NORTH CAROLINA WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION APPROVED PROCEDURE FOR THE ANALYSIS OF TOTAL RESIDUAL CHLORINE

This document provides an approved procedure for the colorimetric analysis of Total Residual Chlorine (TRC) per 15A NCAC 2H .0805 (a) (6) (F) and (g) (3). The procedures in this document, in addition to all requirements of the EPA approved method found in 40 CFR Part 136.3, must be met.

Holding Time:

- Samples must be analyzed within 15 minutes of collection (40 CFR Part 136 Table II).

General Information:

- If there is a limit required by the facility permit, you must have an instrument capable of detecting concentrations at that level, such as a spectrophotometer or filter photometer.

- If a facility has no effluent limit for TRC (just a monitoring requirement), then use of a hand-held meter, sometimes described as a pocket colorimeter, is acceptable. For facilities using these hand-held meters, the North Carolina Division of Water Quality has established the minimum reporting level at 100 µg/L. Any values obtained less than that concentration must be reported as "<100 µg/L". Ref: Division of Water Quality, Point Source Compliance/Enforcement Unit letter dated August 14, 2001.

- Since Hach Method ULR 10014 is approved by EPA as an alternate test procedure, all steps in the method must be followed. This means that the sample must be filtered, liquid reagents must be used and the flow-thru cell must be used.

Instrument Calibration or Standard Curve Verification:

Instruments are to be calibrated according to the manufacturer's calibration procedure or a standard curve verification must be performed prior to analysis of samples each day compliance monitoring is performed. Standard curve verification checks must be performed for the standard curve and/or program used for sample analysis.

Depending upon the meter, you may either construct a laboratory-generated calibration curve or verify the factory-set calibration. 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 must be verified at least **every 12 months**.

The definition of a laboratory-generated calibration; as opposed to a factory-set calibration verification is as follows:

- *Laboratory-generated Calibration* means: A series of standards are analyzed by the permitted facility and the obtained values are programmed into the instrument, computer spreadsheet, scientific calculator, or plotted manually. Sample results are obtained by comparison to the linear regression of those values. The standard materials used must be of an acceptable purity. Each analyst performing the test must generate an individual calibration curve.

- *Factory-set Calibration Verification* means: An internal standard curve, generated by the instrument manufacturer, is checked (i.e., verified) using a series of known standards. The standard materials used to verify the factory-set calibration must be of an acceptable purity. This procedure may be performed by the permitted facility or may be contracted to a vendor or another laboratory. Since a single curve is always used for sample measurement and is verified for accuracy, each analyst does not have to perform factory-set calibration verifications, this may be done per instrument.

The concentrations of the calibration standards must bracket the concentrations of the samples analyzed. One of the standards must have a concentration equal to or below the lower reporting concentration for Total Residual Chlorine. The lower reporting limit must be less than or equal to the permit limit.

Example:

If the laboratory chooses to have a lower reporting limit of 20 µg/L for residual chlorine, you must analyze at least a 20 µg/L or lower standard and report lower concentrations as <20 µg/L or < the concentration of the chosen standard.

If you choose 400 µg/L for the top of your standard curve, all samples above this limit must be diluted and reanalyzed to fall within the range of the chosen lower standard and 400 µg/L.

Blanks:

Generally, for colorimetric analyses, a calibration blank must be analyzed each day to zero the instrument. A calibration blank is a volume of reagent water of the same matrix as the calibration standards, but without the target analyte.

Each day that prepared standards are analyzed, a reagent blank must be analyzed to determine if method analytes or other interferences are present in the laboratory environment, the reagents or the apparatus. This includes annual standard curve verifications as well as daily prepared standards. A reagent blank is an aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, and reagents (e.g., DPD) that are used with other samples. The concentration of reagent blanks must not exceed 50% of the reporting limit, unless otherwise specified by the reference method, or corrective action must be taken.

Calibration and Standard Curve Verification Options:

Option 1 – Annual Factory-set Standard Curve Verification: Analyze a calibration blank to zero the instrument and then analyze a series of five standards (do not use gel or sealed liquid standards for this purpose). The curve verification must check 5 concentrations (not counting the blank) that bracket the range of the sample concentrations to be analyzed. This type of standard curve verification must be performed at least **every 12 months**. The 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 overall correlation coefficient of the curve must be ≥0.995.

If the stored program readings vary by more than the above acceptance criteria, the stored calibration program must not be used for quantitation until troubleshooting is carried out to determine and correct the source of error.

- Each day that prepared standards are analyzed, a reagent blank must be analyzed.
- When a five-standard annual standard curve verification is used, the laboratory must check the calibration curve each analysis day. To do this, the laboratory must analyze a calibration blank to zero the instrument and analyze a check standard each day that samples are analyzed. The value obtained for the check standard must read within 10% of the true value of the check standard. If the obtained value is outside of the ±10% range, corrective action must be taken.
- When performing analyses away from the certified laboratory's primary location, a post analysis calibration verification must be analyzed at the end of the run. The post analysis calibration verification standard concentration must be at mid range. 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 check standard must read within 10% of the true value of the post analysis calibration verification check standard. If the obtained value is outside of the ±10% range, corrective action must be taken.

NOTE: General absorbance standards (i.e., DR/check) supplied by some manufacturers cannot be used for the check standard. Gel-type standards may be used for this purpose.

