

NORTH CAROLINA WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION APPROVED PROCEDURE FOR THE ANALYSIS OF FREE AVAILABLE CHLORINE (DPD COLORIMETRIC)

This document provides an approved procedure for the colorimetric analysis of Free Available Chlorine (FAC) for compliance monitoring per 15A NCAC 2H .0805 (a) (7) and (g) (4).

Holding Time:

- After sampling, avoid excessive light and agitation. Ref: SM 4500 Cl A-2011 (4).
- Samples must be analyzed within 15 minutes of collection (NC WW/GW LC Policy). Sample analysis begins when the reagents are added to the sample.

General Information:

- If there is a Daily Maximum Limit required by the facility permit, you must have an instrument capable of detecting concentrations below that level, such as a spectrophotometer or filter photometer. Per 15A NCAC 02B .0505 (e) (4), facilities must produce detection and reporting levels that are below the Daily Maximum Limit.
- When using a Hach Pocket Colorimeter, follow these instructions to prepare samples for analysis:
 - 10 mL Free Chlorine Powder Pillows are to be used with the 10-mL glass vial under the Low Range (LR) setting on the Pocket Colorimeter. LR range is 0.02 to 2.00 mg/L Cl₂.
 - 25 mL Free Chlorine Powder Pillows are to be used with the 10-mL glass vial under the Mid Range (MR) setting on the Pocket Colorimeter. MR range is 0.05 to 4.00 mg/L Cl₂.
 - 25 mL Free Chlorine Powder Pillows are to be used with the 5-mL plastic vial under the High Range (HR) setting on the Pocket Colorimeter. HR range is 0.1 to 10.0 mg/L Cl₂.
- When using commercially prepared reagents, the laboratory must ensure that Free Available Chlorine reagents are used. Facilities may opt to use liquid reagents and the Pour-Thru Cell, but this is not required. Filtering samples is an allowable modification under Code of Federal Regulations, Title 40, Part 136; Federal Register Vol. 82, No. 165, August 28, 2017; 136.6. (b).
- All standard materials used must be ACS grade or higher purity.
- Do not use the same sample cells (including the Pour-Thru Cell) for Free Available and Total Residual Chlorine. If trace iodide from the Total Residual Chlorine reagent is carried over into the Free Available Chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for Free Available and Total Residual Chlorine measurements.
- Sample duplicates are not a required quality control element for Field parameters.

Definitions

- *Laboratory-generated Calibration Curve:* A linear regression equation generated from the analysis of a series of laboratory-prepared liquid standards. Sample results are obtained by plugging sample absorbance values into the linear regression formula. This is usually performed automatically by direct read-out meters.
- *Factory-set Calibration Curve:* An internal calibration curve, generated and stored as meter programs by the instrument manufacturer.
- *Calibration Blank:* Deionized or Distilled water, without chlorine and without DPD/buffer, that is used to zero the meter when a laboratory-prepared standard is used. A sealed standard (e.g., gel) blank may also be used for this purpose when sealed standards are used for the daily calibration verification.
- *Reagent Blank:* Deionized or Distilled water, from the same source used to make calibration and calibration verification standards, that is analyzed like a sample (i.e., with DPD/buffer added). The concentration of the reagent blank must not exceed 50% of the reporting limit (i.e., the lowest calibration or calibration verification standard concentration), unless otherwise specified by the reference method, or corrective action must be taken. Reagent

blanks would be required when using laboratory-prepared standards [including Proficiency Testing (PT) Samples] and anytime sample dilutions are performed.

- **Second-source Standard:** A standard prepared from a source independent (e.g., different vendor, different lot #, etc.) from that used to prepare the calibration standards.

NOTE: When using a factory-set calibration curve, all other standards are considered to be Second-source.

