Ohio Environmental Protection Agency

Laboratory Manual for Chemical Analyses of Public Drinking Water 2025

This manual is available on Ohio EPA's website at
epa.ohio.gov/static/Portals/28/documents/labcert/CHEMMAN.pdf

This document replaces all previous versions of this manual.

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Table of Contents

Chapter 1 – Purpose and Introduction

A. Purpose of This Manual

The purpose of this manual is to present the requirements, criteria and procedures necessary to obtain laboratory certification to analyze drinking water samples for the purpose of determining compliance with Ohio Administrative Code (OAC) Chapters 3745-81 and 3745-82 and rules 3745-83-01, 3745-91-06 and 3745-9-09. This includes plant control tests and other analyses required by the director of the Ohio Environmental Protection Agency (Ohio EPA).

Ohio's drinking water laboratory certification program requirements are found in OAC Chapter 3745-89.

The requirements, criteria and procedures described in this publication represent current practices of Ohio EPA. They are subject to change when, in the judgment of Ohio EPA, such a change will be more effective in fulfilling its responsibility under the law.

This version of the *Ohio EPA Laboratory Manual for Chemical Analyses of Public Drinking Water* incorporates rule revisions effective on **July 7, 2025,** and replaces all previous versions.

B. Introduction

As authorized by the Safe Drinking Water Act (SDWA), the United States Environmental Protection Agency (U.S. EPA) has set health-based standards in the form of the National Primary Drinking Water Regulations (NPDWR) to protect against analytes that may be found in drinking water. In accordance with the SDWA and the NPDWR, public water systems must conduct periodic analyses of drinking water served to the public.

As delegated by the U.S. EPA, Ohio EPA has primary enforcement responsibility for the SDWA in Ohio. This includes the responsibility to certify laboratory facilities and personnel to perform analytical measurements of all analytes specified in the State primary drinking water regulations and analytes necessary for the operation of public water systems. Ohio EPA's Division of Drinking and Ground Waters implements the drinking water laboratory certification program.

Following OAC rules in Chapters 3745-81, 3745-82, and 3745-89, the laboratory certification section recommends whether to grant or deny certification to laboratories and laboratory personnel.

Ohio EPA's *Laboratory Manual for Chemical Analyses of Public Drinking Water 2025* and *Laboratory Manual for Microbiological Analyses of Public Drinking Water 2025* outline requirements for obtaining and maintaining certification for drinking water analysis. These manuals contain methods and general laboratory facility requirements for the analysis of drinking water necessary for public water system operation.

Chapter 2 – Critical Elements for Certification

A. Laboratory Construction and Remodeling Requirements

Laboratories are encouraged to contact the laboratory certification section staff early in the planning stages for construction or remodeling of a laboratory. Plans must be submitted to the Ohio EPA for review and approval **prior to construction or remodeling**. Laboratory plan approval is covered under OAC rule 3745-89-03.

All items listed below may not be applicable to a particular laboratory. If you have questions or need assistance, contact the laboratory certification section.

1) Chemistry Laboratory Space

- The door(s) entering the laboratory area must be equipped with a locking system keyed separately from the other doors in the building.
- The door(s) entering the laboratory must be equipped with a clear glass pane large enough to allow forced entry in cases of emergency.
- The laboratory must be equipped with heating and air conditioning capable of maintaining an ambient temperature of between 65° and 80°F.
- Electrical outlets must be provided appropriately along the work benches.
- Acid and alkaline resistant sinks are required if concentrated acids or bases are used.
- Stone balance tables or stone balance slabs must be provided for all analytical balances.
- The laboratory must not be constructed or located as to allow thoroughfare, nor have non-emergency doors directly to the outside of building.
- Emergency exit doors must be equipped with an audible alarm and breaker bar.
- The laboratory's analytical and sample storage areas should be isolated from all potential sources of contamination.
- Physical isolation of a microbiological section of the laboratory from chemical analytical sections is not mandatory, except for laboratories conducting either organic or viral analysis, in which case isolation of the areas is required.
- All laboratory facilities must be constructed as to not be adversely affected by vibration or dust.
- Laboratories must not be constructed with windows intended for ventilation purposes.
- Adequate floor or wall type storage cabinets must be provided for glassware and non-corrosive type reagents.

2) Bench Space

- An appropriate amount of work bench space must be provided per certified method for each chemical analytical group.

3) Equipment

- A list of all analytical equipment, including manufacturer and model number, must be submitted to Ohio EPA for evaluation.
- If a dish washing machine is to be used for glassware, it must be installed to provide a final distilled or deionized water rinse.

- Exhaust hoods used for acid digestions must be corrosion resistant. If an exhaust hood is to be used in conjunction with solvents, it must be equipped with explosion-proof motors and switches and must be labeled as such.
- All refrigerator systems to be used for storage of solvents must be suitable for flammable materials storage.
- Commercial gas and electric cooking stoves cannot be used in laboratories as substitutes for drying ovens or for other heating purposes.
- If continuous monitors for turbidimeters, pH meters, or chlorine analyzers are installed in the water treatment plant, a bench model is required for calibrations and reference samples.
- All benchtops and shelving for corrosion storage cabinets must be of alkaline and acid-resistant construction.
- A safety shower and/or emergency eye wash is to be provided and equipped to provide tempered water in the 65° to 80°F range for a minimum of 15 minutes.
- Distilled or deionized water is required for microbiological and chemical laboratories. If a still is provided, it can be mounted on the wall above the work bench area. Adequate work bench area must be provided for either a still or purchased water, ensuring availability of additional work bench area necessary to perform certified methods.
- The laboratory must be equipped with piped hot and cold water.
- Separate full-size or under-the-counter refrigerators must be provided when non-compatible samples and/or standards are stored in the same laboratory space.

B. Quality Assurance Plan (QAP)

1) Requirements for the QAP

The QAP, as required by OAC rule 3745-89-03(A)(2), must include the following information:

- Table of laboratory organization delineating responsibilities of all laboratory personnel.
- Standard operating procedures (SOPs) including identification of the reference methods used to perform the drinking water analysis. These SOPs must be reviewed and/or revised at least annually. To track this information, either track the history on the laboratory's SOPs or use the *Annual Laboratory Manual Review Record* located at the end this manual.
- Sample handling procedures, including:
    - Directions for maintaining sample integrity from collection to receipt, testing to disposal.
    - Directions for sample preservation, as required by the reference method.
    - Directions to ensure sample information accuracy.
    - Chain of custody forms, where applicable.
    - Directions for rejection and notification of samples not meeting method requirements.
- Routine practices to maintain the precision and accuracy of data.
- Corrective analytical action procedures.
- Preventive instrument maintenance procedures.
- Documentation of standard preparation and reagent expiration dates.
- Reporting procedures.

This manual may be used as the QAP by public water system laboratories seeking certification for plant control tests. In addition, these laboratories may use the analytical methods located of this manual as the SOP of record for each analytical method for which the laboratory and its personnel are certified.

Laboratories not using this manual as their QAP or SOPs must develop a QAP/SOPs as described in U.S. EPA's *Manual for the Certification of Laboratories Analyzing Drinking Water*, dated January 2005 and designated EPA 815-R-05-004, as supplemented in June 2008 and designated EPA 815-F-08-006. These documents are available at ***epa.gov/dwlabcert***.

C. Laboratory Contingency Plan

Each certified laboratory must have in place a written contingency plan, with a course of action outlining steps to be taken during an event which might prevent the sample analyses required for daily operation of the public water system as required by OAC rule 3745-85-01.

D. Reporting of Analytical Results

Public water systems and certified laboratories must report results of drinking water samples to Ohio EPA to demonstrate that drinking water meets health-based standards. OAC rule 3745-89-08 requires analytical results to be reported to Ohio EPA electronically via a method acceptable to the director. Ohio EPA created electronic Drinking Water Reports (eDWR) for laboratories to use for submitting drinking water data. Microbiological Sample Submission Reports (SSRs), Chemical SSRs, and Monthly Operating Reports (MORs) must be submitted to Ohio EPA through eDWR. For more information about eDWR, please go to ***epa.ohio.gov/divisions-and-offices/drinking-and-ground-waters/guides-manuals/data-reporting-faqs***.

E. Data Management

1) Document Management

Public water supply laboratories must record all quality control, standardizations, calibrations, and analyses on standardized record forms or bench sheets. Record forms for each method are located on the last few pages following each method in this manual. Record forms are to be completed entirely and entries on the forms must be legible. One record space must contain only one entry or one data result.

All standards and/or reagents prepared in or purchased by the laboratory for use in an analytical method shall be documented on the *Reagent/Standard Receipt/Preparation Record*. A template of this record is located in Appendix 3 of this manual.

Entries or data results must be recorded in ink or an electronic version approved by the Ohio EPA laboratory certification section. Correction products (e.g., tape, liquid, etc.) are not permitted. Incorrect entries should be crossed out using one line through the entire row or column, leaving the crossed-out entry legible. The correction should be entered in the following dated row or column with a statement describing the cause and solution to the previous incorrect entry.

> **Note:** Electronic records must be stored in a time-stamped, non-editable, sustainable document type. If using a laboratory management system, edits must be time-stamped and trackable, including what was changed, who made the change and the reason the change was made.

2) Continuous Monitors

Public water supplies using continuous monitors (e.g., for turbidity, pH, chlorine) in the water treatment plant, must have a bench model in the laboratory for calibrations and reference samples. Requirements and bench sheets are located in Appendix 4 of this manual.

3) Record Retention

All laboratory records including, but not limited to, sample identification records, sample analytical result records, quality control, calibration, and standardization records, and original bench sheets, are to be retained for the following minimum periods in accordance with OAC rule 3745-89-04:

5 Years - Microbiological Laboratory Data Records
10 Years - Chemical Laboratory Data Records
12 Years - Lead & Copper Laboratory Data Records

Records must be kept readily available in the laboratory for a minimum of three years. The records may be kept off-site for the remainder of the retention period.

F. Proficiency Test (PT) Samples

In accordance with OAC rule 3745-89-03, laboratories seeking to obtain or maintain laboratory certification must participate in a proficiency test (PT) sample study at least once annually resulting in an Acceptable evaluation, as described by this rule, for all regulated analytes which the laboratory is certified.

Laboratories seeking initial certification must pass a PT sample for each analyte for which it is seeking certification prior to the scheduled survey. An annual basis is considered January 1 through December 31 of each year. All PT study results must be sent to Ohio EPA directly from the accredited PT provider.

Laboratories with an evaluation of Not Acceptable for the initial PT study for any certified analyte/analyte group must complete a makeup PT within 30 days of receiving the PT provider results report.

Laboratories with evaluations of Not Acceptable for the initial and make-up PT studies for any certified analyte/analyte group must immediately cease analysis for the analyte/analyte group, submit a corrective action report to Ohio EPA, and obtain a second make-up PT sample study for the analyte/analyte group in question.

The corrective action must address why the Not Acceptable result occurred, and how the problem was resolved. The corrective action must be submitted prior to ordering the second make-up PT sample study. Additionally, per the laboratory's quality assurance plan (QAP), the laboratory must notify Ohio EPA where the samples will be sent for analysis. As stated on the certificate, certification will be placed on hold until an Acceptable PT evaluation is received from the PT provider.

All PT samples must be part of an accredited WS study and provided by an accredited PT provider accreditor meeting the National Environmental Laboratory Accreditation Conference (NELAC) requirements. A current list of accredited providers is available at ***nelac-institute.org/content/NEPTP/ptproviders.php***.

Fluoride QC Sample:

Requirements for the fluoride QC sample are detailed in Section 7.3 of the Fluoride Analysis by Ion-Selective Electrode Method and Section 7.5 of the Fluoride Analysis by Hach SPADNS 2 (Arsenic-free) Method 10225, both located in this manual.

G. Laboratory Safety

Ohio EPA strongly recommends that each laboratory seeking certification have a safety program developed to meet its specific requirements. The laboratory safety plan should focus on the methods for which it is seeking certification and the requirements needed to conduct those analyses safely.

While safety criteria are not part of the laboratory certification survey, the safety equipment identified above in the Laboratory Construction and Remodeling Requirements section, is required for a laboratory to be considered for certification.

For a detailed reference on the requirements of a laboratory safety plan, review Standard Methods for the Examination of Water and Wastewater, Part 1090 Laboratory Occupational Health and Safety.

H. Laboratory Integrity

Laboratory personnel must notify Ohio EPA when improper activities regarding laboratory sampling or analyses are suspected or observed.

Chapter 3 - Requirements for Participating in the Laboratory Certification Program

Applications for certification to perform drinking water analysis are to be completed and include all materials and information as detailed in OAC rule 3745-89-03. An application will be considered incomplete and may not be accepted if it is not accompanied by a laboratory plan approval letter or includes the date which laboratory plans were approved by Ohio EPA.

The most recent versions of applications are available at ***epa.ohio.gov/divisions-and-offices/drinking-and-ground-waters/public-water-systems/laboratory-certification***.

A. Initial Certification

A signed application for initial certification, indicating which analysis methods are being requested for certification, must be submitted to ***dwlabcert@epa.ohio.gov***.

The requirements for initial drinking water laboratory certification, in accordance with OAC rule 3745-89-03, include but are not limited to:

- Receive approval for detailed laboratory floor plan.
- Submit a complete application and pay the appropriate fee.
- Submit an acceptable quality assurance plan and an acceptable SOP for the new method.
- Submit documentation of initial QC procedures required by the methods, and if appropriate, any required method detection limit studies and/or initial demonstrations of capability studies.
- Successfully analyze required proficiency test samples.
- Pass a survey.

B. Certification Renewal and Maintenance

The requirements to renew and maintain certification, in accordance with OAC rules 3745-89-04 and 3745-89-05, include but are not limited to:

- Maintain a valid and unexpired laboratory certification.
- Submit results of annual proficiency test sample analyses. See Chapter 2, Section F of this manual.
- Maintain an updated laboratory quality assurance plan.
- Report significant changes in facility, equipment, personnel, or quality assurance plan.
- Submit a renewal application and pay the appropriate fee.
- Electronically submit requested data by the specified deadline.
- Submit to required audits and implement any required corrective actions.

The certification renewal application must be submitted no more than 120 days and no less than 30 days prior to the expiration of the current laboratory certification. When applications for renewal are submitted in accordance with OAC rule 3745-89-04 and deemed complete, the laboratory certification will be extended until the survey is completed. Should failure to follow guidelines result in suspension or loss of certification, the laboratory must have required water analysis completed by a certified lab until certification is reinstated.

C. Fees

Detailed fees are in Ohio Revised Code (ORC) Section 3745.11 and shall be paid upon receipt of the survey invoice. The fee schedule is available at ***epa.ohio.gov/static/Portals/47/facts/feeschedule.pdf***.

Chapter 4 - Surveys

Ohio EPA conducts both announced and unannounced surveys to confirm the information provided by the laboratory on the application, review and evaluate each analyst, and review records maintained by the laboratory.

The following personnel must be available during an announced survey:

- All certified personnel seeking renewal or initial certification.
- All personnel seeking initial operational certification.
- A majority of the operationally certified personnel seeking renewal certification.
    - Exemption of operationally certified personnel may not exceed more than one renewal survey.

Surveys are conducted during normal business hours. Required laboratory records must be in the laboratory, clearly labeled and easily accessible. **Copies of the records must be made available upon request.**

At least two people should be designated as responsible for allowing access to the laboratory (e.g., city hall employee, plant operator, police officer, etc.). Telephone numbers of the responsible personnel must be posted in a location visible outside the facility to allow access for certification officers.

A. Typical Agenda

During the survey, the laboratory must demonstrate acceptable levels of performance including, but not limited to:

- Proficiency in appropriate analytical procedures, methodologies, techniques, and use of equipment by analysts participating in the survey.
- Analysis of samples provided at the time of the survey.
- For laboratories seeking initial certification, demonstration of the laboratory's plan for maintaining records, documenting:
    - All appropriate laboratory equipment is operational and is within acceptable limits.
    - Sufficient practice analyses have been conducted by each analyst participating in the survey to demonstrate the analyst's proficiency.
    - An acceptable quality assurance plan has been documented and implemented.
    - The analyses, QC procedures and preparation of standards were correctly performed by all certified analysts during the survey.
    - The analyses were correctly performed by each operationally certified analyst participating in the survey.
    - Acceptable method detection limit studies have been completed for each method and instrument.
    - Documentation of acceptable proficiency study results.
- Conformance to the approved laboratory plan.
- Conformance to the analytical reporting limits identified in OAC rule 3745-89-03.
- Correction of violations noted in previous survey reports.

B. Review of Survey Findings

At the completion of the survey, the certification officer will meet with the appropriate laboratory representatives to review the findings of the survey.

C. Survey Report

Ohio EPA will issue the report to the applicant within 45 days of the survey. The survey report will indicate the acceptability of the applicant's performance during the survey and will state violations required to be corrected prior to certification of the laboratory. If the survey report includes violations, the director of Ohio EPA may deny, suspend, or revoke certification in accordance with OAC rule 3745-89-06.

In accordance with OAC rule 3745-89-01, a violation is non-compliance with laboratory certification requirements which cover the physical facility, testing equipment, analytical methods, reporting, and all QC requirements whether they are in the method, the laboratory certification manual or the OAC.

Laboratories are generally given 30 days to respond to identified violations.

Chapter 5 - Requirements for Analyst Certification

A. Certified/Operational Certification for Plant Control Tests

There are two types of drinking water certification available for laboratories and personnel performing chemical analyses. Annually, each primary contact for the lab is required to review Chapters 1 through 8, and all analysts must review each method in Chapter 8 of this manual for which they are certified. The review must be documented and kept with the laboratory records. To track this information, use the *Annual Laboratory Manual Review Record* located at the end this manual.

1) Certified

Each certified analyst is required to perform all QC requirements, including calibrations, standardizations and verifications as detailed in Chapter 8 of this manual for each plant control test method. Each certified analyst must complete drinking water sample analysis at a minimum rate of three days per month for all methods which the analyst is certified.

> **Note:** Analysts who are certified for the same method(s) at multiple laboratories within a public water system may meet the minimum rate when performing analysis at any of the laboratories within the system.

