003	0.014	**0.014**
Known Standard	50	50	1	0.06	0.103	**0.103**
Effluent x/x/04	50	50	1	0.047	0.083	**0.083**
Effluent Replicate	50	50	1	0.051	0.089	**0.089**
Effluent Spike	50	50	1	0.109	0.180	**0.180**
	10	mLs	Sample Volume used in the Spiked sample			
	10.031	mLs	Total volume sample + spike			
	26.1	mg/L	Concentration of spike solution			
	0.031	mLs	Volume of spike solution added			0.08

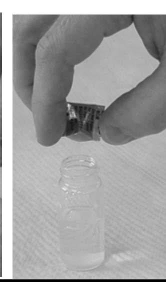
Developing Color with Powder Pillows

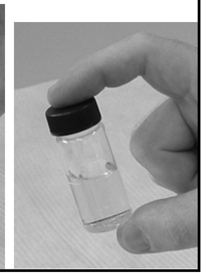
Standards





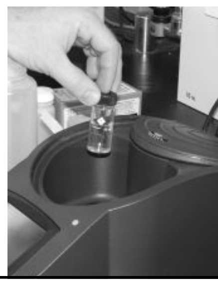






Developing Color with Powder Pillows





Calibration data by approach







GeneSys10

mg/L TRC	Abs
0	0
0.03	0.007
0.05	0.01
0.075	0.019
0.1	0.029
0.2	0.055
0.4	0.101

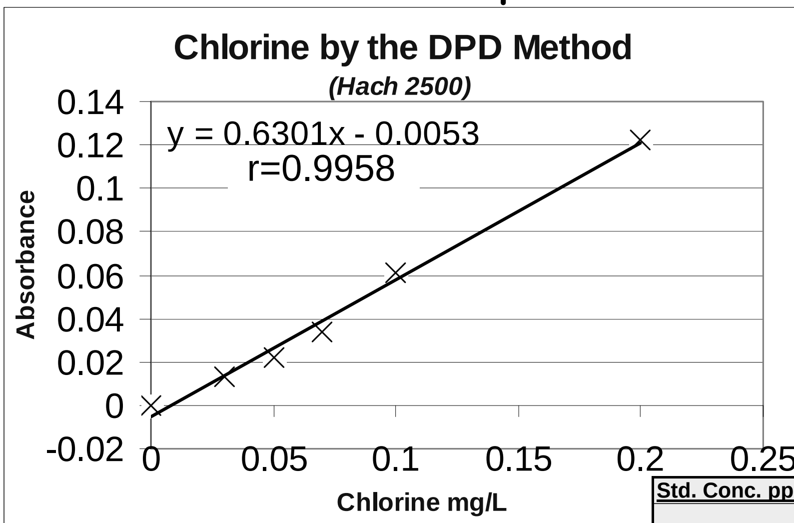
HACH DR890

mg/L TRC	Abs
0	0
0.03	0.006
0.05	0.016
0.075	0.032
0.1	0.043
0.2	0.098
0.4	0.208

HACH DR890

mg/L TRC	Abs
0	**0.000**
0.03	**0.016**
0.05	**0.029**
0.1	**0.056**
0.15	**0.080**
0.2	**0.100**
0.25	**0.135**

Recent update



Std. Conc. ppm	ABS.
0	0
0.03	0.013
0.05	0.022
0.07	0.034
0.1	0.061
0.2	0.122

Calibration data by approach - 2

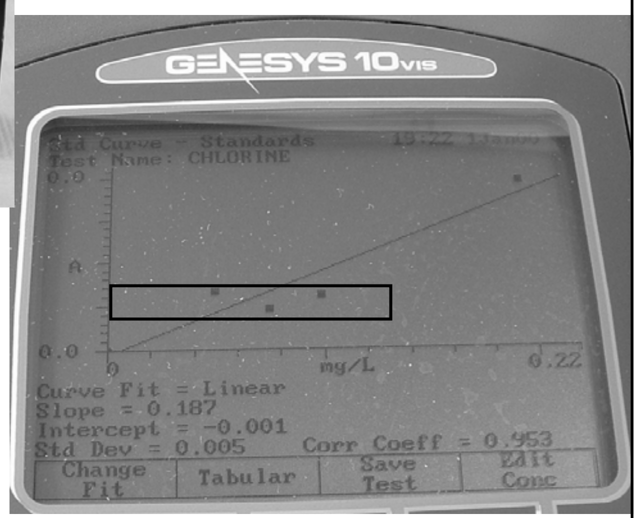
GeneSys10			HACH DR890			HACH DR890			HACH DR890 (internal curve)	
TRUE	CURVE	Bias	TRUE	CURVE	Bias	TRUE	CURVE	Bias	TRUE	Bias
0	-0.001		0	0.014		0	-0.002		**0**	
0.03	0.027	-12%	0.03	0.026	-14%	0.03	0.028	-5%	**0.03**	67%
0.05	0.038	-24%	0.05	0.044	-11%	0.05	0.053	6%	**0.05**	40%
0.075	0.073	- 2%	0.075	0.074	- 1%	0.075	0.105	5%	**0.1**	20%
0.1	0.112	12%	0.1	0.095	- 5%	0.1	0.151	1%	**0.15**	10%
0.2	0.213	7%	0.2	0.198	- 1%	0.2	0.189	-5%	**0.2**	5%
0.4	0.392	- 2%	0.4	0.404	1%	0.4	0.256	2%	**0.25**	- 3%