- **Daily Check Standard:** A sealed standard (e.g., gel) or a laboratory-prepared standard of known concentration of the analyte of interest. A Daily Check Standard is used to evaluate laboratory performance and analyte recovery in a blank matrix.
- **Post-Analysis Calibration Verification Standard:** A Daily Check Standard that is analyzed after all sample analyses.

Instrument Calibration or Calibration Curve Verification:

Depending upon the meter, you may either construct a Laboratory-generated Calibration Curve or verify the Factory-set Calibration Curve initially, at least every 12 months and any time the instrument optics are serviced. Most field photometric instruments have factory-set calibration programs, which when selected in combination with the optimum wavelength for a particular analysis, give a direct readout in concentration. These factory-set calibration programs are acceptable for quantitation, but due to possible analyst error, variation in sample or standard preparation, variation in reagents or malfunction of the instrument, the Factory-set Calibration Curve must be verified as described below.

Calibration curve verification checks must be performed with the calibration curve and/or program used for sample analysis. All compliance monitoring samples and PT Samples must be analyzed on the prepared or verified calibration curve.

For all calibration options, the range of standard concentrations must bracket the permitted discharge limit concentration, the range of sample concentrations to be analyzed and anticipated PT Sample concentrations. One of the standards must have a concentration less than the permitted discharge limit. The lower reporting limit concentration is equal to the lowest standard concentration. Sample concentrations that are less than the lower reporting limit must be reported as a less-than value.

Example:

If a facility has an FAC compliance limit of 0.120 mg/L (120 µg/L), they must demonstrate they can accurately quantify FAC concentrations below the Daily Maximum Limit. To do this, a standard concentration less than 0.120 mg/L (120 µg/L) must be analyzed. This will be their lower reporting limit.

If the laboratory chooses 2.00 mg/L (2000 µg/L) as the highest concentration in the calibration curve or calibration curve verification, all samples above this concentration must be diluted and reanalyzed to fall within the range of the chosen lower reporting limit and 2.00 mg/L (2000 µg/L).

Calibration and Calibration Curve Verification Options: Option 1 is the most widely used calibration curve verification option. Another certified laboratory may be able to provide assistance with the meter calibration curve and calibration curve verification options listed below. All documentation must be maintained by the meter user.

If the factory-set readings (Options 1 and 2 below) vary by more than the stated acceptance criteria, the stored calibration program must not be used for compliance monitoring until troubleshooting is carried out to determine and correct the source of error.

NOTE: Possible corrective actions include: re-zeroing the meter; ensuring glassware is clean and not scratched; preparing fresh calibration standards; having the meter serviced, etc.

NOTE: General Absorbance Standards (i.e., standards with specific absorbance values plus a tolerance range that are used to check absorbances at specific wavelengths) sometimes referred to as a "HACHDR/Check Absorbance Standard Kit", cannot be used for the Daily Check Standard or as a calibration standard.

Option 1 – Annual Factory-set Calibration Curve Verification: This type of calibration curve verification must be performed **initially, at least every 12 months and any time the instrument optics are serviced.** Zero the instrument with a Calibration Blank and then analyze a Reagent Blank and a series of five standards (do not use gel or sealed liquid standards for this purpose). The calibration standard values obtained must not vary by more than 10%.

Each day compliance samples are analyzed, perform the following:

- When an annual five-standard Factory-set Calibration Curve verification is used, the laboratory must check the calibration curve each analysis day. To do this, the laboratory must zero the instrument with a Calibration Blank and analyze a Daily Check Standard (gel-type standards are most widely used for these purposes). The value obtained for the Daily Check Standard must read within 10% of the true value of the Daily Check Standard. If the obtained value is outside of the $\pm 10\%$ range, corrective action must be taken.
- If preparing standards, analyzing a PT Sample or analyzing diluted samples, a Reagent Blank is required.
- When performing analyses at multiple sample sites in a single day, a Post-analysis Calibration Verification Standard must be analyzed after the last sample. It is recommended that a mid-day calibration verification be performed when samples are analyzed over an extended period of time. The value obtained for the Post-analysis Calibration Verification Standard must read within 10% of the true value of the Post-analysis Calibration Verification Standard. If the obtained value is outside of the $\pm 10\%$ range, corrective action must be taken.

