*Name of Facility*

Total Residual Chlorine

Low-level Amperometric Titration

Method: SM 4500 Cl E-2011

Effective Date:

Supervisor Signature Date

Supervisor Name (print)

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*Blue text is replaceable instructional language to be customized for your facility.*

1. Summary of Method
   1. This method modifies the general amperometric titration procedure by using more dilute phenylarsine oxide. Also, the endpoint is determined through a graphical procedure. The phenylarsine oxide causes the cell to become more and more polarized because of the decrease in chlorine. The cell consists of a nonpolarizable reference electrode that is immersed in a salt solution and a readily polarizable noble-metal electrode that is in contact with both the salt solution and the sample being titrated.
   2. *State what type of samples are analyzed, e.g., wastewater effluent, ground water monitoring well, etc. and the permit limits if applicable*
   3. *State what your reporting range is with units*
2. Definitions
   1. 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.
   2. 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.
   3. NC WW/GW LC: North Carolina Wastewater Groundwater Laboratory Certification
   4. *Add any other applicable acronyms or terms used by your facility*
3. Safety and Waste Handling
   1. Phenylarsine oxide is a known poison and suspected cancer agent*. state the steps that are taken for personal safety*
   2. Other items that would be included in this section are things such as:

* Precautionary measures (list here and at the critical steps in the procedure)
* Personal protective equipment (e.g., gloves, eye protection, lab coat, work in a hood, etc.)
* Hazardous chemicals/reagents
* Storage and disposal of samples and reagents
* Reference to Chemical Hygiene Plan, if applicable
* Location of SDSs

1. Apparatus, Equipment and Reagents

*Note: Include storage conditions and expiration dates for standards and reagents. It is recommended catalog numbers also be included*

* 1. *List your instruments/electrodes etc.*
  2. Agitator *(list what you are using)*
  3. Buret *(describe)*
  4. Daily check standard: *If it is purchased, state the concentration. If it is prepared, state that analysts refer to Appendix 1*
  5. Lab water: *state what type of water is used e.g., purchased distilled water, etc.*
  6. Low-strength phenylarsine oxide titrant (0.000564*N*) **Caution: Phenylarsine oxide is a cancer-suspect agent**: *state if it is purchased and if prepared, include instructions in Appendix 1*
  7. Potassium iodide, KI, crystals.
  8. Potassium bi-iodate, 0.002256*N: state if it is purchased and if prepared, include instructions in Appendix 1*
  9. Acetate buffer solution, pH 4 SU: *state if it is purchased and if prepared, include instructions in Appendix 1*

1. Interference
   1. Interference from copper has been noted in samples taken from copper pipe or after heavy copper sulfate treatment of reservoirs, with metallic copper plating out on the electrode. Silver ions also poison the electrode.
   2. Interference occurs in some highly colored waters and in waters containing surface-active agents.
   3. Very low temperatures slow response of measuring cell and longer time is required for the titration, but precision is not affected.
   4. The violent stirring of some commercial titrators can lower chlorine values by volatilization.
2. Sample Collection, Preservation and Holding Time
   1. Samples must be collected in glass or polyethylene containers.
   2. There is no preservation requirement for Total Residual Chlorine.
   3. The holding time is 15 minutes.
3. Standardization
   1. *Delete one of the following:(for lab prepared titrant)* Follow the steps in 7.1.1 and 7.1.2 to standardize the phenylarsine oxide titrant each time the titrant is prepared and every 30 days thereafter. *(for purchased titrant)* When the phenylarsine oxide titrant is purchased already prepared, initial standardization is not necessary, but it must be re-standardized every 30 days following the steps in 7.1.1 and 7.1.2.
      1. The potassium bi-iodate used for standardization must be freshly prepared.
      2. Dilute5.00 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. Calculate the normality using the following equation.

Normality = 0.002256 x 5/A

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

1. Procedure
   1. *If using an auto titrator, describe the process of setting it up. \*note: when using this method, the auto-titrator must be using the low-strength PAO and forward titration\* If manually titrating, describe filling the buret.*
   2. Rinse buret with titrant several times. Check there are no air bubbles in the buret or line of auto-titrator (if using). Rinse sample container with chlorine-free water then with sample.
   3. Select a sample volume requiring no more than 2 mL of phenylarsine oxide titrant (approximately 200 mL)

* 1. Analyze the method blank. See Section 12 for the acceptance criterion.
  2. Analyze a freshly prepared Daily Check Standard. See Section 12 for the acceptance criterion. This needs to be 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.
  3. Add approximately 1.5 g KI to sample and dissolve using (state what you are using)
  4. Add 1 mL acetate buffer solution and place sample container in end-point detection apparatus.
  5. If using auto titrator- describe that process and how the result is determined, and delete the directions below
  6. When the current stabilizes, record the reading.
  7. Initially adjust meter to near full-scale deflection.
  8. Titrate by adding small, known, volumes of titrant.
  9. After each addition, record cumulative volume added and current reading when the signal stabilizes.
  10. If meter reading falls to near or below 10% of full-scale deflection, record low reading, readjust meter to near full-scale deflection, and record difference between low amount and readjusted high deflection.
      1. Add this value to all deflection readings for subsequent titrant additions.
  11. Continue adding titrant until no further meter deflection occurs.
  12. If fewer than 3 additions were made before meter deflection ceased, discard sample and repeat analysis using smaller titrant increments.
  13. Determine equivalence point by plotting total meter deflection against titrant volume added. (if an auto-titrator can determine the equivalence point automatically, describe that process)
      1. Draw 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 2 lines
  14. Calculate the concentration of Cl2 with the following equation:

