Getting the Best Chlorine Residual Data

DPD Colorimetric Testing for Chlorine

Using vacuum ampuls to test for total residual chlorine

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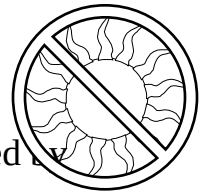
Getting the Best Chlorine Residual Data

- Measurement of total residual chlorine at levels low enough to meet wastewater discharge limits is 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.
- Wisconsin's wastewater rules (NR218) do not allow the use of commercial test kits unless they are used properly.
- This presentation will provide step by step instructions for making total residual chlorine measurements with a commercially available kit using the DPD method.
- Each attendee will be given a CD containing streaming video instructions for performing the chlorine test.

Technical Considerations



- Do not work in direct sunlight.
  - Chlorine (among other halides) is affected by intense light, leading to errors.
  - If working outdoors (on-site), be sure to work in the shade.
- Dilute precisely and accurately.
  - Solutions less than 0.1mg/l in concentration are especially vulnerable to error.
  - At low concentrations, errors as little as 0.05% can change absorbance measurements by over 15%.
  - Dirty glassware will significantly effect low-concentration solutions.

Technical Considerations

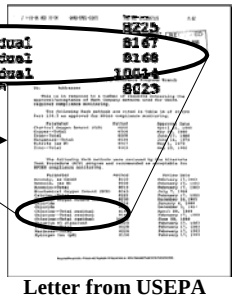
- Use good pipet technique.
  - Ideally, use an automated pipet.
  - Use a new pipet tip for each solution.
  - Never pipet from the stock solution, this can contaminate the whole lot. Pour the solution into a smaller beaker first.
  - If using a pipet bulb, be sure not to draw solution into the bulb itself.
- Use consistent technique.
  - Dilutions
  - Timing
  - Readings
- Consistency = less error

Approved and Accepted Methods

If a commercial method is accepted by the USEPA as equivalent to one (usually both) of the methods listed in NR219, than it can be used for reporting purposes to the WDNR for NR 219 (in addition to NR 809).

NR 219
EPA
330.5
OR
Std. Mthds.
4500-Cl G

NR 219.05



Commercial Test

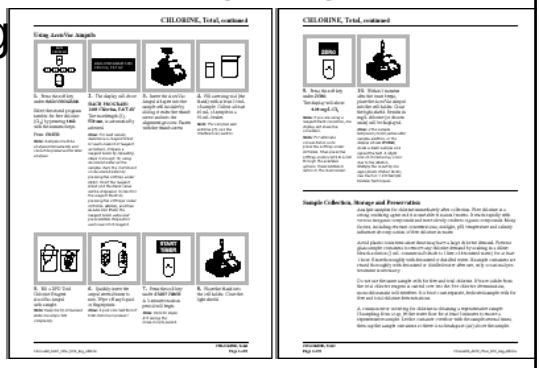
Letter from USEPA indicating acceptance of commercial test method

<u>If you are going to use a commercial test, their must be documentation that the test method is approved.</u>

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.

Quick Tests for Chlorine Testing

- Colorwheels are NOT acceptable.
- "Pocket colorimeters" are NOT acceptable.
  - These colorimeters use an insufficient, preprogrammed calibration.
- Must use true spectrophotometers or colorimeters with a USEPA-accepted method.

These are NOT acceptable for compliance testing

Preparing Potassium Permanganate Standard

Standard is of correct concentration and labeled appropriately

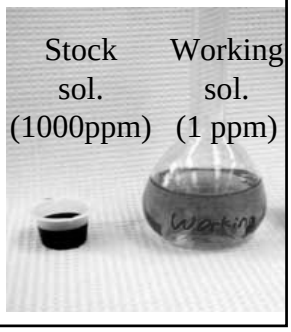
Dark bottle prevents degradation due to light

Preparing Potassium Permanganate Standard

- Dilute the 1000 ppm stock solution to 1 ppm working solution (1:1000) as follows:
  1) Dilute 10.00 ml stock solution to 100.0 ml (with distilled water in a volumetric flask)
  2) Take 1.00 ml of this new solution and dilute it to 100.0 ml.
  - Be sure to mix each dilution thoroughly.