Option 2 – Daily Factory-set Calibration Curve Verification: This type of calibration curve verification must be performed each day compliance samples are analyzed. Zero the instrument with the Calibration Blank and then analyze a Reagent Blank and a series of three standards (do not use gel or sealed liquid standards for this purpose). The values obtained must not vary by more than 10%.

- When performing analyses at multiple sample sites in a single day, a Post-analysis Calibration Verification Standard must be analyzed after the last sample. It is recommended that a mid-day calibration verification be performed when samples are analyzed over an extended period of time. The value obtained for the Post-analysis Calibration Verification Standard must read within 10% of the true value of the Post-analysis Calibration Verification Standard. If the obtained value is outside of the $\pm 10\%$ range, corrective action must be taken.

Option 3 – Annual Laboratory-generated Calibration Curve: This type of calibration curve must be generated initially, at least every 12 months and any time the instrument optics are serviced. Zero the instrument with the Calibration Blank and then analyze a Reagent Blank and a series of five standards (do not use gel or sealed liquid standards for this purpose). The obtained values are programmed into the instrument, computer spreadsheet, scientific calculator, or plotted manually. The correlation coefficient of the calibration curve must be ≥ 0.995 . Back calculate the concentration of each calibration point. For standards $\leq 50 \mu\text{g/L}$, the back-calculated value and standard true value must agree within $\pm 25\%$. For standards $> 50 \mu\text{g/L}$, the back-calculated value and standard true value must agree within $\pm 10\%$. The calibration curve must then be verified by analyzing a Second-source Standard (gel-type standards may not be used). The Second-source Standard must read within $\pm 10\%$ of its true value. Sample results are obtained from the linear regression equation of the calibration curve.

Each day compliance samples are analyzed, perform the following:

- When an annual five-standard Laboratory-generated Calibration Curve is used, the laboratory must check the calibration curve each analysis day. To do this, zero the instrument with a Calibration Blank and analyze a Daily Check Standard (gel-type standards are most widely used for this purpose). The value obtained for the Daily Check Standard must read within 10% of the true value of the Daily Check Standard. If the obtained value is outside of the $\pm 10\%$ range, corrective action must be taken.
- If preparing standards, analyzing a PT Sample or analyzing diluted samples, a Reagent Blank is required.
- When performing analyses at multiple sample sites in a single day, a Post-analysis Calibration Verification Standard must be analyzed after the last sample. It is recommended that a mid-day calibration verification be performed when samples are analyzed over an extended period of time. The value obtained for the Post-analysis Calibration Verification Standard must read within 10% of the true value of the Post-analysis Calibration Verification Standard. If the obtained value is outside of the $\pm 10\%$ range, corrective action must be taken.

Option 4 – Daily Laboratory-generated Calibration Curve: This type of calibration curve must be generated each day compliance samples are analyzed. Zero the instrument with the Calibration Blank and then analyze a Reagent Blank and a series of three standards (do not use gel or sealed liquid standards for this purpose). The obtained values are programmed into the instrument, computer spreadsheet, scientific calculator, or plotted manually. The correlation coefficient of the calibration curve must be ≥ 0.995 . Sample results are obtained from the linear regression equation of the calibration curve.

Each day compliance samples are analyzed, perform the following:

- When a daily three-standard Laboratory-generated Calibration Curve is used, the laboratory must verify the calibration curve each analysis day with a Daily Check Standard prepared from a second source. The calibration check is performed immediately after calibration. The value obtained for the Daily Check Standard must read within 10% of the true value of the Daily Check Standard. If the obtained value is outside of the $\pm 10\%$ range, corrective action must be taken.
- When performing analyses at multiple sites, a Post-analysis Calibration Verification Standard must be analyzed at the end of the run. It is recommended that a mid-day calibration verification be performed when samples are analyzed over an extended period of time. The value obtained for the Post-analysis Calibration Verification Standard must read within 10% of the true value of the Post-analysis Calibration Verification Standard. If the obtained value is outside of the $\pm 10\%$ range, corrective action must be taken.

