NORTH CAROLINA WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION BRANCH APPROVED PROCEDURE FOR THE ANALYSIS OF TOTAL RESIDUAL CHLORINE (DPD COLORIMETRIC by Hach 10014 ULR)

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

Holding Time:

- Samples must be analyzed within 15 minutes of collection (40 CFR Part 136 Table II). 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 NPDES permit section D. 4, facilities must produce detection and reporting levels that are below the Daily Maximum Limit.
    - **NOTE:** Even though permits for stormwater monitoring do not have Daily Maximum Limits, stormwater permittees must use an instrument and analytical method capable of detecting concentrations below the specified stormwater benchmark concentration of 28 µg/L to properly assess pollutants and the effectiveness of Best Management Practices (BMPs).
- The Reagent Blank value must be determined each analysis day and must be < 5 µg/L. The Reagent Blank value must be subtracted from the Method Blank and all sample and standard results. Powder reagents may be used in place of liquid reagents, and the sample filtration step and use of the Pour-Thru Cell may be omitted. A laboratory wishing to use these modifications must demonstrate acceptable method performance by performing and documenting all applicable initial demonstrations of capability and ongoing QC tests and meeting all applicable QC acceptance criteria as described in 40 CFR § 136.7.
- All standard materials used must be ACS grade or higher purity.
- 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*: A blank that is used to zero the meter. When using a laboratory-prepared standard, the calibration blank is Deionized or Distilled water, without chlorine and without DPD/buffer. When using a gel-type Daily Check Standard, the calibration blank is the gel-type blank.
- *Reagent Blank*: Deionized or Distilled water, from the same source used to make calibration and calibration verification standards, to which 1.0 mL of Blanking Reagent is added. The Blanking Reagent removes chlorine and chloramines from the water. It is then analyzed like a sample (i.e., with DPD/buffer added). The concentration of the reagent blank must not exceed 5 µg/L.
- *Method 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 Method Blank, after the Reagent Blank concentration is subtracted, must be ≤ ½ the concentration of the lowest calibration, or calibration verification, standard.
- *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 and PT Samples must be analyzed on the prepared or verified calibration curve and/or program.

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 Daily Maximum 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 a Total Residual Chlorine Daily Maximum Limit of 28 µg/L, they must demonstrate they can accurately quantify TRC below the Daily Maximum Limit. To do this, a standard concentration less than 28 µg/L must be analyzed. Most laboratories choose a standard concentration below their Daily Maximum Limit that is easy to prepare, such as 20 µg/L in this example. This will be their lower reporting limit. Anytime a compliance sample measures less than this value (e.g., 18 µg/L), it is reported on the Discharge Monitoring Report (DMR) as <20 µg/L.

If the laboratory chooses 400 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 400 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 "HACH DR/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, a Method Blank and a series of five standards (do not use gel or sealed liquid standards for this purpose). The value of the Reagent Blank is subtracted from the value of each standard. The adjusted calibration standard values obtained must not vary by more than ±10% from the known value for standard concentrations greater than or equal to 50 µg/L and must not vary by more than ±25% from the known value for standard concentrations less than 50 µg/L. The concentration of the Method Blank (with the Reagent Blank value subtracted) must be ≤½ the concentration of the lowest calibration curve verification standard.

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 Reagent Blank and a Daily Check Standard. The value of the Reagent Blank is subtracted from the Daily Check Standard value when using a laboratory-prepared standard (not applicable when using a gel-type standard). The adjusted value obtained for the Daily Check Standard must read within ±10% of the true value of the Daily Check Standard for standards ≥50 µg/L and within ±25% of its true value for standards <50 µg/L. If the obtained value is outside of the acceptance limits, corrective action must be taken.

- Analyze a Method Blank when using a laboratory-prepared standard (not applicable when using a gel-type standard). The concentration of the Method Blank (with the Reagent Blank value subtracted) must be ≤½ the concentration of the lowest calibration curve verification standard.

- 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 for standards ≥50 µg/L and within ±25% of its true value for standards <50 µg/L. If the obtained value is outside of the acceptance limits, corrective action must be taken.

<u>Option 2</u> – 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, a Method Blank and a series of three standards (do not use gel or sealed liquid standards for this purpose). The value of the Reagent Blank is subtracted from the value of each standard. The adjusted values obtained must not vary by more than ±10% of the known value for standard concentrations greater than or equal to 50 µg/L and must not vary by more than ±25% of the known value for standard concentrations less than 50 µg/L. The concentration of the Method Blank (with the Reagent Blank value subtracted) must be ≤½ the concentration of the lowest calibration curve verification standard.

- 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 (with the Reagent Blank value subtracted if using a laboratory-prepared standard) must read within ±10% of the true value of the Post-analysis Calibration Verification Standard for standards ≥50 µg/L and within ±25% of its true value for standards <50 µg/L. If the obtained value is outside of the acceptance limits, corrective action must be taken.

<u>Option 3</u> – Annual Laboratory-generated Calibration Curve: This type of calibration curve must be generated **<u>initially, at least every 12 months and any time the instrument optics are serviced.</u>** Zero the instrument with the Calibration Blank and then analyze a Reagent Blank, a Method Blank and a series of five standards (do not use gel or sealed liquid standards for this purpose). The absorbance value of the Reagent Blank is subtracted from the absorbance value of each standard. The adjusted absorbance 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 <50 µg/L, the back-calculated value and standard true value must agree within ±25%. For standards ≥50 µg/L, the back-calculated value and standard true value must agree within ±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 ±10% of its true value for standards ≥50 µg/L and within ±25% of its true value for standards <50 µg/L. 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 Reagent Blank and a Daily Check Standard. The value of the Reagent Blank is subtracted from the Daily Check Standard value when using a laboratory-prepared standard. The adjusted value obtained for the Daily Check Standard must read within ±10% of the true value of the Daily Check Standard for standards ≥50 µg/L and within ±25% of its true value for standards <50 µg/L. If the obtained value is outside of the acceptance limits, corrective action must be taken.