Slope=	0.25692	0.53456	0.522974
intercept=	0.00019	-0.00772	0.001154
“r”=	0.99766	0.99868	0.998079

LOD data by approach

Spikes level:	0.090 mg/L		0.090 mg/L		0.090 mg/L	
	GeneSys10		HACH DR890		HACH DR2500	
	Abs.	CURVE	Abs.	CURVE	Abs.	CURVE
rep #1	0.023	0.089	0.041	0.091	0.053	0.092
rep #2	0.021	0.081	0.037	0.084	0.048	0.084
rep #3	0.021	0.081	0.039	0.087	0.047	0.083
rep #4	0.023	0.089	0.040	0.089	0.049	0.086
rep #5	0.022	0.085	0.036	0.082	0.047	0.083
rep #6	0.021	0.081	0.038	0.086	0.054	0.094
rep #7	0.021	0.081	0.041	0.091	0.049	0.086
mean	**0.084**		**0.087**		**0.0868**	
stdev	**0.00370**		**0.00365**		**0.0044**	
LOD=	**0.0116**		**0.0115**		**0.0133**	

Vacu-Vials--Another Option



Collecting a Sample for Total Residual Chlorine

- Collect samples in amber, glass bottles treated with bleach to remove chlorine demand.
  - *Treat bottles by filling with DI water, adding a few mL of household bleach, allow to soak about 30 minutes and then rinse thoroughly with tap water followed by DI water.*
- Minimize the time between sampling and analysis (preferably ***= ≤ 15 mins***.)
- Warm samples to room temperature before testing with the ISE method.
- Fill sample completely to minimize contact with the air until samples are tested.

Method Startup Costs

Cost Comparison for Equipment Needed to Test for
Total Residual Chlorine in Water and Wastewater

ISE	Approximate Cost		DPD	Approximate Cost
ISE meter	**$ 1,300.00**		Spectrophotometer	**$ 2,200.00**
Orion Chlorine Electrode	**$ 450.00**		Holder for 1" cells	$ 100.00
Optional printer	**$ 600.00**		Cells, 2.5 cm (1"), pk of 8	$ 18.00
12-150 mL Glass beakers	$ 30.00		DPD Power Pillows, 100 pk	$ 17.00
6-Magnetic stir bars	$ 18.00		0.1-1.0 mL pipettor	$ 225.00
Magnetic stirrer	$ 130.00		1-10 mL pipettor	$ 225.00
0.1-1.0 mL pipettor	$ 225.00		6-100 mL volumetric flasks	$ 110.00
0.5-5 mL or 1-10 mL pipettor	$ 225.00		KMN04 chlorine standard, 1000 ppm	$ 12.00
Chlorine standard 100 ppm (iodate)	$ 15.00			
Acid reagent	$ 15.00			
Iodide reagent	$ 15.00			
2-Glass bottles for collecting samples	$ 5.00			
Total estimated cost	$ 3,028.00		**Total estimated cost**	$ 2,907.00
Total cost without ISE meter/printer	$ 1,128.00		Total cost without spectrophotometer	$ 707.00

Conclusions

- An LOD of less than 0.037ppm IS achievable
- 0.100 ppm is certainly a realistic LOQ.
- Quality low level calibrations CAN be easily developed.
- The use of electronic or mechanical pipettors is required to obtain quality data at these trace levels.
- Either technique will get the results you need
- Effective chlorination WILL kill E. coli
- Use tools to fine-tune dosing rate and disinfection process...allowing more efficient disinfection/dechlorination & reducing costs

More Conclusions

DPD

- The best DPD data will be obtained using a technique providing a path-length of $\geq$ 2 cm.
- Both hand-held and table-top spectrophotometers are available that will meet your needs.
- Internal calibrations not sufficiently accurate.
- Vacu-vials (< 2 cm path) may not be suitable at low levels required for compliance monitoring.

ISE

- Use the more stable potassium iodate standard for calibration
- Avoid calibrating below 0.1 ppm due to non-linearity
- Check the slope from 0.2 to 2.0 (start above 0.1)
- 30-45 minutes for 5-pt calibration
- ISE method is extremely temperature-sensitive

Advantages/Disadvantages: ISE v. DPD

DPD

Advantages

- Most labs have a spectrophotometer
- Fewer reagents; can be purchased
- Temperature not critical factor
- May not need full daily calibration
- Less costly initial set-up (*assuming have spectrophotometer*)
- Less equipment required
- Calculations easier
- Same instrumentation allows free & total chlorine measurement

Disadvantages

- Color & turbidity interfere
- Color correction is critical step
- Need at least 2 cm cell

ISE

Advantages

- Few interferences

Disadvantages

- Higher initial set-up cost (electrode)
- Requires full calibration daily
- Slower
- More reagents
- Temperature is **critical**
- Can only measure total residual

Acknowledgements

We'd like to thank the following for their assistance in developing this session:

- **Graham Anderson**…for "doing" while we "managed"
- **Micah Berman**, DNR Intern and "Piano Guy"…for his DPD work
- **Mike Raynovic & Jerry Cookle of North Central Laboratories**... for loaning us the spectrophotometer and pipettes
- **Ryan Wittrock and Thermo-Orion...** for providing a chlorine electrode for us to play with