Standard Solutions:

You may prepare a stock standard solution of potassium permanganate or chlorine and subsequent standard solutions as described in Standard Methods 4500-Cl G – 2011, DPD Colorimetric Method, Sections 4 (a) (1) and (2), page 4-69.

If liquid chlorine standard solutions with a stated range and average value are used, the average value must be used for the true value of the standard. These standards may only be used for the Daily Check Standard and may not be used for generating or verifying a calibration curve.

Purchased “gel-type” or sealed liquid standards may be used only for daily calibration curve verifications. These standards must have a true value assigned **initially** and with each subsequent calibration curve generation/verification thereafter. When this is done, these standards may be used after the manufacturer’s expiration date. It is only necessary to assign a true value to the gel-type or sealed liquid standard which falls within the concentration range of the calibration curve used to measure sample concentrations. For example, if you are measuring samples against a low-range calibration curve, a 200 $\mu\text{g/L}$ standard would be verified, and not the 800 $\mu\text{g/L}$ standard since the 800 $\mu\text{g/L}$ standard would be measured using a high-range calibration curve.

To assign a true value to the gel-type or sealed liquid standard:

1. Zero the instrument with the calibration blank.
2. Read and record gel standard values.
3. Repeat steps 1 and 2 at least two more times.
4. Assign the average value as the true value.

The assigned true value will be used until a new calibration curve verification is performed and the true value is reassigned. The gel/sealed liquid standard true value assignment must be performed for each instrument on which they are to be used. If multiple instruments and/or standard sets are used, each must have assigned true values specific for the instrument and standard set. Documentation must link the gel/sealed liquid standard identification to the meter with which the assigned value was determined.

Equipment Maintenance:

As cited in the Laboratory Certification rules, “Each facility must have glassware, chemicals, supplies, equipment, and a source of distilled or deionized water that will meet the minimum criteria of the approved methodologies.” Ref: 15A NCAC 2H .0805 (g) (4). Meeting the minimum criteria means the equipment must also be properly maintained. Clean and maintain equipment as indicated by the manufacturer’s instructions. Sample lines and the Pour-Thru Cell can become discolored and clogged due to a buildup of colored reaction products or algae growth.

Hach offers the following instructions for cleaning the pour-thru cell:

Cleaning the Pour-Thru Cell

The Pour-Thru Cell may accumulate a buildup of colored reaction products, especially if the reacted solutions are allowed to remain in the cell for long periods after measurement. Remove the buildup by rinsing the cell with 5.25 N sulfuric acid followed by rinsing with deionized water.

If your facility does not have access to or is not comfortable using sulfuric acid cleaning solution, a contract laboratory or vendor may perform this service. Please exercise proper safety precautions when handling acid solutions.

Check condition of sample cells prior to use. They must be clean, clear of fingerprints and free of scratches. Also note orientation of cells in the instrument. Ensure proper placement of indexed cells. Note that there are two options for Pour-Thru Cell placement. One gives a 1-inch cell path length and when rotated 90°, gives a ½-inch cell path length. Ensure the 1-inch cell path length is used. **Do not use the same sample cells for free and total chlorine.** If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine measurements.

