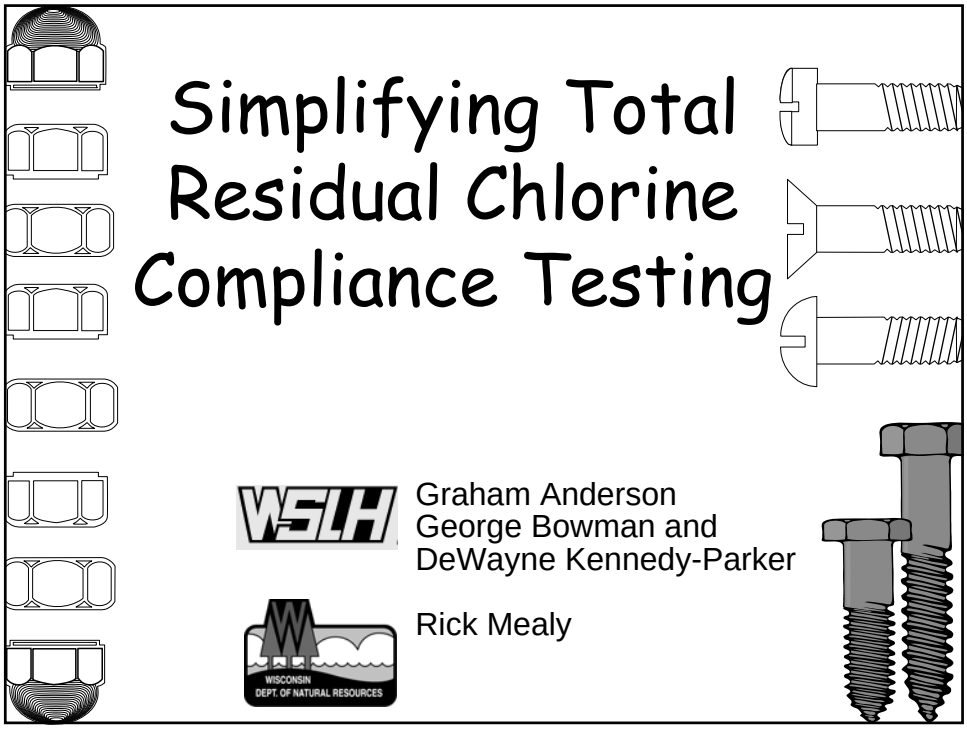


Simplifying Total Residual Chlorine Compliance Testing

Graham Anderson
George Bowman and
DeWayne Kennedy-Parker

Rick Mealy

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.

What Other States Are Doing

Wisconsin:

- current permit limits set at 0.038 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)

Challenges in Testing Chlorine at levels required to meet discharge limits

- NR219 states the chlorine must be analyzed immediately (within 15 minutes of collection)
- The 15 minute time frame is very restrictive
  - Difficult to calibrate, warm sample to room temperature and test within 15 minutes
  - Almost precludes analysis by the ISE method-ISE is extremely temperature sensitive
  - Sampling and analysis to achieve the 0.038 ppm discharge limit becomes a logistical challenge

Today's Objectives

- Discuss wastewater chlorine compliance testing requirements
- Discuss logistics to achieve quality chlorine results:
  - Working with your DNR engineer
  - Optimizing sampling
- Describe testing options available
- Two part session:
  - DPD method-Part 1
  - ISE method-Part 2
- Break into 4 groups for hands-on demos for DPD Method
  - Compare standard curves among groups
- Live demonstration of the ISE method
- Discussion-which approach best meets your needs?

Collecting a Sample for Total Residual Chlorine

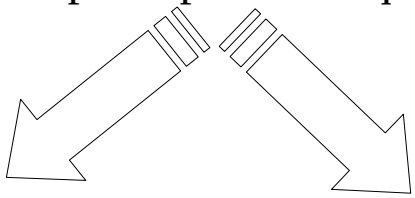
- Collect samples in amber, glass bottles treated with bleach to remove chlorine demand.
  - *Treat bottles by filling with DI water, adding a few mL of household bleach, allow to soak about 30 minutes and then rinse thoroughly with tap water followed by DI water.*
- Minimize the time between sampling 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.