Remember:

The concentrations are equivalents. They solutions are not ACTUALLY chlorine, but behave like chlorine at the equivalent concentration.



Preparing Calibration Standards

- Fresh working solution for use in calibration standards must be prepared fresh for that day.
- Range of calibration standards must include the anticipated sample range.
  - If you expect samples between 0.030 – 0.150 ppm (typical for wastewater and drinking water analysis), then calibrate from 0.020 – 0.200 ppm.
- Do not prepare calibration standards below 0.020 ppm. These will lead to error.
- Set up a table to help calculate dilutions

Preparing Calibration Standards

- Example dilution table.

  Dilute working solution (1ppm) with DI water up to the final volume in a 100 ml volumetric flask:

Working Solution 1ppm	Final Volume	Final Concentration	
3.00 ml	100 ml	0.03 ppm	**DNR LOD goal 0.037ppm**
5.00 ml	100 ml	0.05 ppm	
7.00 ml	100 ml	0.07 ppm	
10.00 ml	100 ml	0.10 ppm	**DNR req'd LOD 0.100 ppm**
20.00 ml	100 ml	0.20 ppm	

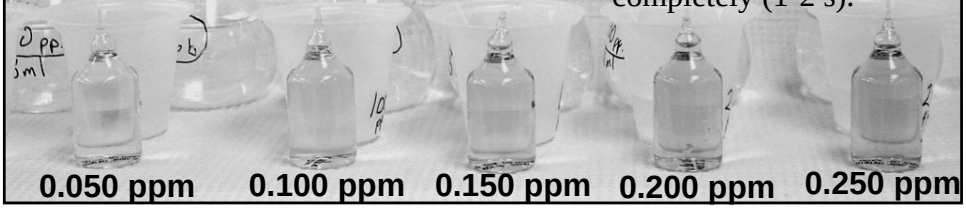
Preparing Calibration Standards

- ✓ Calibration standards are labeled, filled to meniscus, and thoroughly mixed.
- ✓ Calibration blank (DI water) is included, and prepared like all other standards.

Note: this photograph reflects concentrations in ppb, not ppm

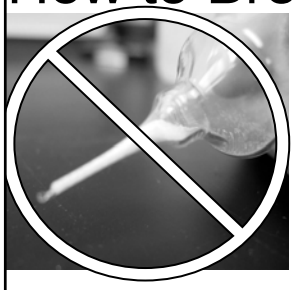
Developing Calibration Standards

- Pour a small amount of calibration standard from the volumetric flask into a small beaker and place the beaker in front of the flask.
- Do this for each calibration standard, including the calibration blank (DI water).
- Begin a timer – break one ampul upside down in the beakers.
  - Be sure that reagent is not in ampul tip.
  - Break tip against bottom or wall of beaker.
  - Allow ampul to fill completely (1-2 s).



0.050 ppm **0.100 ppm** **0.150 ppm** **0.200 ppm** **0.250 ppm**

How to Break an Ampul



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

Ampul is handled carefully to avoid reagent falling into tip.

- Ampul is too vertical.
- Reagent is likely to fall into tip before it breaks.