2) Operational Certification

Operational certification is defined in OAC rule 3745-89-01 as certification granted by the director for an analyst to perform one or more of the plant control tests for alkalinity, stability, chloride, chlorine, chlorite, chlorine dioxide, fluoride, hardness, pH, or turbidity, including daily calibration and standardization, but does not include the preparation of standards or reagents, the required monthly/every three-month calibrations and standardizations, or other QC activities unless otherwise noted in Chapter 8, Section 6.0 of each method in this manual. Each operationally certified analyst must complete drinking water sample analysis at a minimum rate of three days per month for all methods which the analyst is certified.

> **Note:** Analysts who are operationally certified for the same method(s) at multiple laboratories within a public water system may meet the minimum rate when performing analysis at any of the laboratories within the system.

Operational certification is not available to commercial laboratory personnel.

B. Interim Authorization for Plant Control Tests

A laboratory with a valid and unexpired certification may apply for interim authorization for an analyst to perform one or more of the plant control tests for pH, turbidity, alkalinity, stability, hardness, fluoride, chloride, chlorine dioxide, chlorite and chlorine, according to the following requirements:

- Interim Authorization will be granted to the applying analyst(s) upon demonstration of acceptable performance in a 20-day parallel testing period. Acceptable performance is defined as follows.
    - For each plant control test other than pH and turbidity, obtaining results within ±10% of the certified analyst.
    - For pH, obtaining results within ±0.1 pH units of the certified analyst.
    - For turbidity results less than 0.3 NTU, obtaining results within ±0.03 NTU of the certified analyst.
    - For turbidity results equal to or greater than 0.3 NTU, obtaining results within ±10% of the certified analyst.

- A laboratory must apply for interim authorization including the following information:
    - The name, address, and telephone number of the laboratory and of the individual(s) responsible for the laboratory.
    - The list of analysts specified on the laboratory's applicable certificates and the plant control tests which each analyst currently performs.
    - The list of individuals and the plant control tests for which interim authorization is sought.
    - Documentation for each individual on each plant control test requested for interim authorization of at least 20 days of analytical results generated in parallel testing with an analyst included on a certificate for those same plant control tests.
    - To decrease the number of parallels required, labs may request that previous certification of an individual to perform plant control tests be considered.

> **Note:** Only currently certified or operationally certified analysts may serve as trainers (i.e., personnel with interim authorization are not acceptable trainers for new personnel).

A survey will be scheduled within six months of an interim authorization. Unless an extension is granted, interim authorization shall remain in effect for a period not to exceed six months.

Chapter 6 - Issuance of Laboratory Certification

Based on the results of the survey, laboratory certification section staff provide a recommendation to the Ohio EPA director concerning the certification status of the laboratory in the following categories:

Certified

A certificate will be issued by Ohio EPA for the analytical method(s) identified on the application for certification. Certificates are valid for a period not to exceed three years from the date of issuance.

Analysts are only certified at a laboratory for methods noted on their certificate. An analyst must undergo a survey to add additional certified methods for drinking water analysis. Analysts must be certified during a survey or obtain interim authorization prior to analyzing drinking water samples for reporting purposes.

Provisionally Certified

Provisional certification is limited to laboratories which have been previously certified for analytical method(s) identified in the application. Provisional certification may be granted to a laboratory with violations noted on the survey report. The provisional certification will remain in effect during the period between the completion of the survey and the deadline allotted for the lab to respond to the violations listed on the survey report. The laboratory will be certified for the analytical method(s) by Ohio EPA if the laboratory provides an acceptable response addressing the violations by the deadline. Failure to respond or to provide an acceptable response will result in a loss of certification. Provisional certification is not available to laboratories requesting initial certification.

Not Certified

The laboratory, personnel or equipment did not meet minimum requirements for drinking water analysis certification as detailed in OAC Chapter 3745-89.

Certificates

Certificates are nontransferable. It is the laboratory's responsibility to notify Ohio EPA of all personnel changes. All certificates of approval remain the property of Ohio EPA and must be destroyed upon analyst separation from the certified laboratory.

Certification will remain in effect for a laboratory changing facility locations if the certified personnel are retained and the new laboratory plans are approved in writing by Ohio EPA prior to the move.

Denial, Suspension, or Revocation of Laboratory Certification

In accordance with OAC rule 3745-89-06, the director may deny, suspend, or revoke a laboratory certification upon finding:

- The laboratory or any laboratory personnel has falsified laboratory data.
- The laboratory failed to meet laboratory certification requirements as described in OAC rules 3745-89-03 to 3745-89-05.
- The laboratory fails to meet the reporting requirements in OAC rule 3745-89-08.
- The laboratory has submitted unacceptable data.
- The laboratory has submitted a proficiency test sample to another laboratory for analysis and reported the data as its own.
- Analysis of a drinking water PT sample for purposes of retaining a valid laboratory certification is performed by a person who does not hold a valid certification for the laboratory, or the analyte reported.

- The laboratory or any laboratory personnel is performing, reporting or failing to report drinking water analyses in such a manner as to threaten public health or welfare.
- The laboratory failed to satisfactorily correct violations.
- Failure to maintain at least one certified analyst for each method.
- Any facility changes to approved laboratory plans without prior Ohio EPA approval.

Should failure to follow requirements result in loss of certification, it will be the laboratory's responsibility to have the required analysis completed by a certified laboratory during that time.

Chapter 7 - Standard Operating Procedures for Plant Control Tests

OAC rule 3745-81-27 references all approved methods for analyzing drinking water in the State of Ohio.

Public water system laboratories may use the methods in Chapter 8 of this manual as the SOP of record for each method which laboratory personnel are certified.

Each method in this manual includes the following sections:

1. General method summary
2. Equipment
3. Reagents
4. Sample collection/preservation/holding time
5. Analysis procedure
6. Analyst requirements
7. Quality control requirements
8. Required documentation

   > **Note:** If an acceptable range is listed to one or more decimal places, recorded data must use the same number of decimal places
9. Any notes detailing unique aspects of individual SOPs

Any use of product or firm names in this publication is for descriptive purposes only and does not imply endorsement by the Ohio Environmental Protection Agency.

Chapter 8 – Analytical Methods

Alkalinity Analysis by Sulfuric Acid Titration Method

Quick Reference	**Standard/Reagent**	**Requirements**
Standard/Reagent Storage	0.020 N Sulfuric Acid (H_2SO_4)	Manufacturer's Recommendations
	Indicator (Bromcresol Green/Methyl Red)	Manufacturer's Recommendations
	0.1 N Sodium Thiosulfate	Manufacturer's Recommendations
	0.020 N Sodium Carbonate (Na_2CO_3) Standard	Manufacturer's Recommendations
Standard/Reagent Expiration	**Standard/Reagent**	**Expiration**
	0.020 N Sulfuric Acid (H_2SO_4)	1 Year After Opening/ Manufacturer's Expiration Date
	Indicator (Bromcresol Green/ Methyl Red)	1 Year After Opening/ Manufacturer's Expiration Date
	0.1 N Sodium Thiosulfate	1 Year After Opening/ Manufacturer's Expiration Date
	0.020 N Sodium Carbonate (Na_2CO_3) Standard	1 Year After Opening/ Manufacturer's Expiration Date
Required Quality Control	**QC Procedure**	**Frequency**
	Standardize Titrant	Once Per Month
	pH 4.5 Endpoint Verification	Once Per Month
Sample Collection	**Preservation**	**Maximum Hold Time**
	4°C	14 Days

Method Reference

Standard Methods 22nd Edition (2320)

Survey Requirements

- Each certified analyst must be able to perform the alkalinity titrant standardization described in this method.
- Operationally certified analysts will be required to analyze a plant tap sample and may be required to analyze a performance sample.
- Procedural technique will be observed.
- All reagents, standards and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

A titration is performed with 0.020 N sulfuric acid (H_2SO_4) to specified pH endpoints. The pH endpoints are determined either with a pH meter or by color in the presence of a suitable endpoint indicator solution. Phenolphthalein indicator is used to indicate an endpoint at a pH of 8.3. The mixed indicator bromcresol green/methyl red is used to indicate an endpoint at a pH of 4.5. Phenol alkalinity and total alkalinity can then be calculated. Samples must not be filtered or diluted.

Interferences

Suspended solids, precipitates, and dirty glassware may affect results. Chlorinated samples with more than 1.0 mg/L chlorine can affect the mixed indicator. Samples with more than 1.0 mg/L chlorine must be dechlorinated with 1 to 3 drops of 0.1 N sodium thiosulfate solution prior to analysis.

2.0) Equipment

1. 25 to 50 mL digital or self-leveling automatic burette.

   > **Note:** Burette with sufficient capacity so that all tests and standardizations can be performed without refilling the burette.

2. 20.0 mL Class A volumetric pipet(s).
3. Titration vessels of appropriate volume.
4. Graduated cylinders (50 to 100 mL).
5. Magnetic stirring device and stir bars.
6. Balance.

3.0) Reagents

1. Sulfuric Acid Titrant 0.020 N (H_2SO_4): Commercially available.
2. Mixed Bromcresol Green-Methyl Red Indicator: Commercially available.
   Prepare with alcoholic solution.
3. Phenolphthalein Alcoholic Solution.
4. Reagent Water.
5. 0.1 N Sodium Thiosulfate Solution: Commercially available.
6. Sodium Carbonate 0.020 N (Na_2CO_3): Commercially available as 0.020 N Na_2CO_3 or dry 2 to 3 g primary standard grade Na_2CO_3 at 250° C for four hours and cool in a desiccator. Weigh 1.0599 g and transfer to a 1-liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Alkalinity sample may be collected in a clean plastic or glass screw top container (250 to 1,000 mL). Alternatively, the sample may be collected directly into a graduated cylinder if the sample is analyzed immediately.
2. Preservation: 4°C.
3. Maximum sample holding time: 14 days. Ohio EPA recommends analyzing samples immediately after collection.

5.0) Alkalinity Analysis Procedure

A. Colorimetric Titration

1. Fill the burette with 0.020 N H_2SO_4 titrant. Zero the burette reading.
2. Rinse out the titrating vessel with sample and discard.
3. Measure 50 mL or 100 mL of sample with an appropriately sized graduated cylinder.
4. If the sample pH is greater than 8.3, add 2 to 4 drops of phenolphthalein indicator to the sample. If pH is less than 8.3 go to Step 9.
5. Slowly add titrant to the sample until color is dissipated, mixing with a magnetic stir bar or glass rod.

6. Record the volume of titrant needed to reach color endpoint.
7. Multiply the volume of titrant (mL) needed to reach color endpoint by a multiplier factor.
    - 50 mL sample titrated: multiply mL of titrant by 20.
    - 100 mL sample titrated: multiply mL of titrant by 10.
8. Record the value as phenol alkalinity in mg/L $CaCO_3$.
9. If sample free chlorine concentration is >1 mg/L, add 1 to 3 drops of a 0.1 N sodium thiosulfate solution to de-chlorinate the sample. Otherwise, proceed to Step 10.
10. Add 2 to 4 drops of mixed bromcresol green-methyl red indicator to the sample.
11. Slowly add titrant to the sample, mixing with a magnetic stir bar or glass rod until color endpoint is reached.
12. Record the volume of titrant needed to reach color endpoint.
13. Multiply the volume of titrant (mL) needed to reach color endpoint by a multiplier factor.
    - 50 mL sample titrated: multiply mL of titrant by 20.
    - 100 mL sample titrated: multiply mL of titrant by 10.
14. Record the value as total alkalinity in mg/L as $CaCO_3$.

B. Potentiometric Titration

1. Calibrate the pH meter (Section 7.0 of the pH method).
2. Fill the burette with 0.020 N H_2SO_4 titrant. Zero the burette reading.
3. Rinse out the titrating vessel with sample and discard.
4. Measure the sample with an appropriately sized graduated cylinder.
5. Place the pH electrode in the sample container.
6. Slowly add titrant to the sample, mixing with a magnetic stir bar.
7. Stop adding titrant when a stable pH of 8.3 ±0.2 pH units is reached.
8. Record the volume of titrant used for phenol alkalinity determination.
9. Multiply the volume of titrant (mL) needed to reach color endpoint by a multiplier factor.
    - 50 mL sample titrated: multiply mL of titrant by 20.
    - 100 mL sample titrated: multiply mL of titrant by 10.
10. Record the value as phenol alkalinity in mg/L $CaCO_3$.
11. Slowly add titrant to the sample, mixing with a magnetic stir bar.
12. Stop adding titrant when a stable pH of 4.5 ±0.2 pH units is reached.
13. Record the volume of titrant used for total alkalinity determination.
14. Multiply the volume of titrant (mL) needed to reach color endpoint by a multiplier factor.
    - 50 mL sample titrated: multiply mL of titrant by 20.
    - 100 mL sample titrated: multiply mL of titrant by 10.
15. Record the value as total alkalinity in mg/L as $CaCO_3$.

6.0) Analyst Requirements

All certified and operationally certified analysts must perform sample analysis at a minimum of at least three days per month.

Certified Analyst Requirements

All certified analysts must perform the monthly titrant standardization procedure at least once every three months. (Refer to Section 7.0 of this method.) Standardizations must be dated and initialed by all certified analysts participating in each standardization procedure. Analysts must verify and record the endpoint pH value of a total alkalinity sample at least once every month for the colorimetric titration only. The pH must be 4.5 ±0.2 pH units.

Operationally Certified Analyst Requirements

Analysts must verify and record the endpoint pH value of a total alkalinity sample at least once every month for the colorimetric titration only.

7.0) Quality Control Requirements

The titrant standardization procedure must be completed initially upon opening or preparation of titrant and at least once per month thereafter. Each standardization procedure must be dated and recorded.

7.1) Blank Verification of Alkalinity Free Reagent Water (Not required for potentiometric analysis)

1. Add 30 mL of reagent water using a graduated cylinder, then add sufficient mixed bromcresol green-methyl red indicator to the vessel to produce a distinctive color.
2. Slowly add 0.020 N H2SO4 titrant to the sample, mixing with a magnetic stir bar, until color endpoint is reached.
3. If less than 0.2 mL (approximately 4 drops) of titrant is needed to reach the endpoint, the reagent water is acceptable to use for the Titrant Check (Section 7.2).
4. If more than 0.2 mL (approximately 4 drops) of titrant is needed to reach the endpoint, obtain acceptable reagent water, and repeat the Titrant Standardization Procedure.
5. Record the volume of titrant used for blank determination on the *Monthly Alkalinity Titrant Standardization Record*.

7.2) Titrant Check

A. Colorimetric Titration

1. Add 30 mL of reagent water using a graduated cylinder and the mixed bromcresol green–methyl red indicator to the vessel.
2. Deliver 20.0 mL of standard solution 0.020 N Sodium Carbonate (Na2CO3) using a Class A volumetric pipet into the titrating vessel.
3. Slowly add titrant to the sample, mixing with a magnetic stir bar until color endpoint is reached.
4. Record the volume of titrant used for total alkalinity determination on the *Monthly Alkalinity Titrant Standardization Record*.
5. Repeat Steps 1 through 4 using a fresh portion reagent water and standard solution.

B. Potentiometric Titration

1. Add 30 mL of reagent water using a graduated cylinder to the vessel.
2. Deliver 20.0 mL of standard solution 0.020 N Sodium Carbonate (Na2CO3) using a Class A volumetric pipet into the titrating vessel.
3. Slowly add titrant to the sample, mixing with a magnetic stir bar until the pH endpoint of 4.5 ±0.2 pH units is reached.
4. Record the volume of titrant used for total alkalinity determination on the *Monthly Alkalinity Titrant Standardization Record*.
5. Repeat Steps 1 through 4 using a fresh portion reagent water and standard solution.

7.3) Titrant Standardization Acceptance Limits

The acceptable range for the adjusted amount of titrant used is ±5% of theoretical value.

When using 20.0 mL of 0.020 N Sodium Carbonate (Na_2CO_3) standardizing solution the acceptable range is 19.0 mL to 21.0 mL.

If the amount of the laboratory-prepared titrant used is outside of the acceptable range replace or remake the titrant. Do not use correction factors. Titrants must be within range or replaced.

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review by Ohio EPA and must be available upon request.

- Monthly Alkalinity Titrant Standardization Record
- Alkalinity pH 4.5 Endpoint Verification Record

Monthly Alkalinity Titrant Standardization Record

Laboratory _____

Standard Concentration _____

Analyst	Date	Reagent Water Volume (mL)	Blank Verification Result * (mL/drops)	Standard Volume (mL)	Titration #1	Titration #2	Titrant Lot Number/Date Prepared	Corrective Action Taken If Out of Range

*Blank verification must be <0.2 mL or 4 drops.

Alkalinity pH 4.5 Endpoint Verification Record

This must be completed by all analysts once per month.

Laboratory _____

Analyst	Date	Alkalinity (mg/L)	Endpoint (pH 4.5)	Result Within ±0.2 pH Units (Y/N)	Comments

Chloride Analysis by Silver Nitrate Titration Method

Quick Reference	**Standard/Reagent**	**Requirements**
Standard/Reagent Storage	0.0141 N Silver Nitrate Titrant	Manufacturer's Recommendations, Away from Light
	Potassium Chromate Indicator	Manufacturer's Recommendations
	0.0141 N Sodium Chloride Standard	Manufacturer's Recommendations
Standard/Reagent Expiration	**Standard/Reagent**	**Expiration**
	0.0141 N Silver Nitrate Titrant	1 Year After Opening/ Manufacturer's Expiration Date
	Potassium Chromate Indicator	1 Year After Opening/ Manufacturer's Expiration Date
	0.0141 N Sodium Chloride Standard	1 Year After Opening/ Manufacturer's Expiration Date
Required Quality Control	**QC Procedure**	**Frequency**
	Titrant Standardization	Once Per Month
Sample Collection	**Preservation**	**Maximum Hold Time**
	None	28 Days

Method Reference

Standard Methods 22nd Edition (4500-Cl^- B)

Survey Requirements

- Each certified analyst must be able to perform the chloride titrant standardization described in this method.
- Operationally certified analysts will be required to analyze a plant tap sample and may be required to analyze a performance sample.
- Procedural technique will be observed.
- All reagents, standards, and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

After collecting a known sample volume, add approximately 1.0 ml of potassium chromate indicator. A titration is performed with 0.0141 N silver nitrate. The titration is complete when the sample solution color changes from yellow to red/orange. The volume of titrant is recorded, and the chloride concentration is calculated.