Sampling Logistics

- Calibrate your instrument before sampling
  - Have it ready to roll when you arrive with the sample
- Collect sample in stabilized amber glass bottle
- Work with you DNR engineer:
  - Collect some test data to see how time delays affect results
  - Your engineer may be able work with you through the permit process

Chlorine Analysis Options

Two principal techniques



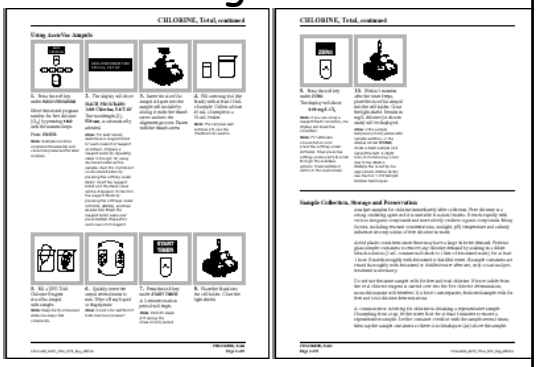
DPD Colorimetric

Ion Selective Electrode (ISE)

DPD

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

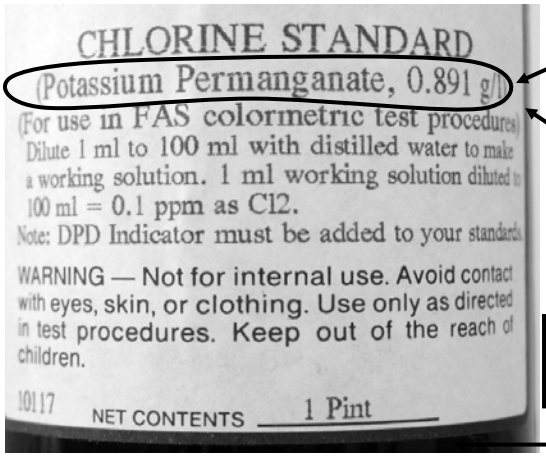


Generic Instruction

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

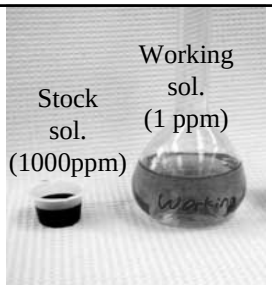
1000 ppm Cl_2

Dark bottle prevents degradation due to light

$$\frac{0.891\ g\ KMnO_4}{L} \times \frac{1\ mole}{158\ g\ KMnO_4} \times \frac{5\ moles\ I_2}{2.5\ moles\ I_2} \times \frac{2\ equivalents\ Cl_2}{mole}$$

$$= 0.028093\ \frac{equivalents}{L} \times \frac{1\ mL}{100\ mL} = 0.0002819\ N\ as\ Cl_2$$

Preparing Calibration Standards with Class A Pipets



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	**DNR LOD goal 0.038 ppm**
5.00 ml	100 ml	0.05 ppm	
10.00 ml	100 ml	0.10 ppm	**DNR req'd LOD 0.100 ppm**
15.00 ml	100 ml	0.15 ppm	
20.00 ml	100 ml	0.20 ppm	

Preparing Calibration Standards with a Variable Volume Pipettor

Prepare a 10 ppm working standard by diluting 1 mL of 1000 ppm to 100 mL with DI water. Must use pipettor

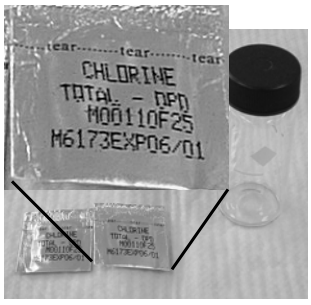
Working Solution 10 ppm	Final Volume	Final Concentration	
0.30 ml*	100 ml	0.03 ppm	
0.5 ml*	100 ml	0.05 ppm	**DNR LOD goal 0.038 ppm**
1.0 ml*	100 ml	0.10 ppm	**DNR req'd LOD 0.100 ppm**
0.75 ml*	50 ml	0.15 ppm	
1.0 ml*	50 ml	0.20 ppm	