µg Cl as Cl2/L = 1000 \* (A \* 200 \* *N*) ÷ (B \* 0.00564) where

A = mL titrant at equivalence point,

B = sample volume, mL and

*N* = phenylarsine oxide normality (approximately 0.000564 *N)*

1. 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
  3. Facility name, sample site (ID or location), and permit number
  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. Normality of the low-strength phenylarsine oxide
  10. Volume of sample analyzed
  11. Volume of titrant used at each increment
  12. Initial meter reading and meter reading with each titrant addition
  13. Plot of meter deflection vs titrant volume
  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)

1. Proficiency Testing (PT) Procedure
   1. Analysis of a PT Sample is required at least once during every 9-month PT calendar year (January 1- September 30).
      1. A list of approved PT Providers may be found on the NELAC website at <http://nelac-institute.org/content/NEPTP/ptproviders.php>. Check this list yearly to assure the chosen vendor is approved.
      2. A PT Sample can be analyzed as early as January 1 and the graded result must be reported to NC WW/GW LC office from the PT Provider no later than September 30.
   2. PT Samples must be analyzed in accordance with the routine testing, calibration and reporting procedures, unless otherwise specified in the instructions supplied by the PT Sample Provider.
      1. PT Samples are logged in and analyzed using the same staff, sample tracking systems, standard operating procedures including the same equipment, reagents, calibration techniques, analytical methods, and the same quality control acceptance criteria.

* + 1. PT Sample preparation must be documented. The instruction sheet provided with the PT Sample will be signed and dated.
    2. PT Samples shall not be analyzed with additional quality control. They are not to be replicated beyond what is routine for Compliance Sample analysis.
    3. PT Sample analysis must be documented on the laboratory’s daily benchsheet.
  1. The PT Provider’s instructions for preparing the PT Sample must be followed and the practice documented by the analyst. The instruction sheet will be initialed and dated when the PT Sample is prepared and retained for 5 years.
  2. The following information must be included when reporting the PT Samples.
     1. EPA Lab Code: (enter here so it is easy to retrieve)
     2. State Lab Certification number: (enter here so it is easy to retrieve)
     3. Method description (refer to CPL for current method description):
     4. Mailing address for NC WW/GW LC: 1623 Mail Service Center, Raleigh, NC 27699-1623

1. Calculations and Reporting
   1. Percent Recovery

% Recovery = Value Obtained x 100

True Value

* 1. Report in units of µg/L
  2. *Describe number of significant figures and rounding procedures*

1. Quality Assurance and Quality Control
   1. The method blank value must not exceed half the reporting limit.
   2. The Daily Check Standard recovery must be within ± 10% of the true value.
   3. See Section 14 for corrective actions if any acceptance criteria fail.
   4. *State who is transcribing the data to the eDMR and whether anyone peer reviews (checks) it. Peer review is recommended, but if that is not possible, it is recommended that the analyst rechecks their own transcription for errors after a certain amount of time has passed.*
2. Preventative Maintenance
   1. *State if a maintenance log or record is maintained.*

* 1. *Include any directions for maintenance per manufacturer’s instructions*

1. Troubleshooting and Corrective Action
   1. *State what will be done if the Daily Check Standard or method blank do not meet acceptance criteria*
2. Employee Training

Employee training must be documented and kept on file.

* 1. *Include required education, training, experience and/or demonstrated skills*
  2. Employee must have read this SOP *– may also include reading the Approved Procedure for the Analysis of Total Residual Chlorine*
  3. *Employee must obtain acceptable results on Proficiency Testing samples or other demonstrations of proficiency (e.g., Initial Demonstration of Capability (IDOC), side-by-side comparison with established analyst, etc.) before analyzing compliance samples for reporting.*

1. References
   1. Standard Methods, 4500 Cl E-2011.
   2. North Carolina Wastewater/Groundwater Laboratory Certification Approved Procedure for the Analysis of Total Residual Chlorine by Low-level Amperometric Titration, Rev. 6/2019
   3. 15A NCAC 02H .0800
2. Revision History

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| Type: Review or Revision | Date | Summary of Changes Made if Revision |
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Appendix 1 – Reagent Preparation Instructions

(the following are examples from Standard Methods, delete the appendix if everything is purchased. If they are prepared, assure the instructions match the lab’s process)

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* Na2S2O3 titrant is equivalent to about 900 µg chlorine. Titrate with standardized 0.025*N* Na2S2O3titrant 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* Na2S2O3 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* Na2S2O3 and record the difference. B is added in the following equation.

µg Cl as Cl2/mL = x 1000

A = mL titration for sample

B = mL titration for blank (add or subtract)

*N* = normality of Na2S2O3

Potassium bi-iodate, 0.002256*N:* Dissolve 0.7332 g anhydrous potassium bi-iodate, KH(IO3)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 NaC2H3O2, or 243 g NaC2H3O2 • 3H2O, 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 Na2S2O3 · 5H2O 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 (CHCl3) to minimize bacterial decomposition.

Standardize 0.1*N* Na2S2O3 by one of the following:

1. Iodate method—Dissolve 3.249 g anhydrous potassium bi-iodate, KH(IO3)2, primary standard quality, or 3.567 g KIO3 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 H2SO4, 10.00 mL 0.1000*N* KH(IO3)2, and 1 g KI. Titrate immediately with 0.1*N* Na2S2O3 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, K2Cr2O7, 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* K2Cr2O7 for iodate and let reaction mixture stand 6 min in the dark before titrating with 0.1*N* Na2S2O3 titrant.

Standard sodium thiosulfate titrant, 0.01*N* or 0.025*N*: Improve the stability of 0.01*N* or 0.025*N* Na2S2O3 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 K2Cr2O7. 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 Cl2/1.00 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.