> **Note:** The color change in this method is subtle. A blank with 0.5 mL of titrant added may assist as a reference for the final color endpoint of titrated samples.

Interferences

Suspended solids, precipitates, and dirty glassware may affect results.

2.0) Equipment

1. Amber or aluminum foil-wrapped, self-zeroing, automatic burette of adequate size to perform titration without refilling.
2. Titration vessels of appropriate volume.
3. Class A volumetric glassware for standardization.
4. Graduated cylinder (50 or 100 mL).
5. Magnetic stirring device and stir bars (optional).

3.0) Reagents

1. Silver Nitrate Titrant (0.0141 N): Commercially available. This titrant is light-sensitive and should be stored away from light.
2. Potassium Chromate Indicator: Commercially available.
3. Sodium Chloride Standard (0.0141 N): Commercially available.
4. Reagent Water.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Collect in a clean plastic or glass screw-top container (250 to 1000 mL). Alternatively, samples may be collected in a graduated cylinder if they are analyzed immediately.
2. Preservation: None.
3. Maximum sample holding time: 28 days. Ohio EPA recommends analyzing samples immediately after collection.

5.0) Chloride Analysis Procedure

1. Fill the burette with 0.0141 N silver nitrate titrant. Zero the burette reading.
2. Rinse out the titrating vessel with sample.
3. Measure 50 mL of sample using a graduated cylinder.
4. Add about 1.0 mL of potassium chromate indicator to the sample.
5. Slowly add silver nitrate titrant to the sample, mixing with a magnetic stir bar or glass rod.
6. Stop adding silver nitrate titrant when color endpoint is reached. The sample will go from yellow to red/orange.
7. Record the volume (mL) of silver nitrate titrant needed to change color from yellow to red/orange.
8. Multiply the volume (mL) of silver nitrate titrant used by a multiplier factor of 10 (see note below).
9. Record this value as chloride concentration in mg/L, using the formula:

   Chloride Concentration (mg/L) = mL titration for sample x multiplier factor

> **Note: Multiplier factor = [0.0141N x 35450] ÷ 50 mL**, where 35450 is the atomic mass of chloride. If using a different normality of silver nitrate or a different sample volume, make adjustments to the multiplier factor formula.

6.0) Analyst Requirements

All certified and operationally certified analysts must perform sample analysis for at least three days per month.

Certified Analyst Requirements

All certified analysts must perform the monthly titrant standardization procedure at least once every three months. (Refer to Section 7.0 of this method.) Standardizations must be dated and initialed by all certified analysts participating in each standardization procedure.

Operationally Certified Analyst Requirements

There are no operationally certified personnel QC requirements for this method.

7.0) Quality Control Requirements

The titrant standardization procedure must be completed upon opening or preparing the titrant and at least once per month thereafter. Each standardization procedure must be dated and recorded.

7.1) Blank (Verification of chloride-free reagent water)

1. Add 45 mL of reagent water using a graduated cylinder, then add 1.0 mL potassium chromate indicator to the vessel to produce a distinctive color.
2. While mixing with a magnetic stir bar, slowly add 0.0141 N silver nitrate titrant, until a red/orange color is reached.
3. If less than 0.6 mL (approximately 12 drops) of titrant is needed to reach the endpoint, the reagent water is acceptable to use for Titrant Standardization Procedure (Section 7.2).
4. Obtain acceptable reagent water if more than 0.6 mL (approximately 12 drops) of titrant is needed to reach the endpoint.
5. Record the volume of titrant used for blank determination on the *Monthly Chloride Titrant Standardization Record*.

7.2) Titrant Standardization Procedure

1. Add 45 mL of reagent water using a graduated cylinder, then add 1.0 mL potassium chromate indicator to the vessel to produce a distinctive color.
2. Add 5.0 mL of the (0.0141 N) sodium chloride standard solution using a Class A volumetric pipet.
3. While mixing with a magnetic stir bar, slowly add 0.0141 N silver nitrate titrant until a red/orange color is reached.
4. Record the volume of titrant used.
5. Repeat Steps 1 through 4 for the second titrant standardization.

The blank result (Section 7.1) is the chloride in the reagent water. Subtract the blank value (in mL) from each standard titration value.

7.3) Titrant Standardization Acceptance Limits

The acceptable range for the adjusted amount of titrant used is ±5% of theoretical value.

The acceptable range for using 5.0 mL of 0.0141 N sodium chloride (NaCl) standard solution is 4.75 to 5.25 mL.

If the amount of the laboratory-prepared titrant used is outside of the acceptable range, replace or remake the titrant. Do not use correction factors. Titrants must be within range or replaced.

8.0) Required Documentation

Each of the following records contains the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review by Ohio EPA and must be available upon request.

- Monthly Chloride Titrant Standardization Record

Monthly Chloride Titrant Standardization Record

Laboratory _____

Standard Concentration _____

Analyst	Date	Reagent Water Volume (mL)	Blank Verification Volume* (mL/drops)	Standard Volume (mL)	Titration #1	Titration #2	Titrant Lot Number/Date Prepared	Corrective Action Taken if out of range

*Blank verification must be <0.6 mL or approximately 12 drops.

Chlorine Analysis by Amperometric (PAO Titration Method)

Quick Reference	**Standard/Reagent**	**Requirements**
Standard/ Reagent Storage	Phenylarsine Oxide (PAO) Titrant (0.00564 N)	Manufacturer's Recommendations
	Phosphate buffer solution (pH 7)	Manufacturer's Recommendations
	Potassium Iodide (KI) Solution	Manufacturer's Recommendations
	Acetate Buffer Solution	Manufacturer's Recommendations
	Sulfuric Acid Solution 10%	Manufacturer's Recommendations
	Potassium Biiodate, (0.025 N)	Manufacturer's Recommendations
Standard/ Reagent Expiration	**Standard/Reagent**	**Expiration**
	Liquid Reagents	1 Year After Opening/ Manufacturer's Expiration Date
	Standards	1 Year After Opening/ Manufacturer's Expiration Date
Required Quality Control	**QC Procedure**	**Frequency**
	Titrant Standardization	Once Per Month
	Verify Chlorine-Free Reagent Water	Once Per Month
Sample Collection	**Preservation**	**Maximum Hold Time**
	No Preservation Required	Analyze Within 15 Minutes

Method Reference

Standard Methods 22nd Edition (4500-Cl D)

Survey Requirements

- Each certified analyst must be able to perform the PAO titrant standardization described in this method.
- Operationally certified analysts will be required to analyze a plant tap sample and may be required to analyze a performance sample.
- Procedural technique will be observed.
- All reagents, standards, and solutions used for the method will be audited for proper labeling and dating.
- All records will be audited.
- Amperometric titrator maintenance/condition will be audited.

1.0) General Method Summary

Should a laboratory choose to be certified for chlorine analysis, the requirements of this method would need to be followed. A known volume of potable water is collected and titrated on an amperometric titrator to deflection endpoint, determining free and total chlorine concentrations. Initially, phosphate buffer is added to the sample to adjust it to pH 7.0. The sample is titrated with phenylarsine oxide to a point where the needle on the amperometric titrator stops deflecting. Free chlorine in mg/L is then calculated using the titrant volume needed to reach endpoint. Potassium iodide solution and acetate buffer are added to the sample, adjusting to pH 3.5 – 4.5. Without refilling the burette, the sample is again titrated with phenylarsine oxide (PAO) to a point where the needle on the amperometric titrator stops deflecting. Total chlorine in mg/L is then calculated using the total volume of titrant needed to reach endpoint.

Interferences

Suspended solids, precipitates, and dirty glassware may affect results.

2.0) Equipment

1. Amperometric titrator equipped with the following:
   - Platinum electrode: Follow the manufacturer's recommendations for maintenance.
   - Salt bridge: Follow the manufacturer's recommendations for maintenance.
   - Silver-Silver Chloride reference electrode.
   - Agitator: Follow the manufacturer's recommendations for maintenance.
   - Titrant burette (1.00 mL to 5.00 mL).
   - Sample container with 200 mL graduation.
2. Class A volumetric glassware including:
   - Volumetric pipets - 1.0 mL, 5.0 mL, 10.0 mL, 20.0 mL, 25.0 mL.
   - Volumetric flasks - 100 mL, 500 mL, 1000 mL.

3.0) Reagents

1. Phenylarsine Oxide (PAO) Titrant (0.00564 N): Commercially available.
2. Phosphate buffer solution (pH 7): Commercially available.
3. Potassium Iodide (KI) Solution: Commercially available.
4. Acetate Buffer Solution: Commercially available.
5. Potassium Biiodate, Commercially Prepared Solution (0.025 N). Expires one year after opening or on manufacturer’s expiration date.
6. Potassium Biiodate Titrant Standardization Solution (0.0025 N) From Commercial Solution (0.025 N): Dilute a fresh batch for each standardization procedure. Add 10 mL of commercially prepared potassium biiodate solution (0.025 N) to a 100 mL volumetric flask, half-filled with reagent water. Bring to volume with reagent water.
7. Potassium Biiodate, Laboratory-Prepared Stock Solution (0.100 N): Dry 2 to 4 g of reagent - grade potassium biiodate for two hours at 105°C and desiccate at room temperature. Add 1.6245 g of potassium biiodate to a 500 mL volumetric flask, half-filled with reagent water. Bring to volume with reagent water. Expires one year after preparation.
8. Potassium Biiodate Titrant Standardization Solution (0.0025 N) from laboratory stock solution (0.100 N): Dilute a fresh batch for each standardization procedure. Add 25.0 mL of 0.100 N laboratory-prepared potassium biiodate stock solution (0.100 N) to a 1-liter volumetric flask, half-filled with reagent water. Bring to volume with reagent water.
9. Sulfuric Acid Solution (10% or 4 N): Commercially available. It may also be prepared as follows: Slowly add 10 mL of concentrated H_2SO_4 to a 100 mL volumetric flask, half-filled with reagent water. After allowing time for the solution to cool, bring the flask to volume with reagent water. **Caution: H_2SO_4 is a strong acid. Safety glasses, lab coat, and acid-resistant gloves must be worn when handling H_2SO_4.**
10. Reagent water.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Samples may be collected in a clean plastic or glass screw-top container dedicated to chlorine sample collection. Alternatively, if the sample is analyzed immediately, it may be collected directly into the analysis container.
2. Preservation: No preservation required.
3. Maximum sample hold time: Analyze sample within 15 minutes of collection.

5.0) Amperometric Titration Chlorine Analysis Procedure

1. Run the sample tap for at least five minutes to maintain a constant chlorine concentration from the main water supply.
2. Collect a 200 mL sample.
3. **Free Chlorine Analysis:** Add 1.0 mL of pH 7.0 phosphate buffer.
4. While stirring, titrate until the meter's needle movement stops. The titration endpoint is approaching when needle movement becomes sluggish. From this point on, add titrant in increments of 0.05 mL. When nearing the endpoint, record titrant volume before adding additional titrant to avoid over-titration. If there is no needle response after additional titrant, use the previous titrant volume recorded for reporting purposes.
5. Record the final titrant volume needed to reach free chlorine endpoint.
6. Using the calculation in Section 5.1, convert titrant volume to free chlorine concentration in mg/L.
7. Do not refill the burette with titrant.
8. **Total Chlorine Analysis:** Add 1.00 mL of KI solution and 1.00 mL acetate buffer to the sample titrated for free chlorine.
9. Titrate this sample again until the meter's needle movement stops. The titration endpoint is approaching when needle movement becomes sluggish. From this point on, add titrant in increments of 0.05 mL. When nearing the endpoint, record titrant volume before adding additional titrant to avoid over-titration. If there is no needle response after additional titrant, use the previous titrant volume recorded for reporting purposes.
10. Record the final titrant volume (volume of titrant needed to reach free chlorine endpoint plus additional volume of titrant used for total chlorine endpoint).
11. Using the calculation in Section 5.1, convert titrant volume needed to reach titration endpoint to total chlorine concentration in mg/L.
12. Subtract the free chlorine concentration from the total chlorine concentration and record the result as combined chlorine.

5.1) Amperometric Chlorine Calculations

The following formula is used to calculate concentrations for free and total chlorine:

$$\frac{\text{Volume of PAO titrant needed to reach endpoint (mL)} \times 200}{\text{mL of sample analyzed}} = \text{mg/L Chlorine}$$

Free Chlorine Example:

Initial burette reading: 0.00 mL
Final burette reading (free chlorine): 1.20 mL
mL of sample analyzed: 200 mL

$$\frac{1.2 \text{ mL} \times 200}{200 \text{ mL}} = 1.2 \text{ mg/L Free Chlorine}$$

Total Chlorine Example:

Initial burette reading: 1.20 mL
Final burette reading (total chlorine): 1.80 mL
mL of sample analyzed: 200 mL

$$\frac{1.8 \text{ mL} \times 200}{200 \text{ mL}} = 1.8 \text{ mg/L Total Chlorine}$$

Combined Chlorine Example:

Calculate the combined chlorine by subtracting the free chlorine concentration from the total chlorine concentration.

Free chlorine concentration: 1.2 mg/L
Total chlorine concentration: 1.8 mg/L

(1.8 mg/L Total chlorine – 1.2 mg/L Free chlorine) = 0.6 mg/L Combined chlorine

6.0) Analyst Requirements

All certified and operationally certified analysts must perform sample analysis at a minimum of at least three days per month.

Certified Analyst Requirements

All certified analysts must perform the titrant standardization procedure at least once every three months. (Refer to Section 7.0 of this method.) Standardizations must be dated and initialed by all certified analysts participating in each standardization procedure.

Operationally Certified Analyst Requirements

There are no operationally certified personnel QC requirements for this method.

7.0) Quality Control Requirements

The titrant standardization procedure must be completed upon opening or preparing the titrant and at least once per month thereafter. Each standardization procedure must be dated and recorded.

7.1) Blank (Verification of Chlorine-Free Reagent Water)

1. Add 200 mL of reagent water in the sample container and turn on the stirrer.
2. Add 1.0 mL of sulfuric acid solution (10%).
3. Add approximately 1.0 mL of KI solution.
4. Add an initial 0.05 mL of PAO titrant. If the needle does not move, the reagent water is free of chlorine. Record the blank as 0.0 mg/L; go to Section 7.2. If the needle does move after adding more than 0.05 mL of PAO titrant, find an alternative source of reagent water.

7.2) Titrant Standardization Procedure

1. Fill burette with PAO titrant.
2. Add 200 mL of reagent water in the sample container and turn on the stirrer.
3. Add 1.0 mL of sulfuric acid solution (10%).
4. Add approximately 1.0 mL of KI solution.
5. Carefully add 5.0 mL of the 0.0025 N potassium biiodate titrant standardization solution (Section 3.0 Reagents, 5 or 6). A pale-yellow color should develop.
6. Titrate until the meter's needle movement stops. The titration endpoint is approaching when needle movement becomes sluggish. From this point on, add titrant in increments of 0.05 mL. When nearing the endpoint, record titrant volume before adding additional titrant to avoid over titration. If there is no needle response after additional titrant is added, use the previous titrant volume recorded for reporting purposes.
7. Record the final titrant volume.
8. Repeat Steps 1 through 7 for the second titrant standardization.

7.3) Titrant Standardization Acceptance Limits

The true value of the PAO titrant is 2.22 mL. The acceptable range is ±5% of the true value (2.22 mL), which is 2.11 mL to 2.33 mL. If the PAO titrant is outside of the acceptable range, replace it.

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review by Ohio EPA and must be available upon request.

- Monthly Chlorine Amperometric (PAO) Titrant Standardization Record

Monthly Chlorine Amperometric (PAO) Titrant Standardization Record

Laboratory _____

Standard Concentration _____

Analyst	Date	Reagent Water Verification	Standard Volume (mL)	Titration #1	Titration #2	Titrant Lot Number/Date Prepared	Corrective Action Taken if out of range

Chlorine Analysis by Colorimetric/DPD Method

Quick Reference	**Standard/Reagent**	**Requirements**
Standard/Reagent/ Equipment Storage	Commercially Available Secondary Standards	Manufacturer's Recommendations
	Commercially Available Ampules	Manufacturer's Recommendations
	Sealed DPD Powder Pillows	Manufacturer's Recommendations
	DPD Single Dose Dispensers	Manufacturer's Recommendations
	Liquid DPD Indicator	Manufacturer's Recommendations
Standard/ Reagent Expiration	**Standard/Reagent**	**Expiration**
	Commercially Available Secondary Standards	Manufacturer's Expiration Date
	Commercially Available Ampules	Manufacturer's Expiration Date
	Sealed DPD Powder Pillows	Manufacturer's Expiration Date
	DPD Single Dose Dispensers	Manufacturer's Expiration Date
	Liquid DPD Indicator	Manufacturer's Expiration Date or Six Months After Opening
Required Quality Control	**QC Procedure**	**Frequency**
	Colorimeter Calibration Verification	Once Every Three Months
Sample Collection	**Preservation**	**Maximum Hold Time**
	No Preservation Required	Analyze Within 15 Minutes

Method Reference

Standard Methods 22nd Edition (4500-Cl G)

Survey Requirements

- Each certified analyst must be able to perform the calibration verification procedure described in of this method. Alternatively, the analyst must construct a calibration curve if a spectrophotometer is used for chlorine analysis.
- Operationally certified analysts will be required to analyze a plant tap sample and may be required to analyze a performance sample.
- Procedural technique will be observed.
- All reagents, standards, and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

Should a laboratory choose to be certified for chlorine analysis, the requirements of this method would need to be followed. A potable water sample is collected, and a measured amount of chlorine indicator reagent (DPD) is added. The sample is then analyzed. Free chlorine is analyzed with a free chlorine DPD, while total chlorine is analyzed with a total chorine DPD.

Interferences

Bubbles introduced during the sample shaking to dissolve the DPD indicator and dirt collected on the outside of the vial are the most common interferences. Care should be taken to keep the sample free of bubbles and the outside of the vial as clean as possible. Sample turbidity may also cause interference, but it is rarely a factor in finished potable water.

> **Note:** If free chlorine concentration is great than total chlorine concentration, the analysis results are invalid. Free chlorine concentration cannot be greater than total chlorine concentration. Resample and reanalyze both free chlorine and total chlorine.