* Use a 0.1-1 mL variable volume pipettor

Approaches for Color Development

- Commercially available DPD ampules
- Dry powder
  - ✓ Packets “pillows”
  - ✓ Dispenser bottles
- Commercially available DPD Solutions
  (per Standard Methods)

Convenient Dry Reagent Options for Total Residual Chlorine DPD Color*



Powder packets-note use only ones intended for total residual chlorine

Dispenser units for dry reagents

*Note: Prepared liquid reagents in pre-filled vacuum vials or in bulk may also be purchased from most scientific specialty companies.

Instruments for the DPD method



- Most brands of spectrophotometers or filter photometers may be used to measure chlorine in wastewater effluent using the DPD method if they meet the following requirements:
  - The wavelength can be adjusted to the 515-530 ηm range
  - It will accommodate a 2 cm or large cell.
  - Check the instrument manual to confirm the above

Initial Instrument Set-up



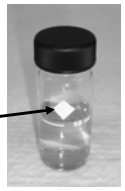
1. Allow instrument to warm up according to manufacturer, generally at least 30 minutes.

2. Select mode (program or absorbance) and set the wavelength to 515 or 530 ηm depending on instrument type.

3. Zero the instrument with lab reagent water with DPD reagent and proceed with the calibration step.

Tips for Calibration

- We recommend using only 1 sample cell when for calibration and sample analysis
- We also recommend calibrating daily
- Always align the cell in the instrument the same way…use mark to align



- If you use more than one cell, make sure they are "matched"
  - Optical quality cells vary from cell to cell
  - Fill all cells with DI water
  - Zero instrument with one cell
  - Measure and record absorbance, and compare
  - Group cells that have similar absorbance – best results when cells vary by <0.005 from each other
- Today's demo-will use multiple cells because of time restrictions

Developing Color with Dry Reagents

1. Prepare standards, pour into disposable beaker.

2. Pipet 10 mL of sample into instrument cell.

Add DPD color reagent using one of the below options

3. Cut open packet, squeeze open the sides and carefully transfer to cell.

or

3. Invert over cell and pull trigger dispenser.

Developing Color with Powder Pillows

4. Cap cell, mix thoroughly and start timer.

5. If using the Hach reagents and wait 3 minutes. Note: HF Science recommends 2 minutes. Our experience shows 3 minutes works best.

6. Wipe-off any smudges from the cell with a soft, lint-free tissue, place in spectrophotometer and observe the absorbance or press read.

7. Remove cell, discard sample, rinse thoroughly with DI water and proceed to the next standard.

Remember to align the cell in the instrument the same way EVERY time!

Note: If using multiple cells, time reagent addition so that you may proceed to the next standard quickly….this takes good timing and lots of practice.