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

DPD Color Levels

"Typical" chlorine sample - light magenta

"Strong" chlorine sample - deep magenta

"Overshot" chlorine sample - reddish brown

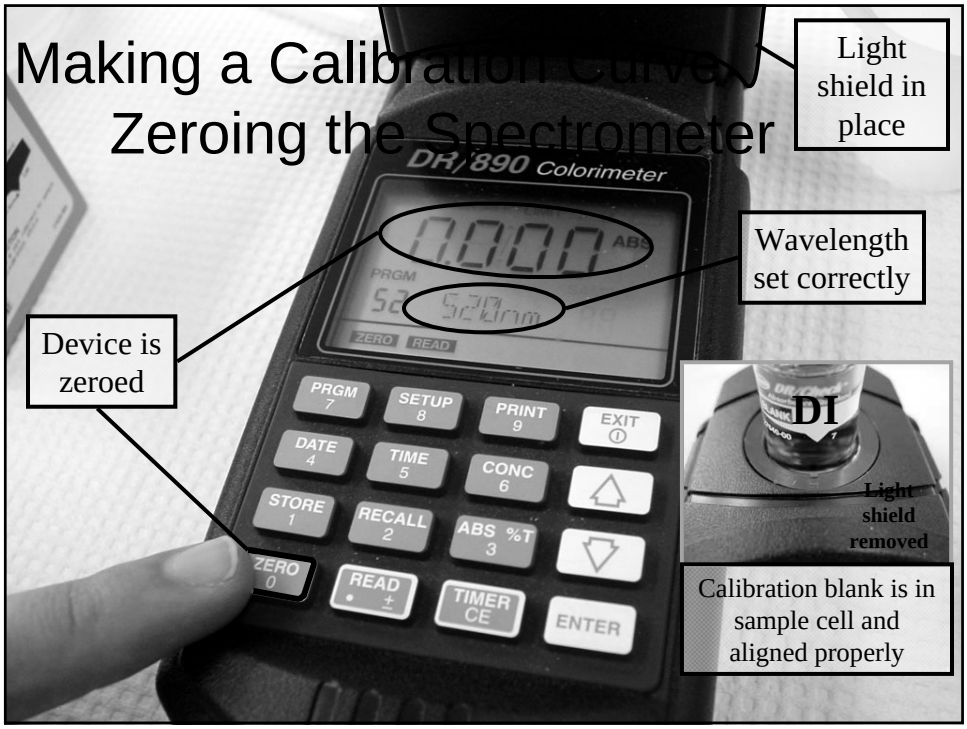
Destroyed DPD - colorless (pure chlorine bleach)

Making a Calibration Curve
Zeroing the Spectrophotometer

- Zero the spectrophotometer using the calibration blank (DI water + reagent)
  - Make sure the spectrophotometer is set to 515 nm. If this is not possible, use a wavelength between 515-540 nm.
  - Zero with the same water (colored) that was used in creating the calibration standards.
  - Pour the water from the flask into a clean sample cell. Wipe the cell clean of fingerprints.
  - Align the reference mark to the light source (or as appropriate), and zero the spectrophotometer.

Fingerprints, dust, and other residues can bias absorbance readings. Be sure to cleanly wipe off the optical surface of any sample cell or ampul that is analyzed with the spectrophotometer.