2.0) Equipment

1. Electronic filter colorimeter or Spectrophotometer. The functional range of the colorimeter must accommodate the highest and lowest concentrations of chlorine observed.
2. An adjustable microliter pipettor.
3. Dedicated plastic or glass screw top container (250 to 1,000 mL).
4. Class A volumetric pipets.
5. Lint-free wipes.

3.0) Reagents

1. N,N-Diethyl-p-phenylenediamine Indicator (DPD): Commercially available in both powder and liquid.
2. Reagent water.
3. Ampule Chlorine Standard Solution: Commercially available. The concentration will vary with each lot. Opened ampules are stable for ½ hour after opening. Discard unopened ampules on the manufacturer's expiration date.
4. Secondary Standards: Commercially available.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Samples may be collected in a clean plastic or glass screw-top container dedicated to chlorine sample collection. Alternatively, if the sample is analyzed immediately, it may be collected directly into the analysis container.
2. Preservation: No Preservation Required.
3. Maximum sample hold time: Analyze sample within 15 minutes of collection.

5.0) Chlorine Analysis Procedure (Hach Pocket Colorimeter)

This procedure is written for using the Hach Pocket Colorimeter on the low range. When using a different range or other chlorine analyzers, please consult the manufacturer's instructions for procedural details.

A. Free Chlorine

1. Run the sample tap to maintain a constant chlorine concentration from the main water supply.
2. Fill a clean 10 mL test vial to the line with water from the sample tap.
3. Wipe the sample vial so that it is dry and clean.
4. Place the vial into the colorimeter. Cover the vial.
5. Zero the colorimeter by pressing ZERO and wait for the colorimeter to display 0.00.
6. Remove the vial from the colorimeter.
7. Immediately add one free chlorine DPD powder packet to the sample.
8. Cap the vial and invert for 10 seconds.

9. Place the vial in the colorimeter. Cover the vial.
10. Immediately analyze the sample by pressing READ. The sample must be read **within one minute** of adding the DPD reagent.
11. Record the displayed result (in mg/L) as free chlorine.

B. Total Chlorine

1. Run the sample tap to maintain a constant chlorine concentration from the main water supply.
2. Fill a clean 10 mL test vial to the line with sample water.
3. Wipe the sample vial so that it is dry and clean.
4. Place the vial into the colorimeter. Cover the vial.
5. Zero the colorimeter by pressing ZERO and wait for the colorimeter to display 0.00.
6. Remove the vial from the colorimeter.
7. Immediately add one total chlorine DPD powder packet to the sample.
8. Cap the vial and invert for 10 seconds.
9. Place the vial in the colorimeter. Cover the vial.
10. **Wait at least three minutes, but no more than five minutes,** then analyze the sample by pressing READ.
11. Record the displayed result (in mg/L) as total chlorine.

C. Combined Chlorine

Calculate the combined chlorine by subtracting the free chlorine concentration from the total chlorine concentration.

Example: **(2.2 mg/L Total Chlorine – 1.6 mg/L Free Chlorine) = 0.6 mg/L Combined Chlorine**

6.0) Analyst Requirements

All certified and operationally certified analysts must perform sample analysis for at least three days per month.

Certified Analyst Requirements

All certified analysts must participate in the calibration verification procedure at least once every three months. (Refer to Section 7.0 of this method.) All participating certified analysts must date and initial calibration verifications.

Operationally Certified Analyst Requirements

There are no operationally certified personnel QC requirements for this method.

7.0) Quality Control Requirements

The DPD colorimeter calibration verification must be completed before initial use for analyzing potable water and at least once every three months thereafter. This must be done for each colorimeter used to report chlorine concentrations for monitoring purposes.

There are two standard solution options for colorimeter verification: (1) Commercially available secondary standards with certified values assigned by the manufacturer; and (2) Commercially available ampules of free chlorine standards.

If option 2 is chosen, the spike concentrations prepared for the calibration verification should span the range of chlorine concentrations observed throughout the entire distribution system. For example: If the lowest chlorine concentration observed in a distribution system is 0.2 mg/L, then the lowest spike concentration in the verification procedure must be near 0.2 mg/L. If the highest chlorine concentration in the distribution system is 2.0 mg/L, then the highest spike concentration in the verification procedure should be near or above 2.0 mg/L. The additional spike(s) will be prepared at concentrations between the lowest and highest spike concentrations.

7.1) DPD Colorimeter Calibration Verification

A. Purchased Secondary Standard Verification Procedure

1. With a lint-free wipe, clean the outside and bottom of standard vials prior to insertion into meter.
2. Zero the instrument with the provided Blank.
3. Place secondary standards into meter.
4. Read and record the value of each secondary standard.
5. Verify the reading is within the acceptable value listed on the Certificate of Analysis, which is specific to each box of secondary standards.

> **Note:** The value may be different for different models of meters.

B. Free Chlorine Standard (purchased in ampules)

1. Using a Class A pipet, add 10.0 mL of reagent water into a clean sample vial.
2. Zero the instrument with the reagent water.
3. Add total chlorine DPD to the reagent water.
4. Wait specified time.
5. Read the reagent water result displayed by colorimeter.
6. If the total chlorine is less than 0.1 mg/L, proceed to the next step. If it is greater than or equal to 0.1 mg/L, obtain a source of chlorine-free reagent water and start with Step 1.
7. Pipet 10.0 mL of reagent water into a clean sample vial.
8. Using an adjustable microliter pipettor, spike the prepared reagent water with a known volume of standard from the ampule and add free chlorine DPD.
9. Mix thoroughly. Analyze immediately.
10. Place into the colorimeter and record the observed concentration. The observed concentration must be within the acceptance limits for each spike concentration. (Refer to Section 7.2 of this method for calculations.)
11. Adjust the microliter pipettor to the next spike volume.
12. Repeat Steps 7 through 11 using five standard concentrations spanning the range of chlorine concentrations observed.

> **Note:** If the spike volume for a concentration is above the range of the microliter pipettor, adding two equal spike volumes totaling the desired spike volume is acceptable. For example: If a spike volume of 300 µL is needed, but the limit of a microliter pipettor is 200 µL, adding two equal spikes at 150 µL is acceptable.

7.2) Expected Calculations for Calibration Verification

A. Calibration Verification with Ampule Chlorine Standard

Standard concentrations are unique to each lot number. Calculations must be completed with each new batch of ampules to determine the expected value for each concentration. The following formula is used to determine the expected concentration:

(Standard Concentration mg/L) x (Volume of Spike Added in µL) = Expected Concentration
(Volume of Water in µL) + (Volume of Spike Added in µL)

> **Note:** 10 mL = 10,000 µL (mL=milliliter, µL=microliter)

Examples: *The following examples assume the ampule standard concentration is 65.35 mg/L.*

Spike with 50 µL **(65.35 mg/L) x (50 µL) = 0.32 mg/L**
(10,000 µL) + (50 µL)

Spike with 150 µL **(65.35 mg/L) x (150 µL) = 0.97 mg/L**
(10,000 µL) + (150 µL)

Spike with 250 µL **(65.35 mg/L) x (250 µL) = 1.59 mg/L**
(10,000 µL) + (250 µL)

> **Note:** Follow the manufacturer's instructions for analyzing water samples containing chlorine concentrations above the colorimeter's analytical range. When performing the standardization, the volume of reagent water used is adjusted, and the result is multiplied by the dilution factor.

Example: *The following assumes a sample vial volume of 25 mL and a dilution factor of 2.5.*

Spike with 150 µL **(65.35 mg/L) x (150 µL) = 0.39 mg/L**
(25,000 µL) + (150 µL)

Multiply by the dilution factor: **0.39 mg/L x 2.5 = 0.97 mg/L**

B. Calibration Verification Acceptance Limits

The observed concentration must not be lower than minus (-) 10% of the expected concentration and must not be higher than plus (+) 10% of the expected concentration of each spike. The colorimeter must be serviced or replaced if the observed concentration results are outside the acceptable range.

Example: If the **Expected Concentration = 0.97 mg/L,** then:

-10% of 0.97 mg/L: 0.97 mg/L x 0.9 = 0.87 mg/L (Lowest Acceptable Observed Conc.)

+10% of 0.97 mg/L: 0.97 mg/L x 1.1 = 1.07 mg/L (Highest Acceptable Observed Conc.)

The acceptance limits for the observed concentration of the 0.97 mg/L spike = **0.87 mg/L to 1.07 mg/L.**

8.0) Required Documentation

Each of the following records contains the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review by Ohio EPA and must be available upon request.

- Three Month DPD Colorimeter Calibration Verification Record for Secondary Standards
- Three Month DPD Colorimeter Calibration Verification Record

9.0) Personnel Acceptable to the Director to Perform Chlorine Analysis

Persons acceptable to the director to conduct chlorine analysis are recommended to undergo a five-day training in chlorine sample collection and analysis with an analyst certified in chlorine sampling and analysis. This training should be completed before reporting chlorine results and documented using the *Training Record for Chlorine Analysis*.

Three-Month DPD Colorimeter Calibration Verification Record*

*For use with secondary standards only

Laboratory _____

Analyst(s)			**Analyst(s)**		
Date			**Date**		
Range of Standard	LR MR HR		**Range of Standard**	LR MR HR	
Standard Expiration Date			**Standard Expiration Date**		
Standard Lot #			**Standard Lot #**		
Standard	**Assigned Value**	**Observed Value**	**Standard**	**Assigned Value**	**Observed Value**
#1			#1		
#2			#2		
#3			#3		
Comments			**Comments**		

Analyst(s)			**Analyst(s)**		
Date			**Date**		
Range of Standard	LR MR HR		**Range of Standard**	LR MR HR	
Standard Expiration Date			**Standard Expiration Date**		
Standard Lot #			**Standard Lot #**		
Standard	**Assigned Value**	**Observed Value**	**Standard**	**Assigned Value**	**Observed Value**
#1			#1		
#2			#2		
#3			#3		
Comments			**Comments**		

Three-Month DPD Colorimeter Calibration Verification Record

Laboratory _____

Analyst(s)			Analyst(s)		
Date			Date		
Standard Concentration			Standard Concentration		
Standard Expiration Date			Standard Expiration Date		
Standard Spike Volume	Calculated Concentration	Observed Concentration	Standard Spike Volume	Calculated Concentration	Observed Concentration
#1			#1		
#2			#2		
#3			#3		
#4			#4		
#5			#5		
Comments			Comments		
Reagent Water Result			Reagent Water Result		

Analyst(s)			Analyst(s)		
Date			Date		
Standard Concentration			Standard Concentration		
Standard Expiration Date			Standard Expiration Date		
Standard Spike Volume	Calculated Concentration	Observed Concentration	Standard Spike Volume	Calculated Concentration	Observed Concentration
#1			#1		
#2			#2		
#3			#3		
#4			#4		
#5			#5		
Comments			Comments		
Reagent Water Result			Reagent Water Result		

Training Record for Chlorine Analysis

Laboratory _____

Trainee Name	Certified Analyst/Trainer Name	Date of Training

Fluoride Analysis by Ion-Selective Electrode Method

Quick Reference	**Standard/Reagent/Equipment**	**Requirements**
Standard/ Reagent Storage	Reference Electrode	Reagent Water
	Fluoride Ion-Sensitive (ISE) Electrode/Combination Electrode	Manufacturer's Recommendations
	TISAB	Manufacturer's Recommendations
	0.5/5.0/1.0 mg/L Standards	Manufacturer's Recommendations
	100 mg/L Standard	Manufacturer's Recommendations
Standard/ Reagent Expiration	**Standard/Reagent**	**Expiration**
	TISAB	1 Year After Opening/ Manufacturer's Expiration Date
	0.5/5.0/1.0 mg/L Standards	1 Year After Opening/ Manufacturer's Expiration Date
	100 mg/L Standard	1 Year After Opening/ Manufacturer's Expiration Date
Required Quality Control	**QC Procedure**	**Frequency**
	Calibrate Meter	Once Per Shift/Once Every 8 Hours
	Linearity (1.0 mg/L Check)	Once Per Week
	QC Sample Analysis	Once Per Month
Sample Collection	**Preservation**	**Maximum Hold Time**
	None or 4°C	48 Hours [See OAC rule 3745-83-01(F)(4)(b)] **or** 1 Month [See OAC rule 3745-81-23(J)]

Method Reference

Standard Methods 22nd Edition (4500-F^- C)

Survey Requirements

- Each certified analyst must be able to perform the calibration procedure described in this method.
- Each operationally certified analyst must be able to perform the calibration procedure described in this method.
- Procedural technique will be observed.
- All reagents, standards and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

Fluoride analysis is one of the most important and frequently performed tests in water chemistry. After acceptable calibration of a fluoride meter, a known volume of drinking water is collected in a clean ion-free container and mixed with an equal volume of fluoride buffer (TISAB). The fluoride meter electrode is immersed in the sample/fluoride buffer mixture. The meter is allowed to stabilize, and the displayed fluoride value is recorded in mg/L.

Interferences

Poorly maintained electrodes (insufficiently filled with electrode solution, having crystalline buildup and/or improperly stored) will cause unacceptable linearity or increase stabilization time. Care should be taken to maintain electrodes following manufacturer's directions.

2.0) Equipment

1. A digital specific ion meter capable of being calibrated with a minimum of two standards and equipped with a slope display.
2. A fluoride ISE combination electrode or a fluoride ISE electrode with a sieve type reference electrode.
3. A magnetic stirring device and a least three TFE-coated (Teflon) stirring bars.
4. Class A volumetric pipets.
5. Class A volumetric flasks.
6. (2) 25 mL graduated cylinders.
7. Plastic beakers (50 - 100 mL).
8. Lint-free wipes.

2.1) General Electrode Maintenance

1. Follow manufacturer's instruction for storing and maintaining electrodes. Alternatively, follow 2 through 6 below.
2. Electrodes should be kept clean and free from crystalline buildup.
3. The ISE electrode should be cleaned periodically (on the bottom only) using fluoride toothpaste to improve response time.
4. The ISE electrode can be stored dry in air when not in use.
5. Store electrodes as they are received until they are put into use.
6. Electrodes taking longer than three minutes to stabilize in calibration solution may need service or replacement.

3.0) Reagents

1. Reagent water.
2. 100 mg/L Stock Fluoride Solution: Commercially available.
3. 0.5 mg/L Calibration Standard: Commercially available. Alternatively, prepare as follows: Pipet 5mL of 100 mg/L stock fluoride solution into a 1-liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.
4. 5.0 mg/L Calibration Standard: Commercially available. Alternatively, prepare as follows: Pipet 50 mL of 100 mg/L stock fluoride solution into a 1-liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.
5. 1.0 mg/L Linearity Verification Standard: Commercially available. Alternatively, prepare as follows: Pipet 10 mL of 100 mg/L stock fluoride solution into a 1-liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.

   > **Note:** Calibration/Linearity Verification Standard must not be mixed with fluoride buffer (TISAB) until immediately prior to calibration procedure. Standards must be stored in suitable plastic containers. Do not store fluoride standards in glass containers.

6. Buffer Solution (TISAB): Commercially available in both powder and liquid.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Collect in a clean plastic screw top container (250 to 1,000 mL). Alternatively, samples may be collected in the analysis container if they are analyzed immediately.
2. Preservation: 4.0°C. No preservation needed if samples are analyzed immediately.
3. Maximum sample holding time: 48 Hours [See OAC rule 3745-83-01(F)(4)(b)] or 1 Month [See OAC rule 3745-81-23(J)]. The hold times are determined by the analytical location. Ohio EPA recommends analyzing samples immediately after collection.

5.0) Fluoride Analysis Procedure

This is a general procedure; each Ion-Selective meter may have a unique procedure. If using a different concentration of fluoride buffer, please reference the manufacturer's instructions for procedural details.

1. Calibrate the fluoride meter following procedure detailed in Section 7.0. If the meter has been calibrated for the current eight-hour shift, go to Step 2.
2. Using a graduated cylinder and/or Class A pipet, measure sample water and TISAB according to manufacturer's instructions (e.g., 25 ml sample and 25 ml TISAB); add to a clean sample beaker/container.

   > **Note:** Each graduated cylinder must be rinsed once with reagent water and then with the solution being measured prior to measuring the solution.

3. Add a stir bar to the beaker containing the mixture and place on magnetic stirrer.
4. Immerse fluoride electrodes in the sample mixture and allow meter to stabilize while stirring.
5. Record the result as fluoride in mg/L.

> **Note:** Rinse electrodes with reagent water and blot dry with a lint-free wipe before and between all analyses of samples/standards. The samples/standards must be stirred during analysis.

6.0) Analyst Requirements

All certified and operationally certified analysts must perform sample analysis at a minimum of three days per month. All calibration slopes must be recorded with dates and analyst initials.

Certified Analyst Requirements

All certified analysts must perform the calibration procedure at least three times per month. (Refer to Section 7.0 of this method.) Calibrations must be dated and initialed by all certified analysts participating in each calibration procedure. Once per week, one of the certified analysts is required to confirm and record the 1.0 mg/L verification standard (second source), with all certified analysts participating at least once every three months.

Operationally Certified Analyst Requirements

All operationally certified analysts must perform the calibration procedure at least three times per month. Calibrations must be dated and initialed by all operationally certified analysts participating in each calibration procedure.

7.0) Quality Control Requirements

7.1) Fluoride Meter Calibration Procedure

The calibration procedure must be performed resulting in an acceptable slope/linearity value in millivolts (mV) prior to initial use for analyzing potable water and at the beginning of each eight-hour shift, if a drinking water sample is to be analyzed during that shift. The slope value must be recorded each time the meter is calibrated. This must be done for each fluoride meter used to report drinking water fluoride results.

> **Note:** Calibrations must be performed once per shift (every eight hours), if a drinking water sample is to be analyzed during that shift. Each calibration requires newly poured standard, which are discarded after calibration.