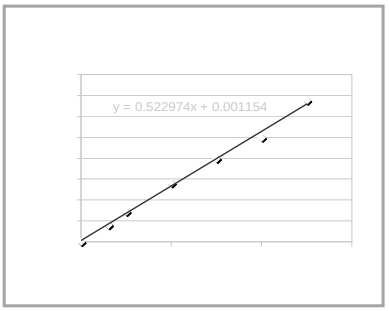
Making a Calibration Curve: Record Data

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

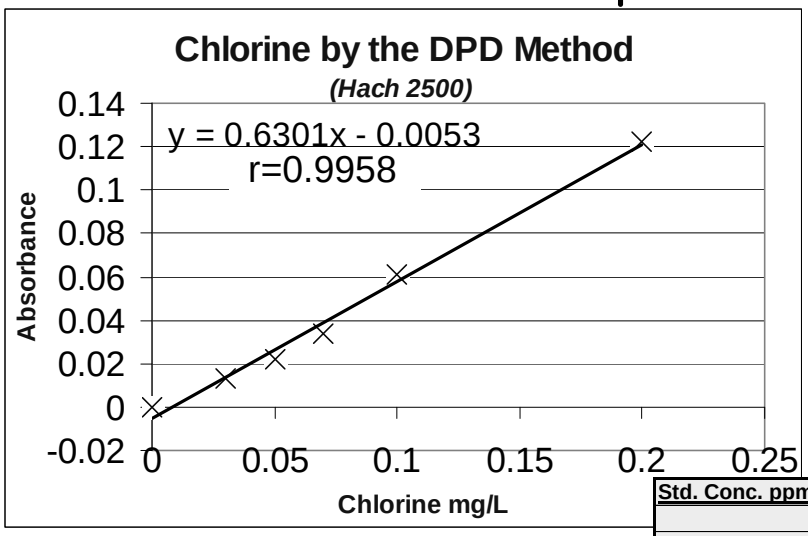
Use a calculator, Excel, or "on-board" software that comes with most spectrophotometers.
In Excel, you can use the CORREL formula.

R = 0.998079

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



Calibration Curve-up close



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

Total Residual Chlorine (DPD) Benchsheet

Sample Location (specific) Final Outfall 1 **Sample Type** (grab, composite) Grab

If composite: ____ Flow proportional ____Time proportional

Sample Date/Time: 09/26/06 08:25 Collected by: G. Anderson

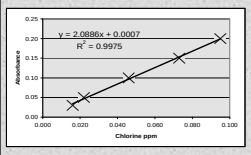
Stock Standard mg/L 1000 Lot # C9B050418 Expires 4/18/07

Working Standard mg/L 10 Lot # 911055* Expires 09/27/06

Spike Standard mg/L 24.9 Lot # A6208 Expires 07/01/07

DPD Reagent Manufacturer: HF Scientific Lot # 60539 Expires 11/01/07

*Lot # convention for WSLH: Logbook#, page #, line #



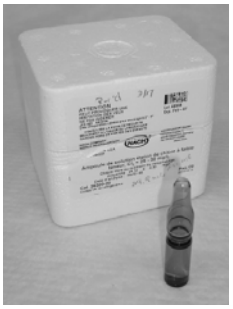
	-----Control Limits------			Criteria
Influent Replicate	NA	%RPD		
Effluent Replicate	15	%RPD		
Influent Spike		to		
Effluent Spike	80.0%	to	120.0%	

Correlation (r)=	0.99915	"r" acceptable	≥ 0.995
Slope=	2.09327		
Intercept=	0.00042	acceptable	< LOD
LOD=	0.015		

Sample	Sample mLs	Final Volume (Sample + DI mLs)	DF	Sample "Blank" Abs	Sample + DPD Abs	Absorbance (or corrected Abs)	Instrument Cl_2 mg/L	Reported Cl_2 mg/L	True Value Notes	Quality Control*
Calibration Blank	10	10	1			0.000	*0.000*		0.0	
Standard 1	10	10	1			0.016	*0.034*		0.03	113.0%
Standard 2	10	10	1			0.022	*0.046*		0.05	92.9%
Standard 3	10	10	1			0.046	*0.097*		0.10	96.7%
Standard 4	10	10	1			0.073	*0.153*		0.15	102.1%
Standard 5	10	10	1			0.095	*0.199*		0.20	99.6%
Method Blank	10	10	1	0	0	0	0.000	0.000	Criteria: <LOD	pass
Known Standard	10	10	1	0	0.029	0.029	0.061	0.061	0.0623 Criteria: 90-110%	98.1% pass
Effluent	10	10	1	0.035	0.054	0.019	0.040	0.040		%RPD
Effluent Replicate 4/1/02	10	10	1	0.035	0.055	0.02	0.042	0.042		5.076 pass
Effluent Spike	10	10	1	0.035	0.122	0.087	0.183	0.183		114.9% pass
	10	mLs	Sample Volume used in the Spiked sample							
	10.05	mLs	Total volume sample + spike							
	24.9	mg/L	Concentration of spike solution							
	0.05	mLs	Volume of spike solution added						0.124 ug/mL	

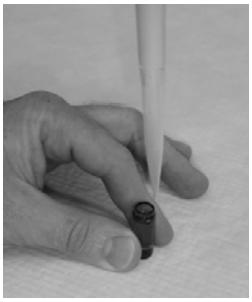
SAMPLE BENCHSHEET

Additional Recommended DPD 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.