- Analyze a Method Blank when using a laboratory-prepared standard (not applicable when using a gel-type standard). The concentration of the Method Blank (with the Reagent Blank value subtracted) must be ≤½ the concentration of the lowest calibration curve standard.

- 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 (with the Reagent Blank value subtracted if using a laboratory-prepared standard) must read within ±10% of the true value of the Post-analysis Calibration Verification Standard for standards ≥ 50 µg/L and within ±25% of its true value for standards <50 µg/L. If the obtained value is outside of the acceptance limits, 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, a Method Blank and a series of three standards (do not use gel or sealed liquid standards for this purpose). The absorbance value of the Reagent Blank is subtracted from the absorbance value of each standard. The adjusted absorbance 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 <50 µg/L, the back-calculated value and standard true value must agree within ±25%. For standards ≥50 µg/L, the back-calculated value and standard true value must agree within ±10%. Sample results are obtained from the linear regression equation of the calibration curve. The concentration of the Method Blank (with the Reagent Blank value subtracted) must be ≤½ the concentration of the lowest calibration curve standard.

The laboratory must then verify the calibration curve 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 (with the Reagent Blank value subtracted if using a laboratory-prepared standard) must read within ±10% of the true value of the Daily Check Standard for standards ≥50 µg/L and within ±25% of its true value for standards <50 µg/L. If the obtained value is outside of the acceptance limits, 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 (with the Reagent Blank value subtracted if using a laboratory-prepared standard) must read within ±10% of the true value of the Post-analysis Calibration Verification Standard for standards ≥50 µg/L and within ±25% of its true value for standards <50 µg/L. If the obtained value is outside of the acceptance limits, corrective action must be taken.

Standard Solutions:

All standards and PT Samples must be prepared using Class-A volumetric flasks and either a calibrated mechanical pipette or a Class-A volumetric pipette.

Potassium Permanganate Stock Solution: Prepare a stock solution containing 891 mg $KMnO_4$/1000 mL. Dilute 10.00 mL stock solution to 100 mL with chlorine-free water in a volumetric flask. When 1 mL of this solution is diluted to 100 mL with chlorine-free water, a chlorine equivalent of 1.00 mg/L will be in the DPD reaction. Store in an amber glass bottle and refrigerate. Use within the laboratory-assigned expiration date.

Working standards for calibrating the meter or verifying the Factory-set Calibration Curve can be made by serial dilutions of the stock solution.

If commercially prepared 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 verification of a Factory-set Calibration Curve. They may not be used for preparing a Laboratory-generated 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 every 12 months 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 µg/L standard would be verified, and not the 800 µg/L standard since the 800 µg/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 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 water that will meet the minimum criteria of the approved methodologies. Ref: 15A NCAC 02H .0805 (a) (6) (A) and (B) and 15A NCAC 02H .0805 (g) (6). 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 Method 10014 ULR 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. Flush the Pour-Thru Cell with DI water immediately prior to and following use each day. 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.

Daily Sample Analysis Procedure:

- Zero meter with calibration blank
- Analyze a Reagent Blank (Subtract that value from the laboratory-prepared Daily Check Standard, Method Blank and samples)
- Analyze Daily Check Standard
- Analyze Method Blank (only if using a laboratory-prepared Daily Check Standard)
- Collect sample (sample may be collected before or after calibration or calibration check)
- Zero meter with unreacted, filtered sample
- Add DPD/buffer within 15 minutes of collection
- Wait 3 - 6 minutes
- Filter sample
- Read sample result
- Document required information

Documentation:

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

1. Date and time of sample collection
2. Date and time of sample analysis to verify the 15-minute holding time is met [Alternatively, one time may be documented for collection and analysis with the notation that samples are measured immediately at the sample site.]
3. Facility name or permit number, and sample site (ID or location)
4. Collector's/analyst's name or initials
5. Daily Check Standard analysis time(s)
6. Preparation procedure and true values of laboratory-prepared standards, when applicable
7. True value of the Daily Check Standard(s)
8. Value obtained for the Daily Check Standard(s)
9. Value obtained for the Reagent Blank (verification of <5 µg/L)
10. Value obtained for the Method Blank (verification of ≤½ concentration of the lowest calibration curve, or calibration curve verification, standard)
11. Time analyzed, true value and value obtained for the Post-analysis Calibration Verification Standard(s), where applicable

12. Quality control assessments (percent recovery or acknowledgement that observed concentration is within the acceptance range)
13. All data must be documented and reported in units of measure **as specified in the permit** (i.e., µg/L)
14. Traceability for chemicals, reagents, standards and consumables
15. Instrument identification (serial number preferred)
16. Date of most recent calibration curve generation or calibration curve verification
17. Statement that samples were filtered
18. Final value to be reported
19. Parameter analyzed
20. Method reference
21. Data qualifier(s), when applicable
22. Equipment maintenance (recommended)

This document was prepared using Hach Method 10014 ULR as a reference.