Option 2 – Daily Factory-set Standard Curve Verification: Analyze a calibration blank to zero the instrument and then analyze a series of three standard concentrations (not counting the blank) that bracket the range of the sample concentrations to be analyzed (do not use gel or sealed liquid standards for this purpose). The 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 overall correlation coefficient of the curve must be ≥0.995. Each day that prepared standards are analyzed, a reagent blank must be analyzed.

Option 3 – Annual Laboratory-generated Calibration Curve: Analyze a calibration blank to zero the instrument and then analyze a series of five standard concentrations (not counting the blank) that bracket the range of the sample concentrations to be analyzed. The obtained values are programmed into the instrument, computer spreadsheet, scientific calculator, or plotted manually. Sample results are obtained by comparison to the linear regression of those values. The standard materials used must be of an acceptable purity. Each analyst performing the test must have an individual calibration curve. This type of curve must be performed annually (i.e., at least **every 12 months**).

- Each day that prepared standards are analyzed, a reagent blank must be analyzed.
- When a five-standard annual curve is generated, the laboratory must check the calibration curve each analysis day. To do this, the laboratory must analyze a calibration blank to zero the instrument and analyze a check standard each

day that samples are analyzed. The value obtained for the check standard must read within 10% of the true value of the check standard. If the obtained value is outside of the ±10% range, corrective action must be taken.

- When performing analyses away from the certified laboratory's primary location, a post analysis calibration verification must be analyzed at the end of the run. The post analysis calibration verification standard concentration must be at mid range. 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 check standard must read within 10% of the true value of the post analysis calibration verification check standard. If the obtained value is outside of the ±10% range, corrective action must be taken.

NOTE: General absorbance standards (i.e., DR/check) supplied by some manufacturers cannot be used for the check standard. Gel-type standards may be used for this purpose.

Option 4 – Daily Laboratory-generated Calibration Curve: Analyze a calibration blank to zero the instrument and then analyze a series of three standard concentrations (not counting the blank) that bracket the range of the sample concentrations to be analyzed. The obtained values are programmed into the instrument, computer spreadsheet, scientific calculator, or plotted manually. Sample results are obtained by comparison to the linear regression of those values. The standard materials used must be of an acceptable purity. Each analyst performing the test must have an individual calibration curve. This type of curve must be performed each day compliance samples are analyzed.

- Each day that prepared standards are analyzed, a reagent blank must be analyzed.

- When a three-standard daily curve is generated, the laboratory must check the instrument calibration each analysis day. To do this, the laboratory must analyze a calibration blank to zero the instrument and analyze a check standard each day that samples are analyzed. The calibration check is performed immediately after calibration. The value obtained for the check standard must read within 10% of the true value of the check standard. If the obtained value is outside of the ±10% range, corrective action must be taken.
- When performing analyses away from the certified laboratory's primary location, a post analysis calibration verification must be analyzed at the end of the run. The post analysis calibration verification standard concentration must be at mid range. 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 check standard must read within 10% of the true value of the post analysis calibration verification check standard. If the obtained value is outside of the ±10% range, corrective action must be taken.

NOTE: General absorbance standard (i.e., DR/check) supplied by some manufacturers cannot be used for the check standard. Gel-type standards may be used for this purpose.

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 – 2000, DPD Colorimetric Method, Section 4 (a) (2), page 4-69.

If purchased standard solutions in sealed ampules with a stated range and average value are used, the average value must be used for the true value of the standard.

Purchased "Gel-type" or sealed liquid ampoule standards may be used for daily standard curve verification only. These standards must be verified **initially** and **every 12 months** thereafter, with the standard curve. When this is done, these standards may be used after the manufacturer's expiration date. It is only necessary to verify the gel or sealed liquid standard which falls within the concentration range of the curve used to measure sample concentrations. For example, if you are measuring samples against a low range 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 curve.

Immediately following curve verification:

1. Zero the instrument with the gel blank.
2. Read and record gel standard values.
3. Assign the obtained values as the true value.

The assigned values will be used for the next twelve months, or until a new curve verification is performed. The gel/liquid standard verification 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 values specific for the instrument and standard set. Documentation must link the gel standard identification to the meter with which the assigned value was determined. Some commercial laboratory facilities may be able to provide assistance with the field photometric meter curve verifications.

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 build up of colored reaction products.

Hach Method 10014 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.

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 *in situ* or immediately at the sample site.
3. Sample site including facility name and location, ID, etc.
4. Collector's/analyst's name or initials.
5. Meter calibration and meter calibration time(s).
6. True values of the standards used for calibration or standard curve verification.
7. True value of the check standard.
8. Value obtained for the check standard (verification of ± 10% recovery).
9. Value obtained for the reagent blank, when prepared standards are used (verification of <½ the concentration of the lowest calibration standard).
10. All data must be reported in mg/L or µg/L (i.e., as specified in the permit).
11. True value and value obtained for the post analysis calibration verification(s), where applicable.
12. Traceability for chemicals, reagents, standards and consumables.
13. Instrument identification.
14. Parameter analyzed.
15. Data qualifier(s), when applicable.
16. Equipment maintenance (recommended).

Refer to *Quality Assurance Policies for Field Laboratories* (at http://portal.ncdenr.org/web/wq/lab/cert/field/policy) for additional quality assurance and quality control requirements.

Ref: Standard Methods 4500-Cl G - 2000
Hach Method 10014