- Break open the glass vial and pipet between 0.25-0.50 mL into a 100 mL volumetric flask and bring to volume with DI water.
  - •0.25 mL to 100 mL will yield a chlorine level of about 0.06-0.075 mg/L.
- Test just like a real sample.



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)!

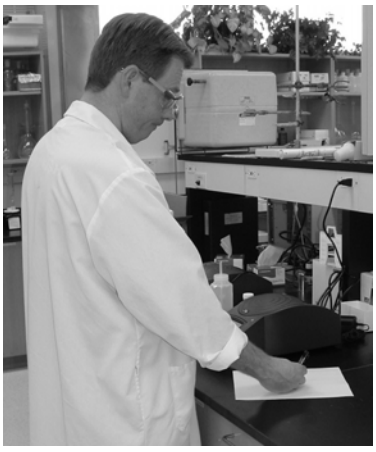
Example

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	Final Volume (Sample + DI mLs)	DF	Sample "Blank" Abs	Sample + DPD Abs	Absorbance (or corrected Abs)	Instrument Cl_2 mg/L	Reported Cl_2 mg/L	True Value Notes	Quality Control*
Calibration Blank	10	10	1			0.000	*0.000*		0.0	
Standard 1	10	10	1			0.016	*0.034*		0.03	113.0%
Standard 2	10	10	1			0.022	*0.046*		0.05	92.9%
Standard 3	10	10	1			0.046	*0.097*		0.10	96.7%
Standard 4	10	10	1			0.073	*0.153*		0.15	102.1%
Standard 5	10	10	1			0.095	*0.199*		0.20	99.6%
Method Blank	10	10	1	0	0	0	0.000	0.000	Criteria: <LOD	pass
Known Standard	10	10	1	0	0.029	0.029	0.061	0.061	0.0623	98.1%
									Criteria: 90-110%	pass
Effluent	10	10	1	0.035	0.054	0.019	0.040	0.040		%RPD
Effluent Replicate 4/1/02	10	10	1	0.035	0.055	0.02	0.042	0.042		5.076
										pass
Effluent Spike	10	10	1	0.035	0.122	0.087	0.183	0.183		114.9%
										pass
	10	mLs	Sample Volume used in the Spiked sample							
	10.05	mLs	Total volume sample + spike							
	24.9	mg/L	Concentration of spike solution							
	0.05	mLs	Volume of spike solution added						0.124 ug/mL	

LOD data by approach

Spikes level: 0.090 mg/L

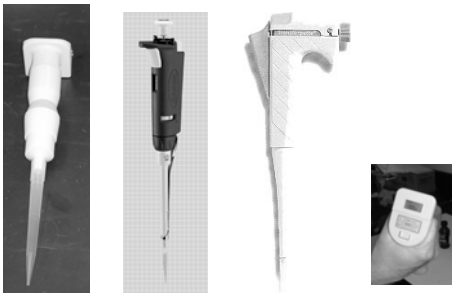
	HACH DR890		HACH DR2500	
	Abs.	CURVE	Abs.	CURVE
rep #1	0.041	0.091	0.053	0.092
rep #2	0.037	0.084	0.048	0.084
rep #3	0.039	0.087	0.047	0.083
rep #4	0.040	0.089	0.049	0.086
rep #5	0.036	0.082	0.047	0.083
rep #6	0.038	0.086	0.054	0.094
rep #7	0.041	0.091	0.049	0.086
mean	**0.087**		**0.0868**	
stdev	**0.00365**		**0.0044**	
LOD=	**0.0115**		**0.0133**	