1. If calibration standards are refrigerated, allow standards to stabilize to room temperature prior to analysis.
2. Prepare 0.5 mg/L calibration standard by using a graduated cylinder to measure and pour equal amounts of 0.5 mg/L calibration standard and TISAB (25 mL 0.5 mg/L calibration standard /25 mL TISAB is common) into a clean sample beaker/container.
3. Prepare 5.0 mg/L calibration standard by using a graduated cylinder to measure and pour equal amounts of 5.0 mg/L calibration standard and TISAB (25 mL 5.0 mg/L calibration standard /25 mL TISAB is common) into a clean sample beaker/container.
4. Once per week, prepare 1.0 mg/L linearity verification standard (second source) by using a graduated cylinder to measure and pour equal amounts of 1.0 mg/L verification standard and TISAB (25 mL 1.0 mg/L verification standard /25 mL TISAB is common) into a clean sample beaker/container. This is required of certified analysts.
5. The results of the 1.0 mg/L verification standard must be within ±10% of the true value. The acceptance limits are 0.9 to 1.10 mg/L.

   > **Note:** Each graduated cylinder must be rinsed once with reagent water and then with the solution being measured prior to measuring the solution.
6. Calibrate the fluoride meter following the manufacturer's instructions for a 2-point calibration using the 0.5 and 5.0 mg/L calibration standard/TISAB mixtures.
7. Record the slope value for the calibration. Refer to Section 7.2 in this method for detailed acceptance limits.
8. If slope value is outside of acceptable range, the calibration procedure must be repeated until an acceptable value is acquired prior to sample analysis. Refer to Section 7.2 for corrective measures.

> **Note:** Rinse electrodes with reagent water and blot dry with a lint-free wipe before and between all analyses of samples/standards. The samples/standards must be stirred during analyses.

7.2) Calibration Acceptance Limits

The slope/linearity value must fall in the acceptable range of 95.0% to 105.0% (slope value displayed in %) or -54.0 to -60.0 mV (value displayed in millivolts). Please reference the manufacturer's instructions for acceptance criteria if otherwise specified.

Corrective Measures

If the calibration results in an unacceptable linearity value, the following steps should be taken to correct the problem:

1. Repeat calibration standard preparation.
2. Check the fill solution level of the electrode and fill if needed. Rinse the electrode with reagent water.
3. Clean the electrode following the manufacturer's recommendations.
4. Service the meter if all other attempts have failed to acquire acceptable results.

7.3) Monthly Fluoride QC Sample Analysis

All laboratories certified for fluoride analysis must successfully analyze and record one QC sample in a range of 0.5 to 1.5 mg/L prior to initial certification and once per month thereafter.

A provider of PT samples must be accredited by a Proficiency Testing Provider Accreditor that meets the National Environmental Laboratory Accreditation Conference requirements. A current list of accredited providers is available at ***nelac-institute.org/content/NEPTP/ptproviders.php***.

The acceptance limits for the QC sample must be within the acceptable range specified by the PT provider. If no range is specified, the acceptance limits are ±10%.

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review by Ohio EPA and must be available upon request.

- Fluoride Slope/Weekly Linearity Verification (1.0 mg/L Standard) Record
- Monthly Fluoride QC Sample Record

Fluoride Slope/Weekly Linearity Verification (1.0 mg/L Standard) Record

Laboratory _____

Standard Concentration _____

Analyst	Date	Slope %	1.0 mg/L ±10% Value	Comments	Analyst	Date	Slope %	1.0 mg/L ±10% Value	Comments

Monthly Fluoride QC Sample Record

Laboratory _____

Analyst	Date	Results (mg/L)	Certified Value Range per PT Provider (mg/L)	Results Within Range (Y/N)	QC Sample Provider Name	Sample Lot #

Fluoride Analysis by SPADNS 2 (Arsenic-Free) Method 10225

Quick Reference	Standard/Reagent/Equipment	Requirements
Standard/Reagent Storage	SPADNS 2 Reagent	Manufacturer's Recommendations
	0.5/1.0/1.5 mg/L Standards	Manufacturer's Recommendations
	100 mg/L Stock Standard	Manufacturer's Recommendations
Standard/Reagent Expiration	Standard/Reagent	Expiration
	Commercially Available Secondary Standards	Manufacturer's Expiration Date
	SPADNS 2 Fluoride Reagent AccuVac ® Ampuls or Fluoride TNTplus Reagent Set	Manufacturer's Expiration Date
	SPADNS 2 Reagent	1 Year After Opening/ Manufacturer's Expiration Date
	0.5/1.0/1.5 mg/L Standards	1 Year After Opening/ Manufacturer's Expiration Date
	100 mg/L Stock Standard	1 Year After Opening/ Manufacturer's Expiration Date
Required Quality Control	QC Procedure	Frequency
	Meter Calibration Verification	Once Every Three Months
	Blank, QCS	Once Per Batch
	QC Sample Analysis	Once Per Month
Sample Collection	Preservation	Maximum Hold Time
	None	48 Hours [See OAC rule 3745-83-01(F)(4)(b)] or 1 Month [See OAC rule 3745-81-23(J)]

Method Reference

Hach Company SPADNS 2 Fluoride Method 10225, Revision 2.0, January 2011

Survey Requirements

- Each certified analyst must be able to perform the calibration verification procedure described in this method.
- Operationally certified analysts will be required to analyze a plant tap sample and may be required to analyze a performance sample.
- Procedural technique will be observed.
- All reagents, standards and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

This method may be performed with SPADNS 2 Reagent Solution, SPADNS 2 Fluoride Reagent AccuVac® Ampuls or Fluoride TNT Vials. Depending on the selected procedure, the method instructions will differ slightly.

Fluoride reacts with a zirconium SPADNS dye. The loss of color during this reaction is proportional to the fluoride concentration in the sample. The SPADNS 2 reagent contains a non-toxic species to prevent chlorine interference. Fluoride values are recorded in mg/L.

Interferences

Chlorine levels above 5 mg/L may interfere. If samples contain more than 5 mg/L chlorine, dilute the sample by a factor that will lower the chlorine level to below 5 mg/L and multiply results by this dilution factor.

2.0) Equipment

1. Electronic filter colorimeter or Spectrophotometer. The functional range of the colorimeter must accommodate the highest and lowest concentrations of fluoride observed.
2. Sample collection bottles: Preferably use polyethylene (plastic) bottles for collecting and storing samples for fluoride analysis.
3. Lint-free wipes.
4. For reagent solution:
   - Adjustable microliter pipettor 2.0 mL and 10 mL capacity.
   - Micropipette tips.
5. For ampuls:
   - Beaker, 50-mL.
   - Stoppers for 18-mm tubes and AccuVac® Ampuls.
6. For TNT vials:
   - Adjustable microliter pipettor, 1.0-5.0 mL capacity.
   - Micropipette tips.

3.0) Reagents

1. Reagent water.
2. 100 mg/L Stock Fluoride Solution: Commercially available.
3. 0.5 mg/L Calibration Standard: Commercially available. Alternatively, prepare as follows: Pipet 5 mL of 100 mg/L stock fluoride solution into a 1-liter volumetric flask, half-filled with reagent water. Bring to volume with reagent water.
4. 1.5 mg/L Calibration Standard: Commercially available. Alternatively, prepare as follows: Pipet 15 mL of 100 mg/L stock fluoride solution into a 1-liter volumetric flask, half-filled with reagent water. Bring to volume with reagent water.
5. 1.0 mg/L Quality Control Sample (QCS): Commercially available. Must be from a different source or different lot than the stock fluoride solution.
6. For reagent solution:
   - SPADNS 2 Reagent: Commercially available.

   > **Note:** Standards must be stored in suitable plastic containers. Do not store fluoride standards in glass containers.
7. For ampuls:
   - SPADNS 2 Fluoride Reagent AccuVac® Ampuls.
8. For TNT vials:
   - Fluoride TNTplus Reagent Set.

9. Secondary Standards: Commercially available.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Collect in a clean plastic screw top container (250 to 1,000 mL). Alternatively, samples may be collected in the analysis container if they are analyzed immediately.
2. Preservation: 4.0°C. No preservation needed if samples are analyzed immediately.
3. Maximum sample holding time: 48 Hours [See OAC rule 3745-83-01(F)(4)(b)] or 1 Month [See OAC rule 3745-81-23(J)]. The hold times are determined by the analytical location. Ohio EPA recommends analyzing samples immediately after collection.

5.0) Fluoride Analysis Procedure

Prior to analysis, refer to Section 7.4 of this method for the quality control requirements of each sample batch.

Reagent Solution Procedure

1. Set the instrument to the appropriate program/channel per the manufacturer's instructions.
2. Pipet 10.0 mL of reagent water into a dry sample cell. This is the blank.
3. Pipet 10.0 mL of 1.0 mg/L F- standard into a dry sample cell. This is the QCS.
4. Pipet 10.0 mL of sample into another dry sample cell. This is the sample.
5. Using a micropipette, carefully pipet 2.0 mL of SPADNS 2 Reagent into each of the sample cells from steps 2, 3, and 4.
6. Swirl and react for 1 minute.
7. With a lint-free wipe, dry the outside and bottom of the sample cells.
8. Insert the sample cell that contains the blank into the instrument.
9. Press ZERO key on the instrument. The display should show 0.00 mg/L F-.
10. Insert the sample cell that contains the QCS into the instrument.
11. Press READ key on the instrument. The display should show concentration as mg/L F-.
12. Record the result as fluoride in mg/L.
13. Insert the sample cell that contains the sample into the instrument.
14. Press READ key on the instrument. The display should show concentration mg/L F-.
15. Record the result as fluoride in mg/L.

AccuVac® Ampul Procedure

1. Set the instrument to the appropriate program/channel per the manufacturer's instructions.
2. Pour at least 40 mL of reagent water into a 50-mL beaker. This is the blank.
3. Pour at least 40 mL of 1.0 mg/L F-standard into a 50-mL beaker. This is the QCS.
4. Pour at least 40 mL of sample into a 50-mL beaker. This is the sample.
5. Using different AccuVac ® Ampul for each of the beakers from steps 2, 3, and 4, fill each AccuVac® Ampul with the reagent water/standard/sample.

> **Note:** Keep the tip immersed while the AccuVac® Ampul fills completely.

6. Cap each of the AccuVac® Ampuls with a stopper.
7. Quickly invert the AccuVac® Ampuls several times to mix and react for one minute.
8. With a lint-free wipe, dry the outside and bottom of the AccuVac® Ampuls.
9. Insert the blank AccuVac® Ampul into the cell holder.
10. Press ZERO key on the instrument. The display should show 0.00 mg/L F-

11. Insert the AccuVac® Ampul that contains the QCS into the instrument.
12. Press READ key on the instrument. The display should show concentration as mg/L F-.
13. Record the result as fluoride in mg/L.
14. Insert the AccuVac® Ampul that contains the sample into the instrument.
15. Press READ key on the instrument. The display should show concentration mg/L F-.
16. Record the result as fluoride in mg/L.

TNT Vial Procedure

1. Set the instrument to the appropriate program/channel per the manufacturer's instructions.
2. Insert the vial into the cell holder and push READ.
3. Remove the vial from the cell holder and pipet 3.0 mL of the sample into the test vial.
4. Cap the vial and invert two to three times.
5. Set and start a timer for one minute to allow the sample to react.
6. When the timer expires, wipe the vial clean and dry with a lint-free wipe.
7. Insert the vial into the cell holder and push READ. Results are displayed in mg/L F-.
8. Repeat steps 2-7 for the QCS (1.0 mg/L F- Standard) and any additional samples.

6.0) Analyst Requirements

All certified and operationally certified analysts must perform an initial precision and recovery procedure to generate acceptable accuracy and precision with this method. (Refer to Section 7.3 of this method.) All certified and operationally certified analysts must perform sample analysis at a minimum of three days per month.

Certified Analyst Requirements

All certified analysts must perform the calibration verification procedure at least once every three months. (Refer to Section 7.1 of this method.)

All certified analysts must participate in the Fluoride QC Sample Analysis at least once every three months. (Refer to Section 7.5 of this method.)

Operationally Certified Analyst Requirements

All operationally certified analysts must perform the fluoride analysis procedure at least three times per month.

7.0) Quality Control Requirements

The spectrophotometer or colorimeter calibration verification must be completed prior to initial use for analyzing potable water and at least once every three months thereafter. This must be done for each spectrophotometer or colorimeter used to report fluoride concentrations for monitoring purposes.

There are two standard solution options for calibration verification: (1) Commercially available secondary standards with certified values assigned by the manufacturer; and (2) Commercially available fluoride standards.

7.1) Spectrophotometer or Colorimeter Calibration Verification Procedure

A. Purchased Secondary Standard Verification Procedure

1. With a lint-free wipe, clean the outside and bottom of standard vials prior to insertion into meter.
2. Zero the instrument with the provided Blank.
3. Place secondary standards into meter.
4. Read and record the value of each secondary standard.
5. Verify the reading is within the acceptable value listed on the Certificate of Analysis, which is specific to each box of secondary standards.

> **Note:** The value may be different for different models of meters.

B. Fluoride Standards

The spectrophotometer or colorimeter must be verified to ensure it is measuring fluoride properly. To do this, 0.5 mg/L and 1.5 mg/L fluoride standards must be analyzed and verified to be within the acceptable range of ±15% of the actual value.

1. If calibration standards are refrigerated, allow standards to stabilize to room temperature prior to analysis.
2. Set the instrument to the appropriate program/channel per the manufacturer's instructions.
3. Prepare and measure a blank, 0.5 mg/L and 1.5 mg/L standards according to the appropriate procedure.
4. With a lint-free wipe, dry the outside and bottom of the sample cells, AccuVac® Ampuls or TNT vials.
5. Insert the prepared vial into the spectrophotometer or colorimeter.
6. Record the result of the 0.5 mg/L and 1.5 mg/L standards onto the *Three-Month Fluoride Calibration Verification Record*. (Refer to Section 7.2 in this method for detailed acceptance limits.)
7. The measured value of the 0.5 mg/L and 1.5 mg/L fluoride standards must be within ±15% of the actual value.
8. If the results of either or both standards are outside of acceptable range, the calibration verification procedure must be repeated until acceptable values are acquired prior to sample analysis. (Refer to Section 7.2 in this method for corrective measures.)

7.2) Calibration Verification Acceptance Limits

The measured value of the 0.5 mg/L and 1.5 mg/L fluoride standards must be within ±15% of the actual value.

Corrective Measures

If the calibration verification results are unacceptable, take the following steps to try to correct the problem:

1. Repeat calibration verification standard preparation(s).
2. Service the spectrophotometer or colorimeter if all other attempts have failed to acquire acceptable results.

7.3) Initial Demonstration of Laboratory Capability

To be certified for this method, an initial demonstration of capability, consisting of an initial method detection limit (MDL) study and an initial precision and recovery (IPR) study, are required as follows:

MDL Determination Procedure (Required to be performed on each meter prior to initial certification for this method.)

1. If calibration standards are refrigerated, allow standards to stabilize to room temperature prior to analysis.
2. Verify the meter calibration using the procedure outlined in section 7.1.
3. Prepare and measure a 0.5 mg/L standard according to the appropriate procedure.
4. With a lint-free wipe, dry the outside and bottom of the sample cell, AccuVac® Ampul or TNT vial.
5. Insert the prepared vial into the spectrophotometer or colorimeter.
6. Measure and record the results onto the *Fluoride MDL Worksheet* provided by Ohio EPA.
7. Repeat steps 3-6 six more times for a total set of seven replicates of the 0.5 mg/L standard.

> **Note:** Each replicate must be separate (i.e., must be a freshly pipetted standard).

8. Calculate the MDL using the provided *Fluoride MDL Worksheet*.
9. If the MDL result is 0.0 mg/L or > 0.5 mg/L, the MDL is unacceptable and the procedure must be repeated.

IPR Procedure (Required to be performed by each analyst prior to initial certification for this method.)

1. If calibration standards are refrigerated, allow standards to stabilize to room temperature prior to analysis.
2. Verify the meter calibration using the procedure outlined in section 7.0.
3. Prepare and measure a 1.0 mg/L standard according to the appropriate procedure.
4. With a lint-free wipe, dry the outside and bottom of the sample cell, AccuVac® Ampul or TNT vial.
5. Insert the prepared vial into the spectrophotometer or colorimeter.
6. Measure and record the results onto the *Fluoride IPR Worksheet provided by Ohio EPA*.
7. Repeat steps 3-6 three more times for a total set of four replicates of the 1.0 mg/L standard.

> **Note:** Each replicate must be separate (i.e., must be a freshly pipetted standard).

8. Calculate the IPR using the provided *Fluoride IPR Worksheet*.
9. If the accuracy is greater than ±10% or the precision of accuracy is >20%, the study is unacceptable and must be repeated by the analyst.

7.4) Requirements with Each Sample Batch (Analytical Sequence)

A sample batch is a set of samples analyzed during a contiguous 8-hour period. Each batch must include a blank, a quality control standard (QCS) and up to 10 samples. The analytical sequence is as follows:

1. Blank (0.0 mg/L): Acceptance: Results must be <0.5 mg/L.
2. QCS (1.0 mg/L F- Standard): Acceptance: Results must be ±10% of the actual value.
3. Sample(s), up to 10.

> **Note:** If the QCS is out of range, a certified analyst must perform and record a meter calibration verification.

7.5) Monthly Fluoride QC Sample Analysis

All laboratories certified for fluoride analysis must successfully analyze and record one QC sample in a range of 0.5 to 1.5 mg/L prior to initial certification and once per month thereafter.

A provider of PT samples must be accredited by a Proficiency Testing Provider Accreditor that meets the National Environmental Laboratory Accreditation Conference requirements. A current list of accredited providers is available at ***nelac-institute.org/content/NEPTP/ptproviders.php***.

The acceptance limits for the QC sample must be within the acceptable range specified by the PT provider.

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review by Ohio EPA and must be available upon request.

