# NORTH CAROLINA WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION APPROVED PROCEDURE FOR THE ANALYSIS OF TOTAL RESIDUAL CHLORINE (Low-Level Amperometric Forward Titration)

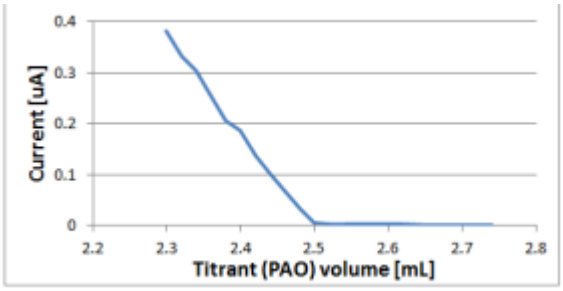
This document provides an approved procedure for the Amperometric Forward Titration analysis of Total Residual Chlorine (TRC) for compliance monitoring per 15A NCAC 2H .0805 (a) (a) (7) and (g) (4).

## Holding Time:

- Samples must be analyzed within 15 minutes of collection (40 CFR Part 136.3 Table II).

## General Information:

- The forward titration follows Standard Methods for the Examination of Water and Wastewater (SM) 4500-Cl E-2011. In this method the chlorine is in the sample at the beginning of the titration which is at a higher µA reading. As the titration runs the chlorine is consumed by the Phenylarsine Oxide (PAO). As the titrant is added and the chlorine is consumed the µA reading decreases. Once all of the chlorine in the sample is consumed, the µA reading will be near zero, and no matter how much more PAO is added, the µA reading won't change. Resulting in a graph like the one below.




The results are calculated with the sample volume used, the concentration of the PAO, and the volume of the PAO needed to reach the end point (which is where the graph goes from sloped to flat and the µA reading no longer changes). [Hach® Document TE728,2 Version 4.0, published 4/10/2018]

- Before using this method or a new instrument, determine its operational range (upper and lower limits), or at least verify the intended range of use. For each analyte, use standard concentrations that provide increasing instrument or other test response. The minimum reporting level (MRL) is set at or above the lowest standard used in the analysis. Quantitation at the MRL must be verified initially and at least quarterly (preferable daily) by analyzing a QC sample. The standard must read within ±10% of the true value.

- The low-strength standard phenylarsine oxide (PAO) titrant must be standardized initially when prepared by the laboratory and every month thereafter (see Appendix A for standardization procedure). Purchased titrant is not required to be standardized initially when the certificate of analysis is retained but must be standardized monthly once it has been opened. All standardizations must be documented. CAUTION: phenylarsine oxide is a cancer-suspect agent.

- All standard materials used must be ACS grade or higher purity.

- Sample duplicates are not a required quality control element for Field parameters.

## Definitions

- *Method Blank*: Chlorine-free water, from the same source used to make the Daily Check Standard, that is analyzed like a sample. The concentration of the method blank must not exceed one half the reporting limit, or corrective action must be taken.

- *Daily Check Standard:* A standard of known concentration of the analyte of interest (chlorine). A Daily Check Standard is used to evaluate laboratory performance and analyte recovery in a blank matrix. The Daily Check Standard must agree within ±10% of the true value, or corrective action must be taken.

**Standard and Reagents**

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.

Only low-strength phenylarsine oxide titrant (**0.000** 564 *N*) may be used with this method.

Refer to Appendix A for standard and reagent preparation instructions.