DPD

Hands on DEMOS

ISE

Key Equipment needed for ISE



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

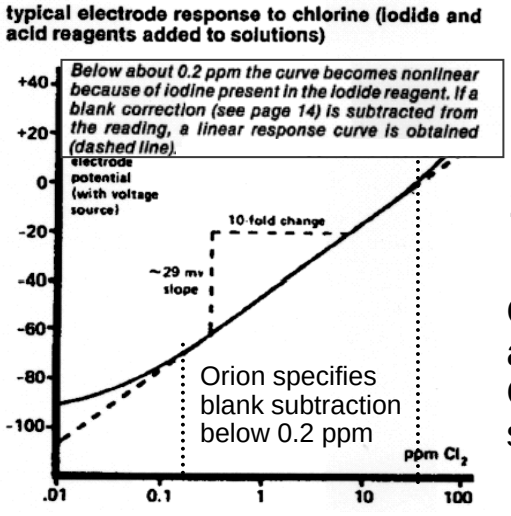
- Orion model 97-70 residual chlorine electrode
- pH/ISE meter
- Magnetic stir plate
- Magnetic stir bar

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 Chlorine Residual electrode Model 97-70-00

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

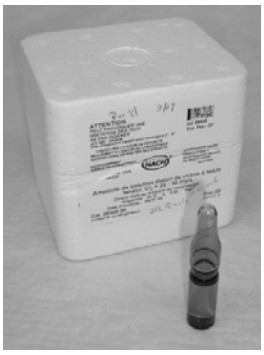
Calibration curve shifts about 0.2 mV per degree C difference between standards and samples

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

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

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

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 Iodate Chlorine Equivalent Standards

Chlorine Conc. (mg/L)	mL of 100 ppm chlorine equivalent standard added directly to analysis beaker **
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

**Must add standard directly to 150 mL beaker and react with iodide and acid reagents before adding 100 mL of DI water.

Standardizing the ISE

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

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

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

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

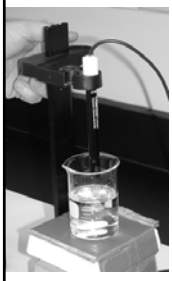
8. Swirl beaker to mix

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.

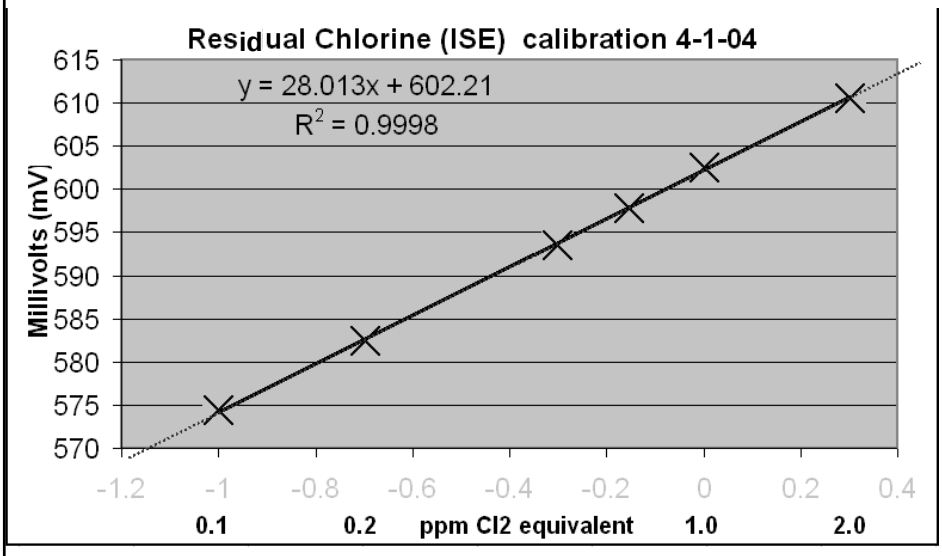


11. Place beaker on magnetic stirrer and allow solution to mix about 20-30 seconds.

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

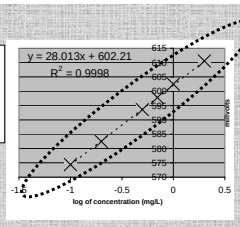
Total Residual Chlorine by ISE

Sample Location (specific) Raw _____ Final _____

Sample Type (Grab, composite) _____ _____

If composite: ____ Flow proportional ____Time proportional

Sample Date/Time: _____ Collected by: _____



Criteria			
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	

Look for points that don't "fit".