- Three-Month Fluoride SPADNS 2 Calibration Verification Record for Secondary Standards
- Three-Month Fluoride SPADNS 2 Calibration Verification Record
- Monthly Fluoride QC Sample Record
- Fluoride SPADNS 2 Quality Control Sample Analysis Record

Three Month Fluoride SPADNS 2 Calibration Verification Record*

*For use with secondary standards only

Laboratory _____

Analyst(s)			**Analyst(s)**		
Date			**Date**		
Standard Expiration Date			**Standard Expiration Date**		
Standard Lot #			**Standard Lot #**		
Standard	**Assigned Value**	**Observed Value**	**Standard**	**Assigned Value**	**Observed Value**
#1			#1		
#2			#2		
#3			#3		
Comments			**Comments**		
Analyst(s)			**Analyst(s)**		
Date			**Date**		
Standard Expiration Date			**Standard Expiration Date**		
Standard Lot #			**Standard Lot #**		
Standard	**Assigned Value**	**Observed Value**	**Standard**	**Assigned Value**	**Observed Value**
#1			#1		
#2			#2		
#3			#3		
Comments			**Comments**		

Three-Month Fluoride SPADNS 2 Calibration Verification Record

Laboratory _____

Analyst(s)			**Analyst(s)**		
Date			**Date**		
Standard(s) Expiration Date			**Standard(s) Expiration Date**		
Standard(s) Lot #			**Standard(s) Lot #**		
Standard	**Assigned Value**	**Observed Value**	**Standard**	**Assigned Value**	**Observed Value**
#1	0.5		#1	0.5	
#2	1.5		#2	1.5	
Comments			**Comments**		
Analyst(s)			**Analyst(s)**		
Date			**Date**		
Standard(s) Expiration Date			**Standard(s) Expiration Date**		
Standard(s) Lot #			**Standard(s) Lot #**		
Standard	**Assigned Value**	**Observed Value**	**Standard**	**Assigned Value**	**Observed Value**
#1	0.5		#1	0.5	
#2	1.5		#2	1.5	
Comments			**Comments**		

Monthly Fluoride QC Sample Record

Laboratory _____

Analyst	Date	Results (mg/L)	Certified Value Range per PT Provider (mg/L)	Results Within Range(Y/N)	QC Sample Provider Name	Sample Lot #

Fluoride SPADNS 2 Quality Control Sample Analysis Record

Laboratory _____

Analyst	Date	Blank (mg/L)	QCS (1.0 mg/L)	Sample Lot #	Analyst	Date	Blank (mg/L)	QCS (1.0 mg/L)	Sample Lot #

Hardness Analysis by EDTA Titration Method

Quick Reference	**Standard/Reagent**	**Requirements**
Standard/Reagent Storage	EDTA	Manufacturer's Recommendations
	Indicator	Manufacturer's Recommendations
	Buffer	Manufacturer's Recommendations
	1000 mg/L Calcium Chloride (as $CaCO_3$) Standard	Manufacturer's Recommendations
	Commercial Dry Reagents	Manufacturer's Recommendations
Standard/Reagent Expiration	**Standard/Reagent**	**Expiration**
	EDTA	1 Year After Opening/ Manufacturer's Expiration Date
	Hardness Indicator	1 Year After Opening/ Manufacturer's Expiration Date
	Buffer	1 Year After Opening/ Manufacturer's Expiration Date
	1000 mg/L Calcium Chloride (as $CaCO_3$) Standard	1 Year After Opening/ Manufacturer's Expiration Date
	Commercial Dry Reagents	6 Years After Opening/ Manufacturer's Expiration Date
Required Quality Control	**QC Procedure**	**Frequency**
	Standardize Titrant	Once Per Month
Sample Collection	**Preservation**	**Maximum Hold Time**
	Adjust to < pH 2.0 with HNO_3, 4°C	28 Days

Method Reference

Standard Methods 22nd Edition (2340 C)

Survey Requirements

- All certified analysts must be able to perform the hardness titrant standardization described in this method.
- Operationally certified analysts will be required to analyze a performance sample and a plant tap sample.
- Procedural technique will be observed.
- All reagents, standards, and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

A titration is performed with 0.010 M (0.020 N) EDTA to a specified color in the presence of Eriochrome black-T indicator and a buffer (to adjust the pH to 10.0 prior to titration). Calcium and magnesium ions are sequestered by the addition of EDTA. The indicator has a red color in the presence of calcium and magnesium ions and a distinct blue color when the cations are sequestered. Hardness can then be calculated.

Perform the titration at room temperature for a rapid, distinct color change endpoint; a slower endpoint will be more evident as sample temperatures approach freezing. The titration must be completed within five minutes from the time the buffer is added to the sample.

Interferences

Suspended solids, precipitates and dirty glassware may affect results. Excessive amounts of heavy metals can interfere. This is usually overcome by complexing the heavy metals with an inhibitor.

2.0) Equipment

1. 25 to 50 mL digital or self-leveling automatic burette.

> **Note:** Burette must be of sufficient capacity so that all tests and standardizations can be performed without refilling the burette.

2. 20.0 mL Class A volumetric pipet(s).
3. Titration vessels of appropriate volume.
4. Graduated cylinders (50 to 100 mL).
5. Magnetic stirring device and stirring bars.
6. Balance.

3.0) Reagents

1. Standard EDTA titrant 0.010 M 0.020 N): Commercially available.
2. Buffer Solution: Commercially available.
3. Mixed Eriochrome Black T Indicator: Commercially available. Prepare with calcium or magnesium ions.
4. Calmagite: Commercially available.
5. Calcium Chloride Standard (0.020 N): Commercially available Calcium Chloride, 1,000 mg/L as $CaCO_3$.
6. Reagent water.

4.0) Sample Collection/Preservative/Storage

1. Sample collection: Hardness samples may be collected in clean plastic or glass screw top container (250 to 1000 mL). Alternately, the sample may be collected directly into a graduated cylinder if sample is analyzed immediately.
2. Preservation: Adjust to pH less than 2.0 with HNO_3, 4°C. Preservation is not required if sample is analyzed immediately.
3. Maximum sample holding time: 28 days. Ohio EPA recommends analyzing samples immediately after collection.

5.0) Analysis Procedure

1. Fill the burette with 0.010 M EDTA titrant if self-leveling burette is used. Zero the burette reading if digital burette is used.
2. Rinse out the titrating vessel with sample and discard.
3. Measure 100 mL of sample with an appropriately sized graduated cylinder.
4. Add 0.5 to 1.0 mL of hardness buffer if not contained in color indicator.
5. Add color indicator.
6. Slowly add titrant to the sample, mixing with a magnetic stir bar.
7. Stop adding titrant when a stable blue color is reached; color persists for 1 minute.
8. Record the volume of titrant used for total hardness determination.

9. Multiply the volume of titrant used by the multiplier factor. 50 mL sample titrated: multiply mL of titrant by 20. 100 mL sample titrated: multiply mL of titrant by 10.
10. Record the values as total hardness mg/L as $CaCO_3$.

Example: Amount (mL) of EDTA titrant needed to change sample color to blue: 7.2 mL

Multiplier factor for 100 mL of sample volume: 10

$CaCO_3$ Concentration (mg/L): 7.2 x 10 = 72 mg/L

6.0) Analyst Requirements

All certified and operationally certified analysts must perform sample analysis at a minimum of at least three days per month.

Certified Analyst Requirements

All certified analysts must perform the titrant standardization procedure at least once every three months. (Refer to Section 7.0 of this method.) Standardizations must be dated and initialed by all certified analysts participating in each standardization procedure.

Operationally Certified Analyst Requirements

There are no operationally certified personnel QC requirements for this method.

7.0) Quality Control Requirements

The titrant standardization procedure must be completed initially upon opening or preparation of titrant and at least once per month thereafter. Each standardization procedure must be dated and recorded.

7.1) Blank (Verification of hardness free reagent water)

1. Add 30 mL of reagent water using a graduated cylinder.
2. Add 0.5 to 1.0 mL of hardness buffer if not contained in color indicator.
3. Add color indicator.
4. Slowly add 0.010 M EDTA titrant to the reagent water, mixing with a magnetic stir bar, until color endpoint is reached.
5. If less than 0.1 mL (approximately 2 drops) of titrant is needed to reach the endpoint, the reagent water is acceptable to use for Titrant Standardization Procedure (Section 7.2).
6. If more than 0.1 mL (approximately 2 drops) of titrant is needed to reach the endpoint, obtain acceptable reagent water, and repeat the Titrant Standardization Procedure.
7. Record the volume of titrant used for blank determination on the Monthly Hardness Titrant Standardization record.

7.2) Titrant Standardization

1. Fill the burette with 0.010 M EDTA titrant if self-leveling burette is used. Zero the burette reading if digital burette is used.
2. Rinse out the titrating vessel with reagent water.
3. Measure 30 mL of reagent water with an appropriately sized graduated cylinder.
4. Add 0.5 to 1.0 mL of hardness buffer if not contained in color indicator.
5. Add color indicator.
6. Add 20.0 mL of calcium chloride standard (0.020 N) with a Class A volumetric pipet.
7. Slowly add titrant to the sample, mixing with a magnetic stir bar.
8. Stop adding titrant when a stable blue color is reached; color persists for one minute.

9. Record the volume of titrant used for total hardness determination on the Monthly Hardness Titrant Standardization record.
10. Repeat Steps 1 through 9 with a fresh portion of reagent water and standard solution.

7.3) Titrant Standardization Acceptance Limits

The acceptable range for the adjusted amount of titrant used is ±5% of theoretical value.

When using 20.0 mL of 0.020 N calcium chloride (as $CaCO_3$) standardizing solution, the acceptable range is 19.0 to 21.0 mL.

If the amount of the laboratory-prepared titrant used is outside of the acceptable range, replace or remake the titrant. Do not use correction factors. Titrants must be within range or replaced.

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review and must be available upon request.

- Monthly Hardness Titrant Standardization Record

Monthly Hardness Titrant Standardization Record

Laboratory _____

Standard Concentration _____

Analyst	Date	Reagent Water Volume (mL)	Blank Verification Result* (mL/drops)	Standard Volume (mL)	Titration #1	Titration #2	Titrant Lot Number/Date Prepared	Corrective Action Taken If Out of Range

*Blank verification must be <0.1 mL or 2 drops.

Nitrate Analysis by Hach TNTplus 835/836 Method 10206

Quick Reference	**Standard/Reagent**	**Requirements**
Standard/Reagent Storage	Hach Company TNTplus Nitrate Reagent, Cat. No. TNT835 or TNT836	Manufacturer's Recommendations
	0.3/1.0/5.0/10.0 mg/L Standards	Manufacturer's Recommendations
	100 mg/L Stock Standard	Manufacturer's Recommendations
Standard/Reagent Expiration	**Standard/Reagent**	**Expiration**
	Hach Company TNTplus Nitrate Reagent, Cat. No. TNT835 or TNT836	Manufacturer's Expiration Date
	0.3/1.0/5.0/10.0 mg/L Standards	1 Year After Opening/ Manufacturer's Expiration Date
	100 mg/L Stock Standard	1 Year After Opening/ Manufacturer's Expiration Date
Required Quality Control	**QC Procedure**	**Frequency**
	Meter Calibration Verification	Once Every Three Months
	QCS	Once Per Batch
Sample Collection	**Preservation**	**Maximum Hold Time**
	None or Acidified 4°C	Immediate **or** 48 hours

Method Reference

Hach Company TNT plus 835/836 Method 10206, Revision 2.0, January 2011

Survey Requirements

- Each certified analyst must be able to perform the calibration verification procedure described in this method.
- Procedural technique will be observed.
- All reagents, standards and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

The Hach TNTplus Nitrate chemistry follows classical electrophilic aromatic substitution in that nitrate in the presence of sulfuric acid yields a nitronium ion (+ NO2) and HSO4 -. Nitronium ions are electrophiles that attack the aromatic ring of the dimethylphenol reagent to form intermediate nitro-carbonium ions. The basic HSO4 - ion then extracts a hydrogen ion from the nitro-carbonium intermediate to yield a stable substitution product (o, or p-nitro-dimethylphenol). The nitrodimethylphenol product is a highly colored (directly related to the nitro functional group), quantifiable by its visible absorption spectra. Test results are measured at 345 nm.

Interferences

Refer to Section 3.0 of the published method for interfering substances. High Iron may be an interference.

2.0) Equipment

1. Spectrophotometer. Hach Company DR 2800, DR 3800, DR 5000 or equivalent.
2. Sample collection bottles. Preferably use polyethylene bottles for collecting and storing samples. Glass bottles that have been acid rinsed may also be used.
3. Adjustable microliter pipettor with tips.
4. Lint-free wipes.

> **Note:** All glassware must be acid rinsed using dilute hydrochloric acid and rinsed thoroughly with reagent water. It is recommended to maintain a dedicated set of glassware for this procedure to reduce the possibilities of contamination.

3.0) Reagents

1. Reagent Water.
2. 100 mg/L Stock Nitrate Solution: Commercially available.
3. 0.3 mg/L Calibration Standard: Commercially available. Alternatively, prepare as follows: Pipet 3 mL of 100 mg/L stock nitrate solution into a 1-liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.
4. 1.0 mg/L Calibration Standard: Commercially available. Alternatively, prepare as follows: Pipet 10 mL of 100 mg/L stock nitrate solution into a 1-liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.
5. 1.0 mg/L Quality Control Sample (QCS): Commercially available. Must be from a different source or different lot than the 1.0 mg/L calibration standard or stock nitrate solution.
6. 5.0 mg/L Calibration Standard: Commercially available. Alternatively, prepare as follows: Pipet 50 mL of 100 mg/L stock nitrate solution into a 1-liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.
7. 10.0 mg/L Calibration Standard: Commercially available. Alternatively, prepare as follows: Pipet 100 mL of 100 mg/L stock nitrate solution into a 1-liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.
8. Hach Company TNTplus Nitrate Reagent, Cat. No. TNT835 or TNT836: Commercially available.

4.0) Sample Collection/Preservation/Storage/Holding Time

1. Sample collection: Collect in clean glass or plastic bottles.
2. Analyze samples as soon as possible. If immediate analysis is not possible, store at 4° C or cooler and analyze within 48 hours.
3. Maximum sample holding time: If longer storage is required (up to 14 days), adjust sample pH to less than 2 with sulfuric acid (about 2 mL per liter). Sample refrigeration is required. If sample is acid preserved, results will be in the form of total nitrate and nitrite.

5.0) Nitrate Analysis Procedure

Prior to analysis refer to Section 7.4 of this method for the quality control requirements of each sample batch.

1. For LR (Low Range) TNT 835: Pipet 1.0 mL of sample into the reagent vial.

   For HR (High Range) TNT836: Pipet 0.2 mL of sample into the reagent vial.
2. For LR TNT835: Pipet 0.2 mL of Solution A into the reagent vial.

   For HR TNT836: Pipe 1.0 mL of Solution A into the reagent vial.

3. Cap and invert the reagent vial 2-3 times until no more streaks can be seen in the reagent vial solution.
4. React for a total of 15 minutes.
5. With a lint-free wipe, dry the outside and bottom of the reagent vials.
6. Insert the prepared vial into the spectrophotometer. The instrument reads the barcode, then selects and performs the correct test. No zero is required. Results are in mg/L NO_3^- N.
7. Repeat steps 1-6 for the QCS (1.0 mg/L nitrate) and any additional samples.

6.0) Analyst Requirements

Certified Analyst Requirements

All certified analysts must perform an initial precision and recovery study to generate acceptable accuracy and precision with this method. (Refer to Section 7.3 of this method.) All certified analysts must perform the calibration verification procedure at least once every three months. All certified analysts must perform sample analysis at a minimum of once per month.

Operationally Certified Analyst Requirements

Operational certification is not available for this method.

7.0) Quality Control Requirements

7.1) Spectrophotometer Calibration Verification Procedure

The nitrate calibration curve of the spectrophotometer must be verified to ensure it is measuring nitrate properly. The required calibration verification must include the analysis of 0.3 mg/L and 10.0 mg/L nitrate standards. The results must be within the acceptable range of ±15% of the actual value.

> **Note:** Calibration verifications must be performed at a minimum of once every three months.

1. If calibration standards are refrigerated, allow standards to stabilize to room temperature prior to analysis.
2. For LR (Low Range) TNT 835: Pipet 1.0 mL of 0.3 mg/L standard into a reagent vial.
   For HR (High Range) TNT836: Pipet 0.2 mL of 0.3 mg/L standard into a reagent vial.
3. For LR (Low Range) TNT 835: Pipet 1.0 mL of 10.0 mg/L standard into a reagent vial.
   For HR (High Range) TNT836: Pipet 0.2 mL of 10.0 mg/L standard into a reagent vial.
4. For LR TNT835: Pipet 0.2 mL of Solution A into each of the vials.
   For HR TNT836: Pipe 1.0 mL of Solution A into each of the vials.
5. Cap and invert the vials 2-3 times until no more streaks can be seen in the vial solutions.
6. React for a total of 15 minutes.
7. With a lint-free wipe, dry the outside and bottom of the reagent vials.
8. Insert the prepared vials into the spectrophotometer beginning with the 0.3 mg/L solution. The instrument reads the barcode, then selects and performs the correct test. No zero is required. Results are in mg/L NO_3^- N.
9. Record the result of the 0.3 mg/L and 10.0 mg/L standards onto the *Three-Month Nitrate Calibration Verification Record*. (Refer to Section 7.2 in this method for detailed acceptance limits.)
10. If the results of either or both standards are outside of acceptable range, the calibration verification procedure must be repeated until acceptable values are acquired prior to sample analysis. (Refer to Section 7.2 in this method for corrective measures.)

7.2) Calibration Verification Acceptance Limits

The measured value of the 0.3 mg/L and 10.0 mg/L nitrate standards must be within ±15% of the actual value.

Corrective Measures

If the calibration verification results are unacceptable, the following steps should be taken to try to correct the problem:

1. Repeat calibration verification standard preparation(s).
2. Service the spectrophotometer if all other attempts have failed to acquire acceptable results.

7.3) Initial Demonstration of Laboratory Capability

To be certified for this method, an initial demonstration of laboratory capability, consisting of an initial method detection limit (MDL) study and an initial precision and recovery (IPR) study, are required as follows:

MDL Determination Procedure (Required to be performed on each meter prior to initial certification for this method.)

1. If calibration standards are refrigerated, allow standards to stabilize to room temperature prior to analysis.
2. For LR TNT 835: Pipet 1.0 mL of 0.3 mg/L standard into a dry reagent vial.
   For HR TNT 836: Pipet 0.2 mL of 0.3 mg/L standard into a dry reagent vial.
3. For LR TNT835: Pipet 0.2 mL of Solution A into the vial.