**Analysis**

- Select a sample requiring no more than 2 mL of phenylarsine oxide titrant (approximately 200 mL).
- Rinse buret with titrant several times. Check there are no air bubbles in the buret or line of auto-titrator. Rinse sample container with chlorine-free water then with sample.
- Analyze a Method Blank.
- Analyze a freshly prepared Daily Check Standard in the range of 10 to 100 µg/L either from a commercially prepared standard or user-prepared standard. If commercially prepared 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.
- Complete the following steps when employing manual titration:
    - Add sample to sample container and approximately 1.5 g KI and dissolve using a stirrer or mixer.
    - Add 1 mL acetate buffer and place container in end-point detection apparatus. When the current stabilizes, record the reading.
    - Initially adjust meter to a near full-scale deflection. Titrate by adding small, known, volumes of titrant.
    - After each addition, record cumulative volume added and current reading when the signal stabilizes.
    - If meter reading falls to near or below 10% of full-scale deflection, and record difference between low amount and readjusted high deflection. Add this value to all deflection readings for subsequent titrant additions.
    - Continue adding titrant until no further meter deflection occurs.
    - If fewer than three titrant additions were made before meter deflection ceased, discard sample and repeat analysis using smaller titrant increments.
    - Determine equivalence point by plotting total meter deflection against titrant volume added. Draw a straight line through the first several points in the plot and a second, horizontal straight line corresponding to the final total deflection in the meter. Read equivalence point as the volume of titrant added at the intersection of these two lines.

$$\text{µg Cl as } Cl_2/L = \frac{A \times 200 \times N}{B \times 0.00564} \times 1000$$

where:
A = mL titrant at equivalence point
B = sample volume
N = phenylarsine oxide normality

- If analyzing with an auto-titrator, follow the manufacturer's instructions making sure the program is using forward titration and low-strength PAO.

**Documentation**

Standardization of titrant and true value, value obtained and recovery for the low-level standard, when performed.

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
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
6. Preparation procedure and true value of the Daily Check Standard
7. Value obtained for the Daily Check Standard (verification of ± 10% true value)
8. Value obtained for the Method Blank
9. Quality control assessments
10. Normality of the low-strength phenylarsine oxide
11. Volume of sample analyzed
12. Volume of titrant used at each increment
13. Initial meter reading and meter reading with each titrant addition
14. Plot of meter deflection vs titrant volume
15. The final value to be reported
16. Units of Measure
17. Traceability for chemicals, reagents, standards and consumables
18. Instrument identification (serial number preferred)
19. Parameter analyzed
20. Method reference or Standard Operating Procedure
21. Data qualifier(s), when applicable
22. 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 E – 2011 as a reference.

**Appendix A**
Standard and Reagent Preparation

Daily check standard preparation instructions:

Place 2 mL acetic acid and 10 to 25 mL chlorine-demand-free water in a flask. Add about 1 g KI. Dissolve using a stirrer or mixer. Measure into the flask a suitable volume of chlorine solution. In choosing a convenient volume, note that 1 mL 0.025*N* $Na_2S_2O_3$ titrant is equivalent to about 900 µg chlorine. Titrate with standardized 0.025*N* $Na_2S_2O_3$ titrant until the yellow iodine color almost disappears. Add 1 to 2 mL starch indicator solution and continue titrating to disappearance of blue color.

Determine blank by adding identical quantities of acid, KI, and starch indicator to a volume of chlorine-demand-free water corresponding to the sample volume used for titration. Perform blank titration 1 or 2, whichever applies.

1) If a blue color develops, titrate with 0.01*N* or 0.025*N* $Na_2S_2O_3$ to disappearance of blue color and record result. B is subtracted in the following equation.

2) If no blue color appears, titrate with 0.0282*N* iodine solution until a blue color appears. Back-titrate with 0.01*N* or 0.025*N* $Na_2S_2O_3$ and record the difference. B is added in the following equation.

$$\text{µg Cl as } Cl_2\text{/mL} = \frac{(A \pm B)\ x\ N\ x\ 35.45}{mL\ sample} \text{ x } 1000$$

A = mL titration for sample
B = mL titration for blank (add or subtract)
*N* = normality of $Na_2S_2O_3$

Potassium bi-iodate, 0.002256*N:* Dissolve 0.7332 g anhydrous potassium bi-iodate, $KH(IO_3)_2$, in 500 mL chlorine-free water and dilute to 1000 mL. Dilute 10.00 mL to 100.00 mL chlorine-free water. Use only freshly prepared solution for the standardization of phenylarsine oxide.