Check slope & intercept

"Back-calculate" stds

± 5% for high std

±10% for mid stds

±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 (or pour-graduated cylinder) 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.

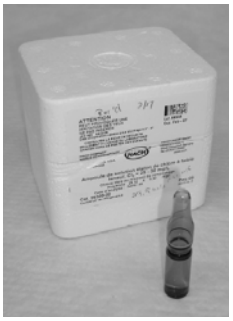
10. Repeat steps 3-9 to measure the remaining samples.

Record all appropriate information on the benchsheet

REMEMBER:

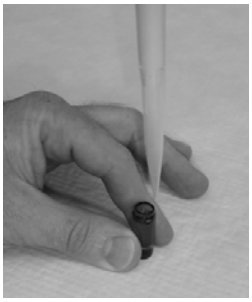
Sample	Sample mLs	Sample + DI mLs	DF	mV	Cl_2 mg/L
Standard 1	50	50	1	**574.4**	**0.10**
Standard 2	50	50	1	**582.4**	**0.20**
Standard 3	50	50	1	**593.6**	**0.49**
Standard 4	50	50	1	**597.8**	**0.70**
Standard 5	50	50	1	**602.5**	**1.02**
Standard 6	50	50	1	**610.6**	**1.99**
Blank	50	50	1	532.3	0.003
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 ISE 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.

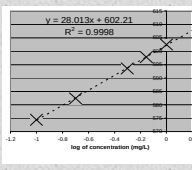


Total Residual Chlorine by ISE

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

Raw NA — NA
Final Outfall 001 — Grab
If composite: ____ Flow proportional ____ Time proportional
Sample Date/Time: 09/25/06 08:50 Collected by: G. Anderson

Stock Standard mg/L 100 Lot # C9A060831 Expiration 08/31/07
Working Std mg/L Same Lot # ____ Expiration ____
Spike Standard mg/L 50 Lot # 911056 Expiration 09/26/06
Iodide Reagent Lot # I55060810 Expiration 02/10/08
Acid Reagent Lot # A13060713 Expiration 07/13/09



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%**
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Standard 3	50	50	1	**593.6**	**0.49**	**0.5**	**98.6%**
Standard 4	50	50	1	**597.8**	**0.70**	**0.70**	**99.5%**
Standard 5	50	50	1	**602.5**	**1.02**	**1.0**	**102.4%**
Standard 6	50	50	1	**610.6**	**1.99**	**2.0**	**99.7%**
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

SAMPLE BENCHSHEET

Special thanks to Graham who <u>can</u> do!
…..Those that can't … manage

Conclusions

- An LOD of <u>less than</u> 0.038 ppm 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

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.
- Commercial powder and liquid DPD reagents are generally satisfactory

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

ISE

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

For more information:

George Bowman
Graham Anderson
DeWayne Kennedy-Parker
(608) 224-6281
State Laboratory of Hygiene
2601 Agriculture Drive
Madison, WI 53718

Rick Mealy
(608) 264-6006
Wisconsin DNR
PO Box 7921
Madison, WI 53707

State Lab web address:
http://www.slh.wisc.edu/outreach/

DNR's LabCert homepage:
http://www.dnr.state.wi.us/org/es/science/lc/

Acknowledgements

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

- **Graham Anderson**…for "doing" while we "managed"
- **Jim Burk and Hach Company...** for loaning us the pipettes and supplies
- **Chris Scott and Thermo-Orion...** for providing a chlorine electrode and meter