Making a Calibration Curve: Zeroing the Spectrometer



Light shield in place

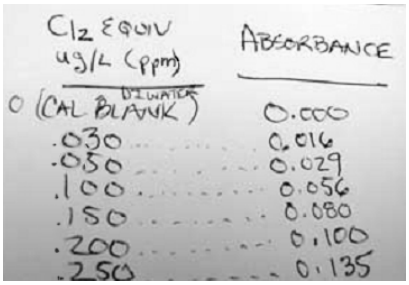
Wavelength set correctly

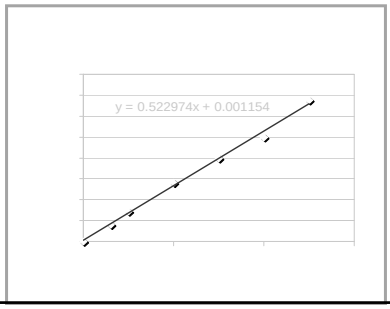
Device is zeroed

Calibration blank is in sample cell and aligned properly

Making a Calibration Curve: Record Data

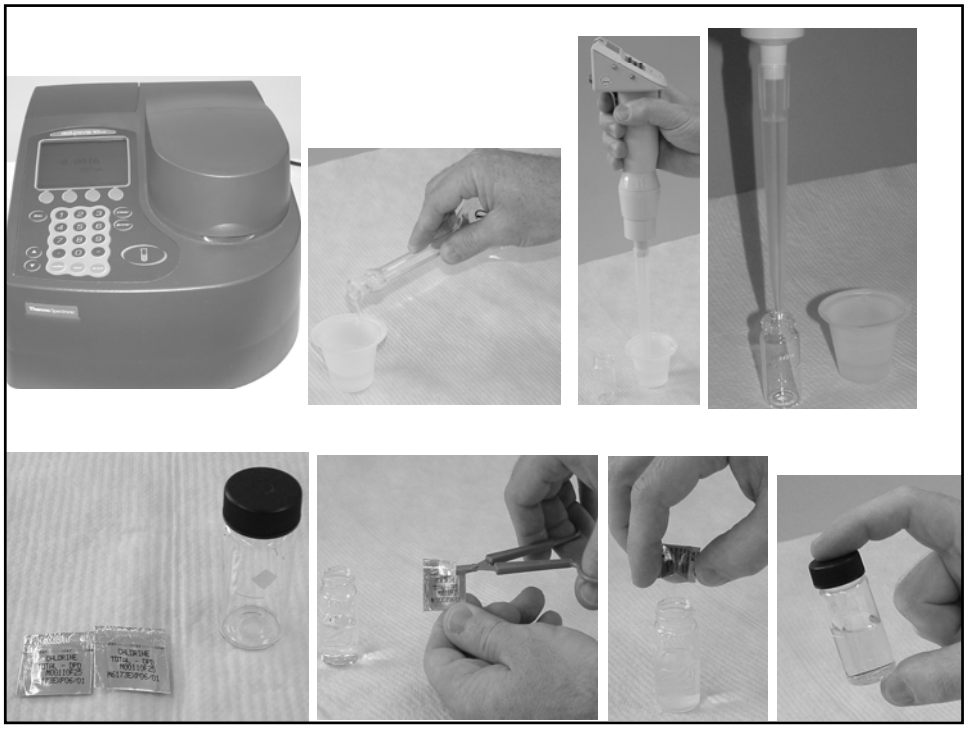
- Record the absorbance of each calibration standard
- This data is used when calculating a calibration curve.





Use a calculator, Excel, or other software.
In Excel, you can use the CORREL formula.

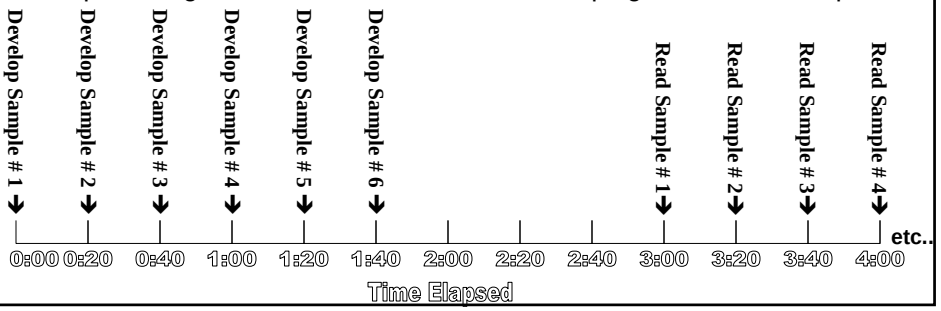
R = 0.998079



Analyzing a Sample - Timing

- Developed (solution + DPD) samples or standards should not be read before three minutes, or after six minutes. Read them between 3-6 minutes.
- Set up a timing schedule to maximize efficiency.
- Ensure that each sample develops for a consistent amount of time before it is read.

Example timing schedule for three minute developing time for six samples.



Analyzing a Sample

- When analyzing a sample record both absorbances (blank and developed) on the data sheet.
- Subtract the blank absorbance from the developed absorbance to get the adjusted absorbance.
- This adjusted absorbance corrects for any natural absorbance of the sample or ampul itself.

Example

Sample no.	Blank	Developed	Adj. Abs.
Outfall no. 1	0.003	0.032	0.029
Outfall no. 2	0.003	0.048	0.045
Outfall no. 3	0.000	0.046	0.046
Outfall no. 4	0.002	0.035	0.033

DEVELOPED - BLANK = Adjusted Absorbance

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**

Calibration data by approach - 2

GeneSys10

TRUE	CURVE	Bias
0	-0.001	
0.03	0.027	-12%
0.05	0.038	-24%
0.075	0.073	- 2%
0.1	0.112	12%
0.2	0.213	7%
0.4	0.392	- 2%