   For HR TNT836: Pipe 1.0 mL of Solution A into the vial.
4. Cap and invert the reagent vial 2-3 times until no more streaks can be seen in the reagent vial solution.
5. React for a total of 15 minutes.
6. With a lint-free wipe, dry the outside and bottom of the reagent vial.
7. Insert the prepared vial into the spectrophotometer. The instrument reads the barcode, then selects and performs the correct test. No zero is required. Results are in mg/L NO_3^- N.
8. Measure and record the results onto the *Nitrate MDL Worksheet* provided by Ohio EPA.
9. Repeat steps 2-8, six more times for a total set of seven replicates of the 0.3 mg/L standard.

   > **Note:** Each replicate must be separate (i.e., must be a freshly pipetted standard).
10. Calculate the MDL using the provided *Nitrate MDL Worksheet*.
11. If the MDL result is 0.0 mg/L or > 0.3 mg/L, the MDL is unacceptable and the procedure must be repeated.

IPR Procedure (Required to be performed by each analyst prior to initial certification for this method.)

1. If calibration standards are refrigerated, allow standards to stabilize to room temperature prior to analysis.
2. For LR TNT 835: Pipet 1.0 mL of 5.0 mg/L standard into a dry reagent vial.
   For HR TNT 836: Pipet 0.2 mL of 5.0 mg/L standard into a dry reagent vial.
3. For LR TNT835: Pipet 0.2 mL of Solution A into the vial.

   For HR TNT836: Pipe 1.0 mL of Solution A into the vial.
4. Cap and invert the reagent vial 2-3 times until no more streaks can be seen in the reagent vial solution.
5. React for a total of 15 minutes.

6. With a lint-free wipe, dry the outside and bottom of the reagent vial.
7. Insert the prepared vial into the spectrophotometer. The instrument reads the barcode, then selects and performs the correct test. No zero is required. Results are in mg/L NO_3^- N.
8. Measure and record the results onto the *Nitrate IPR Worksheet* provided by Ohio EPA.
9. Repeat steps 2-8, three more times for a total set of four replicates of the 5.0 mg/L standard.

> **Note:** Each replicate must be separate (i.e., must be a freshly pipetted standard).

10. Calculate the IPR using the provided *Nitrate IPR Worksheet*.
11. If the accuracy is greater than ±10% or the precision of accuracy is >20%, the study is unacceptable and must be repeated by the analyst.

7.4) Requirements with Each Sample Batch (Analytical Sequence)

An analytical batch is a set of samples processed during a contiguous 8-hour period. Each batch must be accompanied by a quality control standard (QCS) and up to 10 samples. The analytical sequence is as follows:

1. QCS (1.0 mg/L standard). Results must be ±10% of true value.
2. Sample(s), up to 10.

> **Note:** If the QCS is out of range, a meter calibration verification must be performed and recorded.

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review and must be available upon request.

- Three-Month Nitrate Calibration Verification Record
- Nitrate Quality Control Sample Analysis Record

Three-Month Nitrate Calibration Verification Record

Laboratory _____

Analyst(s)			**Analyst(s)**		
Date			**Date**		
Standard(s) Expiration Date			**Standard(s) Expiration Date**		
Standard(s) Lot #			**Standard(s) Lot #**		
Standard	**Assigned Value**	**Observed Value**	**Standard**	**Assigned Value**	**Observed Value**
#1	0.3		#1	0.3	
#2	10.0		#2	10.0	
Comments			**Comments**		
Analyst(s)			**Analyst(s)**		
Date			**Date**		
Standard(s) Expiration Date			**Standard(s) Expiration Date**		
Standard(s) Lot #			**Standard(s) Lot #**		
Standard	**Assigned Value**	**Observed Value**	**Standard**	**Assigned Value**	**Observed Value**
#1	0.3		#1	0.3	
#2	10.0		#2	10.0	
Comments			**Comments**		

Nitrate Quality Control Sample Analysis Record

Laboratory _____

Analyst	Date	QCS (1.0 mg/L)	Sample Lot #	Analyst	Date	QCS (1.0 mg/L)	Sample Lot #

Orthophosphate Analysis by Hach Method 8048 (EPA 365.1)

Quick Reference	**Standard/Reagent**	**Requirements**
Standard/Reagent Storage	PhosVer® 3 Phosphate Reagent AccuVac® Ampuls or Reactive Phosphorus Test 'N Tube Vials	Manufacturer's Recommendations
	0.3/1.0/2.5/3.0/5.0/100.0 mg/L Phosphate Standards as PO_4^{3-}	Manufacturer's Recommendations
	PhosVer® 3 Phosphate Powder Pillows, 10-mL	Manufacturer's Recommendations
Standard/Reagent Expiration	**Standard/Reagent**	**Expiration**
	PhosVer® 3 Phosphate Reagent AccuVac® Ampuls or Reactive Phosphorus Test 'N Tube Vials	Manufacturer's Expiration Date
	0.3/1.0/2.5/3.0/5.0/100.0 mg/L Phosphate Standards	1 Year After Opening/ Manufacturer's Expiration Date
	100 mg/L Stock Standard	1 Year After Opening/ Manufacturer's Expiration Date
	PhosVer® 3 Phosphate Powder Pillows, 10-mL	Manufacturer's Expiration Date
Required Quality Control	**QC Procedure**	**Frequency**
	Meter Calibration Verification	Once Every Three Months
	Blank, QCS	Once Per Batch
Sample Collection	**Preservation**	**Maximum Hold Time**
	None or Filtered/4°C	48 Hours

Method Reference

Hach Method 8048, U.S. EPA-accepted for reporting for drinking water analysis as an acceptable version of EPA Method 365.1.

Survey Requirements

- Each certified analyst must be able to perform the calibration verification procedure described in this method.
- Procedural technique will be observed.
- All reagents, standards and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

This method may be performed with PhosVer® 3 Phosphate Powder Pillows, PhosVer® 3 AccuVac® Ampuls or PhosVer® 3 Reactive Phosphorus Test 'N Tube Vials. Depending on the selected procedure, the method instructions will differ slightly.

Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phosphomolybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by manual sulfuric acid hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by manual persulfate digestion. The developed color is measured automatically.

Interferences

Contaminants in the reagent water, reagents, glassware and other sample processing apparatus that bias analyte response. See Interference Table in Hach Method 8048 for interfering substances.

2.0) Equipment

1. Sample collection bottles – Preferably use polyethylene bottles for collecting and storing samples. Glass bottles that have been acid rinsed may also be used.
2. Spectrophotometer or colorimeter - as appropriate for the procedure selected.
3. For powder pillows alone:
   - Beaker(s)
4. Sample cells appropriate to the instrument in use.
5. For ampuls:
   - PhosVer® 3 Phosphate Reagent AccuVac® Ampuls
   - AccuVac® Ampul Adapter
   - 50-mL beaker(s)
   - Stoppers for 18-mm tubes/AccuVac® Ampuls
6. Sample cells appropriate to the instrument in use.
7. For TNT vials:
   - PhosVer® 3 Reactive Phosphorus Test ‘N Tube Vials with caps: Commercially available.
   - Funnel
   - Test Tube Rack
8. An adjustable microliter pipettor with tips.
9. Lint-free wipes.

> **Note:** All glassware must be acid rinsed with 6 N (1:1) hydrochloric acid and then rinsed thoroughly with reagent water. It is recommended to maintain a dedicated set of glassware for this procedure to reduce the possibilities of contamination.

3.0) Reagents

1. Reagent Water.
2. 100 mg/L Stock Orthophosphate Solution: Commercially available.
3. 0.3 mg/L Standard: Commercially available. Alternatively, prepare as follows. Pipet 3 mL of 100 mg/L stock orthophosphate solution into a 1-liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.
4. 1.0 mg/L Standard: Commercially available. Alternatively, prepare as follows. Pipet 10 mL of 100 mg/L stock orthophosphate solution into a 1-liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.
5. 1.0 mg/L Quality Control Sample (QCS): Commercially available. Must be from a different source or different lot than the 1.0 mg/L calibration standard or stock orthophosphate solution.

6. 2.5 mg/L Standard: Commercially available. Alternatively, prepare as follows. Pipet 25 mL of 100 mg/L stock orthophosphate solution into a 1-liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.
7. 3.0 mg/L Standard: Commercially available. Alternatively, prepare as follows. Pipet 30 mL of 100 mg/L stock orthophosphate solution into a 1-liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.
8. 5.0 mg/L Standard: Commercially available. Alternatively, prepare as follows. Pipet 50 mL of 100 mg/L stock orthophosphate solution into a 1-liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.
9. PhosVer® 3 Phosphate Reagent Powder Pillows, 10 mL (not needed for use with ampuls): Commercially available.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Collect in plastic or glass bottles, preferably polyethylene bottles. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.
2. Preservation: No preservation needed if samples are analyzed immediately. If not able to analyze immediately, filter and keep samples at or below 4.0°C for a maximum of 48 hours.

5.0) Orthophosphate Analysis Procedure

Prior to analysis, refer to Section 7.4 of this method for the quality control requirements of each sample batch.

Powder Pillow Procedure

1. Set the instrument to the appropriate program/channel per the manufacturer's instructions.
2. Rinse a sample cell and cap three times with sample and fill to the 10-mL mark.
3. Add the contents of one PhosVer® 3 Phosphate Reagent Powder Pillow to the sample cell, add the cap and shake vigorously for 20 seconds.
4. Set and start a timer for two minutes to allow the sample to react.
5. Prepare the blank by rinsing a second sample cell and cap three times with sample and fill to the 10-mL mark.
6. Cap the blank and wipe the sample cell clean and dry with a lint-free wipe.
7. Insert the blank into the cell holder, pointing the diamond mark on the sample cell toward the keypad.
8. Install instrument cap over the cell holder and push ZERO. The display should show 0.00 mg/L PO_4^{3-}.
9. Remove the blank.
10. Wipe the prepared sample cell clean and dry with a lint-free wipe.
11. Insert the prepared sample into the cell holder, pointing the diamond mark on the sample cell toward the keypad.
12. Install instrument cap over the cell holder and push READ. Results are displayed in mg/L phosphate (PO_4^{3-}). **Sample must be read within 10 minutes of addition of powder pillow.**
13. Repeat steps 2-4 and 10-12 for the QCS (1.0 mg/L PO_4^{3-}) and any additional samples.

AccuVac® Ampul Procedure

1. Set the instrument to the appropriate program/channel per the manufacturer's instructions.
2. Prepare the blank by filling a sample cell with 10 mL of sample.
3. Prepare the sample by collecting at least 40 mL of sample in a 50 mL beaker and then filling the AccuVac® Ampul with the sample, keeping the tip immersed while the ampul fills completely.
4. Close the AccuVac® Ampul and shake for approximately 30 seconds.
5. Set and start a timer for two minutes to allow the sample to react.
6. When the timer expires, wipe the blank sample cell clean and dry with a lint-free wipe.
7. Insert the blank into the cell holder and push ZERO. The display should show 0.00 mg/L PO_4^{3-}.
8. Remove the blank.
9. Wipe the prepared sample AccuVac® Ampul clean and dry with a lint-free wipe.
10. Insert the prepared sample AccuVac® Ampul into the cell holder and push READ. Results are displayed in mg/L phosphate (PO_4^{3-}).
11. Repeat steps 3-5 and 9-10 for the QCS (1.0 mg/L PO_4^{3-}) and any additional samples.

TNT Vial Procedure

1. Set the instrument to the appropriate program/channel per the manufacturer's instructions.
2. Pipet 5.0 mL of sample to a PhosVer® 3 Reactive Phosphorus Test 'N Tube Vial.
3. Put the cap on the vial. Invert to mix.
4. Wipe the vial clean and dry with a lint-free wipe.
5. Insert the vial into the 16-mm cell holder and push ZERO.
   The display should show 0.00 mg/L PO_4^{3-}.
6. Add the contents of one PhosVer® 3 Phosphate Reagent Powder Pillow.
7. Cap the vial and shake for at least 20 seconds. The powder will not dissolve completely.
8. Set and start a timer for two minutes to allow the sample to react.
9. When the timer expires, wipe the vial clean and dry with a lint-free wipe.
10. Insert the vial into the 16-mm cell holder and push READ. Results are displayed in mg/L phosphate (PO_4^{3-}).
11. Repeat steps 2-10 for the QCS (1.0 mg/L PO_4^{3-}) and any additional samples.

6.0) Analyst Requirements

Certified Analyst Requirements

All certified analysts must perform an initial precision and recovery study to generate acceptable accuracy and precision with this method. (Refer to Section 7.3 of this method.) All certified analysts must perform the calibration verification procedure at least once every three months. All certified analysts must perform sample analysis at a minimum of once per month.

Operationally Certified Analyst Requirements

Operational Certification is not available for this method.

7.0) Quality Control Requirements

7.1) Instrument Calibration Verification Procedure

The instrument calibration must be verified at least once every three months. The required calibration verification must include the analysis of 0.3 mg/L and 1.0 mg/L phosphate standards, and the highest

phosphate standard per the instrument specification (i.e., 2.5 mg/L, 3.0 mg/L or 5.0 mg/L). The results must be within the acceptable range of ±15% of the actual value.

> **Note:** Calibration verifications must be performed at a minimum of once every three months.

1. If calibration standards are refrigerated, allow standards to stabilize to room temperature prior to analysis.
2. Prepare and measure a blank, 0.3 mg/L, 1.0 mg/L and the highest standard per the instrument specification according to the appropriate procedure.
3. React for a total of two minutes.
4. With a lint-free wipe, dry the outside and bottom of the reagent vial.
5. Insert the prepared vial into the instrument.
6. Record the results of the 0.3 mg/L, 1.0 mg/L and highest standard onto the *Three-Month Orthophosphate Calibration Verification Record*. (Refer to Section 7.2 in this method for detailed acceptance limits.)
7. If the results of any of the standards are outside of acceptable range, the calibration verification procedure must be repeated until acceptable values are acquired prior to sample analysis. (Refer to Section 7.2 in this method for corrective measures.)

7.2) Calibration Verification Acceptance Limits

The measured value of the 0.3 mg/L, 1.0 mg/L and highest (2.5 mg/L, 3.0 mg/L, or 5.0 mg/L) phosphate standards must be within ±15% of the actual value.

Corrective Measures

If the calibration verification results are unacceptable, the following steps should be taken to try to correct the problem:

1. Repeat calibration verification standard preparation(s).
2. Service the spectrophotometer if all other attempts have failed to acquire acceptable results.

7.3) Initial Demonstration of Laboratory Capability

To be certified for this method, an initial demonstration of laboratory capability, consisting of an initial method detection limit (MDL) study and an initial precision and recovery (IPR) study, are required as follows:

MDL Determination (Required to be performed on each meter prior to initial certification for this method.)

1. If calibration standards are refrigerated, allow standards to stabilize to room temperature prior to analysis.
2. Prepare and measure a 0.3 mg/L standard according to the appropriate procedure.
3. React for a total of two minutes.
4. With a lint-free wipe, dry the outside and bottom of the reagent vial.
5. Insert the prepared vial into the spectrophotometer.
6. Measure and record the results onto the *Orthophosphate MDL Worksheet provided by Ohio EPA*.
7. Repeat steps 2-6 six more times for a total set of seven replicates of the 0.3 mg/L standard.

   > **Note:** Each replicate must be separate (i.e., must be a freshly pipetted standard).
8. Calculate the MDL using the *Orthophosphate MDL Worksheet*.
9. If the MDL result is 0.0 mg/L or > 0.3 mg/L, the MDL is unacceptable and the procedure must be repeated.

IPR Procedure (Required to be performed by each analyst prior to initial certification for this method.)

1. If calibration standards are refrigerated, allow standards to stabilize to room temperature prior to analysis.
2. Prepare and measure a 1.0 mg/L standard according to the appropriate procedure.
3. React for a total of two minutes.
4. With a lint-free wipe, dry the outside and bottom of the reagent vial.
5. Insert the prepared vial into the spectrophotometer.
6. Measure and record the results onto the *Orthophosphate IPR Worksheet provided by Ohio EPA*.
7. Repeat steps 2-6 three more times for a total set of four replicates of the 1.0 mg/L standard.

> **Note:** Each replicate must be separate (i.e., must be a freshly pipetted standard).

8. Calculate the IPR using the provided *Orthophosphate IPR Worksheet*.
9. If the accuracy is greater than ±10% or the precision of accuracy is >20%, the study is unacceptable and must be repeated by the analyst.

7.4) Requirements with Each Sample Batch (Analytical Sequence)

An analytical batch is a set of samples processed during a contiguous 8-hour period. Each batch must be accompanied by a quality control standard (QCS) and up to 10 samples. The analytical sequence is as follows.

1. Blank (0.0 mg/L): Acceptance: Results must be <0.3 mg/L.
2. QCS (1.0 mg/L Std): Acceptance: Results must be ±10% of the actual value.
3. Sample(s), up to ten.

> **NOTE:** If the QCS is out of range, a meter calibration verification must be performed and recorded.

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review and must be available upon request.

- Three-Month Orthophosphate Calibration Verification Record
- Orthophosphate Quality Control Sample Record

Three-Month Orthophosphate Calibration Verification Record

Laboratory _____

Analyst(s)			Analyst(s)		
Date			Date		
Standard(s) Expiration Date			Standard(s) Expiration Date		
Standard(s) Lot #			Standard(s) Lot #		
Standard	**Assigned Value**	**Observed Value**	**Standard**	**Assigned Value**	**Observed Value**
#1	0.3		#1	0.3	
#2	1.0		#2	1.0	
#3	2.5 3.0 5.0		#3	2.5 3.0 5.0	
Comments			Comments		

Analyst(s)			Analyst(s)		
Date			Date		
Standard(s) Expiration Date			Standard(s) Expiration Date		
Standard(s) Lot #			Standard(s) Lot #		
Standard	**Assigned Value**	**Observed Value**	**Standard**	**Assigned Value**	**Observed Value**
#1	0.3		#1	0.3	
#2	1.0		#2	1.0	
#3	2.5 3.0 5.0		#3	2.5 3.0 5.0	
Comments			Comments		

Orthophosphate Quality Control Sample Analysis Record

Laboratory _____

Analyst	Date	Blank (mg/L)	QCS (1.0 mg/L)	Sample Lot #	Analyst	Date	Blank (mg/L)	QCS (1.0 mg/L)	Sample Lot #

pH Analysis by Electrometric Method

Quick Reference	**Standard/Reagent/Equipment**	**Requirements**
Standard/Reagent/Equipment Storage	pH Electrodes	pH 7 Buffer/Manufacturer's Solution
	pH Buffers	Manufacturer's Recommendation
Standard/Reagent Expiration	**Standard/Reagent**	**Maximum Storage Time**
	pH Buffers	6 Months After Opening/ Manufacturer's Expiration Date
Required Quality Control	**QC Procedure**	**Frequency**
	Calibrate Meter	Once Per Shift/Every 8 Hours
	Linearity (pH 4 Buffer Check)	Once Per Week
Sample Collection	**Preservation**	**Maximum Hold Time**
	No Preservation Required	15 Minutes

Method Reference

Standard Methods 22nd Edition (4500-H^+ B)

Survey Requirements

- Each certified analyst must be able to perform the calibration procedure described in this method.
- Each operationally certified analyst must be able to perform the calibration procedure described in this method.
- Procedural technique will be observed.
- All reagents, standards and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

pH measurement is one of the most important and frequently performed tests in water chemistry. After an acceptable calibration of the pH meter, a sample of drinking water is collected in a clean ion-free container large enough to allow immersion past the shoulder of the pH and ATC electrodes. The meter is allowed to stabilize and the displayed reading (pH values range from 0 to 14) is recorded as pH.

