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

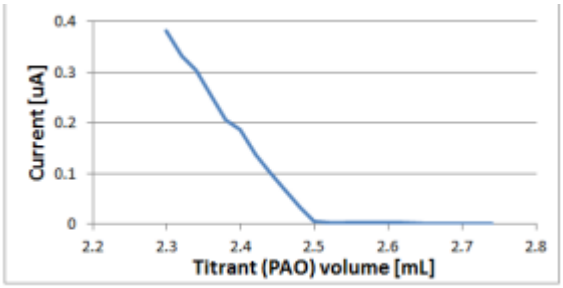
This document provides an approved procedure for the Amperometric Forward Titration analysis of Total Residual Chlorine (TRC) for compliance monitoring per 15A NCAC 2H .0805 (a) (7) and (g) (4).

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 D-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]

- If there is a Daily Maximum Limit required by the facility permit, you must use a procedure capable of detecting concentrations below that level, such as SM 4500-Cl E: Low-Level Amperometric Forward Titration. Per 15A NCAC 02B .0505 (e) (4), facilities must produce detection and reporting levels that are below the Daily Maximum Limit.

- 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 standard phenylarsine oxide (PAO) titrant must be standardized initially when prepared by the laboratory and every month thereafter. 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.

Standards 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.

Refer to Appendix A for standard and reagent preparation instructions.

Analysis

- Select a sample volume requiring no more than 2 mL phenylarsine oxide titrant. For example, for chlorine concentrations of 2 mg/L or less, take a 200-mL sample and for concentrations in excess of 2 mg/L, use 100 mL or proportionately less. If samples containing high chlorine levels are diluted, the dilution water must be free of chlorine, ammonia and chlorine demand.

- Rinse buret with titrant several times. Check there are no air bubbles in the buret or line of auto-titrator.

- Analyze a Method Blank.

- Analyze a freshly prepared Daily Check Standard at a concentration that approximates typical Compliance sample values either from a commercially-prepared standard or user-prepared standard. If commercially-prepared liquid chlorine standard solutions with a stated range and average value are used, the average value is the true value of the standard.

- Complete the following steps when employing manual titration:

    - Add 1 mL KI solution followed by 1 mL acetate buffer solution.

    - Titrate with standard phenylarsine oxide titrant, observing current changes on the microammeter. Add titrant in successively smaller increments until all needle movement ceases. Make successive buret readings when needle action becomes sluggish, signaling approach of endpoint. Subtract last very small increment that causes no needle response because of overtitration.

    - After subtracting the last very small increment, calculate the total residual chlorine concentration using the following equation:

$$\text{mg Cl as } Cl_2/L = \frac{A \times 200}{mL\ sample}$$

where:
A = mL phenylarsine oxide titrant

- If analyzing with an auto-titrator, follow the manufacturer's instructions using 0.005 64*N* PAO (ensuring back-titration is not being performed).

Documentation

Standardization of titrant and true value, value obtained and recovery of 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 standard phenylarsine oxide titrant
11. Volume of sample analyzed
12. Volume of titrant used at each increment when needle action becomes sluggish
13. Total volume of titrant used
14. The final value to be reported
15. Units of Measure
16. Traceability for chemicals, reagents, standards and consumables
17. Instrument identification (serial number preferred)
18. Parameter analyzed
19. Method reference or Standard Operating Procedure
20. Data qualifier(s), when applicable
21. 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 D – 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.

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

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

Phosphate buffer solution, pH 7: Dissolve 25.4 g anhydrous KH_2PO_4 and 34.1 g anhydrous Na_2HPO_4 in 800 mL distilled water. Add 2 mL sodium hypochlorite solution containing 1% chlorine and mix thoroughly. Protect from sunlight for 2 days. Determine that free chlorine still remains in the solution. Then expose to sunlight until no chlorine remains. If necessary, carry out the final dechlorination with an ultraviolet lamp. Determine that no total chlorine remains by adding KI and measuring with one of the colorimetric tests. Dilute to 1 L with distilled water and filter if any precipitate is present.

Potassium iodide, KI, crystals

Potassium iodide solution: Dissolve 50 g KI and dilute to 1 L with freshly boiled and cooled distilled water. Store in the dark in a brown glass-stoppered bottle, preferably in the refrigerator. Discard when solution becomes yellow.

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.

Phenylarsine oxide titrant, 0.00564*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.

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.