Low-strength phenylarsine oxide titrant, 0.**000** 564*N*: Dissolve approximately 0.8 g phenylarsine oxide powder in 150 mL 0.3*N* NaOH solution. After settling, decant 110 mL into 800 mL chlorine-free water and mix thoroughly. Bring to pH 6 to 7 with 6*N* HCl and dilute to 950 mL with chlorine-free water. Dilute 10.00 mL of this solution to 100.00 mL with chlorine-demand-free water.

Standardization – Dilute 5.00 mL 0.002256*N* potassium bi-iodate to 200 mL with chlorine-free water. Add approximately 1.5 g KI and stir to dissolve. Add 1 mL acetate buffer and let stand in the dark for 6 minutes. Titrate using the amperometric titrator and determine the equivalence point.

Normality = 0.002256 x 5/A

A= mL phenylarsine oxide titrant required to reach the equivalence point of standard bi-iodate.

Acetate buffer solution, pH 4: Dissolve 146 g anhydrous $NaC_2H_3O_2$, or 243 g $NaC_2H_3O_2 \cdot 3H_2O$, in 400 mL chlorine-free water, add 480 g concentrated acetic acid, and dilute to 1L with chlorine-demand-free water.

Standard sodium thiosulfate, 0.1*N*: Dissolve 25 g $Na_2S_2O_3 \cdot 5H_2O$ in 1 L freshly boiled chlorine-free water and standardize against potassium bi-iodate or potassium dichromate after at least 2 weeks storage. This initial storage is necessary to allow oxidation of any bisulfite ion present. Use boiled chlorine-free water and add a few milliliters chloroform ($CHCl_3$) to minimize bacterial decomposition.

Standardize 0.1*N* $Na_2S_2O_3$ by one of the following:

1) Iodate method—Dissolve 3.249 g anhydrous potassium bi-iodate, $KH(IO_3)_2$, primary standard quality, or 3.567 g $KIO_3$ dried at 103 ± 2°C for 1 h, in chlorine-free water and dilute to 1000 mL to yield a 0.1000*N* solution. Store in a glass-stoppered bottle. To 80 mL chlorine-free water, add, with constant stirring, 1 mL conc $H_2SO_4$, 10.00 mL 0.1000*N* $KH(IO_3)_2$, and 1 g KI. Titrate immediately with 0.1*N* $Na_2S_2O_3$ titrant until the yellow color of the liberated iodine almost is discharged. Add 1 mL starch indicator solution and continue titrating until the blue color disappears.

2) Dichromate method—Dissolve 4.904 g anhydrous potassium dichromate, $K_2Cr_2O_7$, of primary standard quality, in chlorine-free water and dilute to 1000 mL to yield a 0.1000*N* solution. Store in a glass-stoppered bottle. Proceed as in the iodate method, with the following exceptions: Substitute 10.00 mL 0.1000*N* $K_2Cr_2O_7$ for iodate and let reaction mixture stand 6 min in the dark before titrating with 0.1*N* $Na_2S_2O_3$ titrant.

Standard sodium thiosulfate titrant, 0.01*N* or 0.025*N*: Improve the stability of 0.01*N* or 0.025*N* $Na_2S_2O_3$ by diluting an aged 0.1*N* solution, made as directed above, with freshly boiled chlorine-free water. Add 4 g sodium borate and 10 mg mercuric iodide/L solution. For accurate work, standardize this solution daily in accordance with the directions given above, using 0.01*N* or 0.025*N* iodate or $K_2Cr_2O_7$. Use sufficient volumes of these standard solutions so that their final dilution is not greater than 1 + 4. To speed up operations where many samples must be titrated use an automatic buret of a type in which rubber does not come in contact with the solution. Standard titrants, 0.0100*N* and 0.0250*N*, are equivalent, respectively, to 354.5 µg and 886.3 µg Cl as $Cl_2$/1.00 mL.

Starch indicator solution: To 5 g starch (potato, arrowroot, or soluble), add a little cold water and grind in a mortar to a thin paste. Pour into 1 L of boiling chlorine-free water, stir, and let settle overnight. Use clear supernate. Preserve with 1.25 g salicylic acid, 4 g zinc chloride, or a combination of 4 g sodium propionate and 2 g sodium azide/L starch solution. Some commercial starch substitutes are satisfactory.