HACH DR890

TRUE	CURVE	Bias
0	0.014	
0.03	0.026	-14%
0.05	0.044	-11%
0.075	0.074	- 1%
0.1	0.095	- 5%
0.2	0.198	- 1%
0.4	0.404	1%

HACH DR890

TRUE	CURVE	Bias
0	-0.002	
0.03	0.028	-5%
0.05	0.053	6%
0.075	0.105	5%
0.1	0.151	1%
0.2	0.189	-5%
0.4	0.256	2%

HACH DR890 (internal curve)

TRUE	Bias
0	
0.03	67%
0.05	40%
0.1	20%
0.15	10%
0.2	5%
0.25	- 3%

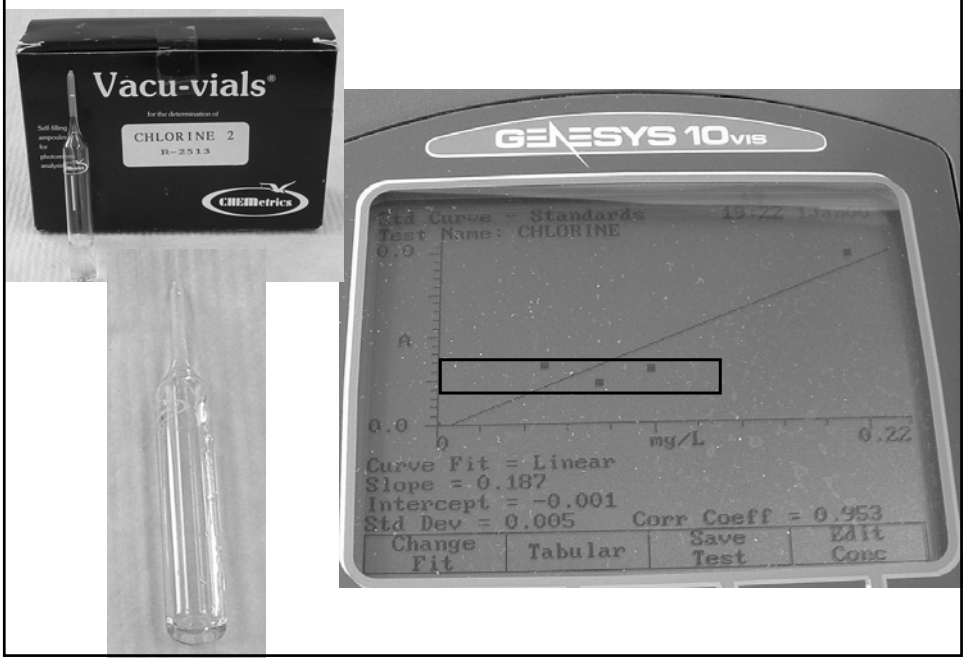
Slope=	0.25692	0.53456	0.522974
intercept=	0.00019	-0.00772	0.001154
"r"=	0.99766	0.99868	0.998079

LOD data by approach

LOD Determination. Spikes prepared at 0.090 mg/L

	GeneSys10		HACH DR890		HACH DR890 (internal calibration)
	Abs.	CURVE	Abs.	CURVE	CURVE
rep #1	0.023	0.089	0.041	0.091	0.11
rep #2	0.021	0.081	0.037	0.084	0.10
rep #3	0.021	0.081	0.039	0.087	0.10
rep #4	0.023	0.089	0.040	0.089	0.11
rep #5	0.022	0.085	0.036	0.082	0.10
rep #6	0.021	0.081	0.038	0.086	0.10
rep #7	0.021	0.081	0.041	0.091	0.11
mean	**0.084**		**0.087**		**0.104**
stdev	**0.00370**		**0.00365**		**0.00535**
LOD=	**0.0116**		**0.0115**		**0.01680**

Vacu-Vials--Another Available Option



Conclusions

- An LOD of 0.037ppm IS achievable
- 0.100 ppm is a realistic LOQ.
- The best data will be obtained using a technique providing a path-length of > 1cm.
- Quality low level calibrations CAN be easily developed.
- Both hand-held and table-top colorimeters are available that meet the needs.
- Internal calibrations are not sufficiently accurate at low levels.
- Vacu-vials may not be suitable at low levels required for compliance monitoring.