Daily Sample Analysis Procedure:

- Zero meter
- Analyze Daily Check Standard
- Analyze Reagent Blank, if applicable
- Collect sample (sample may be collected before or after calibration or calibration check)
- Add Free Available Chlorine DPD/buffer within 15 minutes of sample collection
- Gently swirl sample for 20 seconds, then immediately measure result
- Sample must be measured within 60 seconds of reagent addition
- Document required information

Documentation:

The following must be documented in indelible ink whenever sample analysis is performed:

1. Date and time of sample collection and analysis.
2. Facility name or permit number, and sample site (ID or location)
3. Collector's/analyst's name or initials
4. Daily Check Standard analysis time(s)
5. Preparation procedure and true values of laboratory-prepared standards, when applicable
6. True value of the Daily Check Standard(s)
7. Value obtained for the Daily Check Standard(s)
8. Value obtained for the Reagent Blank, when prepared standards, PT Samples or diluted samples are analyzed (verification of $\leq \frac{1}{2}$ the concentration of the lowest calibration standard)
9. All data must be documented and reported in units of measure **as specified in the permit** (e.g., mg/L for regular level or $\mu\text{g/L}$ for low level)
10. True value and value obtained for the Post-analysis Calibration Verification Standard(s), where applicable
11. Quality control assessments
12. Traceability for chemicals, reagents, standards and consumables
13. Instrument identification (serial number preferred)
14. Date of most recent calibration curve generation or calibration curve verification
15. Statement that samples were filtered, when applicable
16. Final value to be reported
17. Parameter analyzed
18. Method reference
19. Data qualifier(s), when applicable
20. Equipment maintenance (recommended)

Refer to <http://deq.nc.gov/about/divisions/water-resources/water-resources-data/water-sciences-home-page/laboratory-certification-branch/technical-assistance-policies> for additional quality assurance and quality control requirements.

This document was prepared using Standard Methods 4500-Cl G – 2011 and Hach Methods 8021 as references.

FREE AVAILABLE CHLORINE CURVE PREPARATION
Using KMnO₄ (potassium permanganate)

Note: The use of **Class A** Volumetric flasks and pipettes is critical to the accurate preparation of these low-level standards.

Needed Materials

Chlorine-Free Water

Potassium Permanganate (designated as a standard, not as a reagent)

1-Liter Class A Volumetric Flask (Quantity = 1)
100-mL Class A Volumetric Flasks (Quantity = 7)
50-mL Class A Volumetric Pipette (Quantity = 1)
40-mL Class A Volumetric Pipette (Quantity = 1)
30-mL Class A Volumetric Pipette (Quantity = 1)
20-mL Class A Volumetric Pipette (Quantity = 1)
10-mL Class A Volumetric Pipette (Quantity = 2)
1-mL Class A Volumetric Pipette (Quantity = 1)

1000 mg/L Stock Standard – Prepare by dissolving 891 mg KMnO₄ (potassium permanganate) in 1 liter of chlorine-free water.

100 mg/L Intermediate Standard – Prepare by diluting 10 mL of the Stock Standard to 100 mL with chlorine-free water.

1.0 mg/L (1000 µg/L) Working Standard - Prepare by diluting 1 mL of the Intermediate Standard to 100 mL with chlorine-free water.

The Working Standard will be used to prepare your 5-Standard Curve.

Add 50 mL of the Working Standard to a 100-mL volumetric flask and dilute to volume with chlorine-free water. **This is your 0.5 mg/L (500 µg/L) Standard.**

Add 40 mL of the Working Standard to a 100-mL volumetric flask and dilute to volume with chlorine-free water. **This is your 0.4 mg/L (400 µg/L) Standard.**

Add 30 mL of the Working Standard to a 100-mL volumetric flask and dilute to volume with chlorine-free water. **This is your 0.3 mg/L (300 µg/L) Standard.**

Add 20 mL of the Working Standard to a 100-mL volumetric flask and dilute to volume with chlorine-free water. **This is your 0.2 mg/L (200 µg/L) Standard.**

Add 10 mL of the Working Standard to a 100-mL volumetric flask and dilute to volume with chlorine-free water. **This is your 0.1 mg/L (100 µg/L) Standard.**