Interferences

Poorly maintained electrodes (insufficiently filled with electrode solution, crystalline buildup, stored improperly) will cause unacceptable linearity or increased stabilization time. Care should be taken to maintain electrodes following manufacturer's directions.

2.0) Equipment

1. pH Meter. Meter must be designed for a minimum of a 2-point standard calibration and % slope or mV efficiency display. Minimum specifications: Accuracy to 0.1 pH unit, expanded scale millivolt capability accurate to 1 millivolt, or a direct reading concentration scale providing the equivalent or accurate to at least 1 millivolt. Digital display meters are required. Automatic temperature compensation (ATC) electrodes are required for pH meters.
2. Refillable combination electrodes are preferred; however, a combination of a separate pH sensing electrode and a reference electrode is acceptable.
3. Magnetic stirring devices/stir magnets.

2.1) General pH Electrode Maintenance

1. Follow manufacturer's instruction for storing and maintaining electrodes. Alternatively, follow 2. through 3. below.
2. Electrodes should be kept clean and free from crystalline build-up. Sensing and reference electrodes must be stored in either pH 7 or in a manufacturer recommended storage solution.

> **Note:** Storing electrodes in reagent water is not acceptable.

3. Electrodes taking longer than one minute to stabilize in pH buffer may need service or replacement.

3.0) Reagents

1. pH buffers at pH 4.0, 7.0 and 10.0: These are available through numerous supply companies and are available as liquids or in powder packets (powder packets require preparation, follow manufacturer's instructions).

> **Note:** These buffers expire 6 months after opening or 4 weeks after preparation.

2. Reagent water.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Collect in a clean plastic or glass screw top container (250 to 1000 mL). Sample containers should be completely filled and kept sealed prior to analysis. Alternatively, samples analyzed immediately after collection may be collected in the analysis container.
2. Sample preservation: No Preservation Required.
3. Maximum sample holding time: Analyze sample within 15 minutes of collection.

5.0) pH Analysis Procedure

This is a general procedure; each pH meter may have a unique procedure. Please reference the manufacturer's instructions for specific instructions.

1. Calibrate pH meter following procedure in Section 7.0. If the meter has been calibrated for current shift go to Step 2.
2. Rinse and discard sample container with drinking water source to be analyzed.
3. Collect a sample volume of drinking water sufficient to cover the shoulder of the electrode.
4. Open the fill hole on the electrode.
5. Place the electrodes in the sample while stirring and allow the display to stabilize.
6. Record the reading as the pH of the sample.
7. Close the fill hole on the electrode after completing analysis.

> **Note:** Electrodes must be rinsed with reagent water before and between all analyses of samples/standards. The samples/standards must be stirred during analysis.

6.0) Analyst Requirements

All certified and operationally certified analysts must perform sample analysis at a minimum of three days per month. All calibration slopes must be recorded with dates and analyst initials.

Certified Analyst Requirements

All certified analysts must perform the calibration procedure at least three times per month. (Refer to Section 7.0 of this method.) Calibrations must be dated and initialed by all certified analysts participating in each

calibration procedure. Once per week, certified analysts are also required to confirm and record the pH 4.0 verification buffer, with all certified analysts participating at least once every three months.

Operationally Certified Analyst Requirements

All operationally certified must perform the calibration procedure at least three times per month. Calibrations must be dated and initialed by all operationally certified analysts participating in each calibration procedure.

7.0) Quality Control Requirements

7.1) pH Meter Calibration Procedure

The calibration procedure must be performed resulting in an acceptable linearity value, % slope or millivolts (mV), prior to initial use for analyzing potable water and at the beginning of each eight-hour shift if a drinking water sample is analyzed during that shift. The slope value must be recorded each time the meter is calibrated. This must be done for each pH meter used to report drinking water pH values.

> **Note:** Calibration must be performed at the beginning of each shift (every 8 hours). Each calibration requires newly poured buffers, which are discarded after calibration.

1. 4.0, 7.0 and 10.0 buffers stabilize best at room temperature.
2. Calibrate the pH meter following the manufacturer's instructions for 2-point calibrations (pH buffers 7.0 and 10.0) or 3-point calibrations (pH buffers 4.0, 7.0 and 10.0).
3. If a 2-point calibration is performed, analyze and record the pH 4.0 verification buffer value once per week. This is required of certified analysts.
4. The results of the pH 4.0 verification buffer must be within ±0.10 pH units of the true value. The acceptance limits are 3.9 to 4.1 pH units.

   > **Note:** If the laboratory has decided to adopt a 3-point calibration for all analyses, the pH 4.0 verification buffer analysis is not required.

5. Record the slope value for the calibration. Refer to Section 7.2 in this method for detailed acceptance limits.
6. If slope value is outside of acceptable range, the calibration procedure must be repeated until an acceptable value is acquired or refer to Section 7.2 for corrective measures.

   Meters capable of a 3-point calibration may be calibrated with pH buffers 4.0, 7.0 and 10.0.

> **Note:** All laboratory personnel must consistently use the same calibration procedure, either a 2-point or 3-point calibration.
>
> **Note:** Electrodes must be rinsed with reagent water before and between all analyses of samples/standards. The samples/standards must be stirred during analyses.

7.2) Calibration Acceptance Limits

The slope/linearity value must fall in the acceptable range of 95.0% to 105.0%, for pH slope value displayed in percent, or -56.0 to -62.0 mV, for pH value displayed in millivolts. Please reference the manufacturer's instructions for acceptance criteria if otherwise specified.

Corrective Measures

If the calibration results in an unacceptable linearity value, the following steps should be taken in an effort to correct the problem:

1. Replace the buffers. The 10.0 is usually the first buffer to be affected due to overexposure to air.
2. Check the fill solution level and fill if needed. Rinse the electrode with reagent water to remove all internal crystalline build-up or follow the manufacturer's recommendations for electrode cleaning. Replace the electrode if needed.
3. Clean the electrode following the manufacturer's recommendations.
4. Service the pH meter if all other attempts have failed to acquire acceptable results.

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review and must be available upon request.

- pH Meter Slope/Weekly Linearity Verification (4.0 Buffer) Record

pH Meter Slope/Weekly Linearity Verification (4.0 Buffer) Record

Laboratory _____

Calibration Buffers _____

Analyst	Date	Slope %	pH 4 Ver.	Analyst	Date	Slope %	pH 4 Ver.	Analyst	Date	Slope %	pH 4 Ver.

Phosphorous (Total) Analysis by Ascorbic Acid/Spectrophotometric Method

Quick Reference	**Standard/Reagent**	**Requirements**
Standard/Reagent Storage	Liquid Reagents	Manufacturer's Recommendation
	Standards	Manufacturer's Recommendation
Standard/Reagent Expiration	**Standard/Reagent**	**Maximum Storage Time**
	Reagents	1 Year After Opening/ Manufacturer's Expiration Date
	50 mg/L Stock Standard	6 Months After Preparation/ Manufacturer's Expiration Date
	0.50 mg/L Calibration Standard	28 Days At 4°C
Required Quality Control	**QC Procedure**	**Frequency**
	Generate Calibration Curve	Once Every Three Months
	Blank Verification	With Each Analysis/Digestion
	Reporting Limit Verification	With Each Analysis/Digestion If Calibration Curve Is Not Generated
	Midpoint Calibration Verification	With Each Analysis/Digestion If Calibration Curve Is Not Generated
Sample Collection	**Preservation**	**Maximum Hold Time**
	Adjust Sample pH < 2.0 With H_2SO_4, 4°C	28 Days

Method Reference

Standard Methods 22nd Edition (4500-P B & E)

Survey Requirements

- Each certified analyst must be able to generate a calibration curve described in this method.
- Procedural technique will be observed.
- All reagents, standards and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

For the determination of phosphate, total phosphorous, a preliminary digestion step is necessary. Ammonium molybdate and antimony potassium tartrate react in acid medium with orthophosphate to form phosphomolybdic acid that is reduced to intensely colored molybdenum blue by ascorbic acid. The absorbance of the sample is analyzed on a spectrophotometer at a wavelength of 880 nanometers. Both standards and samples must be carried through the entire digestion procedure. A fume hood must be used for this type of digestion to exhaust caustic fumes and to contain samples in case of an accident.

Interferences

If a hot plate is used for the digestion, extreme caution must be taken to prevent any bumping of the samples. If sample loss occurs due to bumping, that sample or standard cannot be used for the analysis.

2.0) Equipment

1. A spectrophotometer capable of reading 880 nm with a cell light path width of at least 1 cm.
2. Spectrophotometer vials.
3. Computer with software capable of generating linear regressions.
4. Class A volumetric pipet(s).
5. Standard laboratory glassware.
6. A hot plate large enough to hold all the standards and samples at the same time for digestion.
7. Heating blocks may be used as long as reagent proportions are not changed.
8. A fume hood for use with the hot plate digestion.
9. Autoclave (acceptable alternative to hot plate for the digestion procedure).
10. Balance.

> **Note:** All glassware must be acid rinsed using dilute hydrochloric acid and rinsed thoroughly with reagent water. It is highly recommended to maintain a dedicated set of glassware for this procedure to reduce the possibilities of phosphorous contamination.

3.0) Reagents

1. 50 mg/L Phosphorous Stock Standard: Commercially available.
2. 0.5 mg/L Phosphorous Calibration Standard: Prepare as follows: Add 10.0 mL of 50 mg/L phosphorous stock standard to a 1-liter Class A volumetric flask, half filled with reagent water. Add 2 mL of concentrated H_2SO_4. Bring to volume with reagent water.
3. Sulfuric Acid Solution H_2SO_4 (5 N): Commercially available. It may also be prepared as follows: Dilute 70 mL of concentrated H_2SO_4 to 500 mL with reagent water. Always add the acid to the water.
4. Antimony Potassium Tartrate ($K(SbO)C_4H_6O_6 \times 0.5H_2O$) Solution: Commercially available. Prepare as follows: Dissolve 1.3715 g $K(SbO)C_4H_6O_6$ to 400 mL with reagent water in a 500 mL volumetric flask and dilute to volume.
5. Ammonium Molybdate ($(NH_4)_6Mo_7O_{24} \times 4H_2O$) Solution: Commercially available. Prepare as follows: Dissolve 20 g $(NH_4)_6Mo_7O_{24} \times 4H_2O$ to 400 mL with reagent water in a 500 mL volumetric flask and dilute to volume.
6. Ascorbic Acid Solution (0.10 M): Commercially available. Prepare as follows: Dissolve 1.76 g ascorbic acid in 100 mL reagent water.
7. Combined Reagent: Mix the above reagents (3, 4, 5 and 6) in the following proportions for 100 mL of combined reagent: 50 mL Sulfuric Acid Solution (5 N); 5 mL Antimony Potassium Tartrate Solution; 15 mL Ammonium Molybdate Solution; and 30 mL Ascorbic Acid Solution (0.10 M). Mix after each addition. This combined reagent is stable for 4 hours after preparation.
8. Sodium Hydroxide Solution NaOH (1 N): Commercially available.
9. Phenolphthalein Indicator: Commercially available.
10. Reagent water.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Collect in a clean plastic or glass screw top container (250 to 1,000 mL).
2. Preservation: Adjust to pH < 2.0 with H_2SO_4, 4°C. No preservation needed if samples are analyzed/digested immediately after collection.
3. Maximum sample holding time: 28 days. Ohio EPA recommends analyzing samples immediately after collection.

5.0) Phosphorous Analysis Procedure

1. Measure 50 mL of sample(s) into an Erlenmeyer flask(s).
2. Add 1 drop of phenolphthalein indicator to the sample(s). Mix flask. If a red color develops, add H_2SO_4 (5 N) solution drop wise until the color dissipates.
3. Add 0.5 mL H_2SO_4 (5 N) solution and 0.4 g ammonium persulfate to the sample(s).
4. Gently boil the sample(s) on a hot plate or in an autoclave for 30 to 40 minutes or until a volume of 10 mL is reached. The hot plate/autoclave must be large enough to evaporate all samples and any standards that will be analyzed/digested in the sample batch simultaneously. A fume hood is required if a hot plate is used for this procedure.
5. Remove the sample(s) from heat and cool to room temperature.
6. Dilute sample(s) to about 30 mL with reagent water.
7. Add 1 drop phenolphthalein solution to the sample(s).
8. Add NaOH solution drop wise to each sample until a faint pink color develops.
9. Carefully, transfer the sample(s) to Class A 50 mL volumetric flask(s).
10. Add 8.0 mL of combined reagent to the sample(s). Bring the sample(s) to volume. Mix thoroughly.
11. Let stand for 10 minutes.
12. Read the absorbance at 880 nanometers for each sample against the most recently generated calibration curve stored in the spectrophotometer. Alternatively, compare to a manually generated calibration curve on an Excel spreadsheet.

> **Note:** For orthophosphate analysis omit Steps 3 through 6 and 9.

6.0) Analyst Requirements

All certified analysts must perform sample analysis at a minimum of at least three days per month.

Certified Analyst Requirements

All certified analysts must perform the calibration curve generation procedure at least once every three months. (Refer to Section 7.0 of this method.) Generations must be dated and initialed by all certified analysts participating in each procedure.

Operationally Certified Analyst Requirements

Operational certification is not available for this method.

6.1) QC Requirements with Each Analysis

With each sample batch digestion/analysis the following QC samples must be digested and analyzed:

1. Blank (0.0 mg/L): Acceptance: Results < ½ the reporting limit.
2. Reporting limit verification (0.03 mg/L): Acceptance: ±30% of true value.
3. Midpoint calibration verification (0.10 mg/L): Acceptance: ±10% of true value.

> **Note:** A blank sample is required with each sample analysis. QC samples 2 and 3 are required only if an entire calibration curve is not analyzed/digested with the sample batch.

7.0) Quality Control Requirements

The calibration curve generation procedure must be performed prior to initial use for analyzing potable water and at least once every three months thereafter. Each calibration curve generation procedure must be dated and recorded.

> **Note:** An Initial Demonstration of Capability (IDC) study and initial Method Detection Limit (MDL) study must be completed and documented for this method.

Calibration Curve Generation Procedure

A minimum of three calibration standard concentrations and a blank must be analyzed to generate a calibration curve. The lowest concentration point prepared should be at least the reporting limit for phosphorous (0.03 mg/L). Alternatively, a reporting limit verification sample may be prepared in addition to the three calibration standard concentrations if the curve generation does not include the reporting limit concentration (0.03 mg/L). The reporting limit verification sample results must be within ±30% of the true value.

1. Prepare three 50 mL volumetric flasks containing a known volume of 0.5 mg/L phosphorous calibration standard and reagent water according to Table 1 (below). Label each flask with the calibration concentration it contains.
2. Prepare a blank by adding 50 mL reagent water to a fourth volumetric flask.
3. Pour each calibration standard into an Erlenmeyer flask. Label each Erlenmeyer flask with the calibration concentration it contains.
4. Add 1 drop of phenolphthalein indicator to each standard. Mix flasks. If a red color develops, add H_2SO_4 (5 N) solution drop wise until the color dissipates.
5. Add 1.0 mL H_2SO_4 (5 N) solution and 0.4 g ammonium persulfate to each standard.
6. Gently boil the standards on a hot plate or in an autoclave for 30 to 40 minutes or until a volume of 10 mL is reached. The hot plate/autoclave must be large enough to evaporate all samples and any standards that will be analyzed/digested in the sample batch simultaneously. A fume hood is required if a hot plate is used for this procedure.
7. Remove the standards from heat and cool to room temperature.
8. Dilute standards to about 30 mL with reagent water.
9. Add 1 drop phenolphthalein solution to the standards.
10. Add NaOH solution drop wise to each sample until a faint pink color develops.
11. Carefully transfer the standards to Class A 50 mL volumetric flasks.
12. Add 8.0 mL of combined reagent to the standards. Bring the standards to volume. Mix thoroughly.
13. Let stand for 10 minutes.

14. Read absorbance of each calibration standard and blank at 880 nm. Follow the spectrophotometer manufacturer's instructions to generate and store a calibration curve using the blank and prepared calibration standards.
15. If the spectrophotometer does not have the capability to store calibration curves, read absorbance for each calibration standard at 880 nm on spectrophotometer. Record absorbance.
16. Using the absorbance and concentration for each calibration standard, generate a calibration curve manually on an Excel spreadsheet.

> **Note:** For orthophosphate analysis, omit Steps 5 through 8 and 11.

Correlation Coefficient (R)/Coefficient of Determination (R^2)

Once the calibration curve has been generated, acceptance of the curve is determined by the correlation coefficient (R) or the coefficient of determination (R^2). For the curve to be acceptable for sample analysis, the correlation coefficient (R) must be greater than 0.995 or the coefficient of determination (R^2) must be greater than 0.990. The spectrophotometer may display this value after the calibration curve has been stored. Alternatively, the calibration curve may be generated on an Excel spreadsheet using the correlation coefficient function to determine the correlation coefficient (R) or the coefficient of determination (R^2).

7.1) Calibration Standard Concentration Calculations

0.50 mg/L phosphorous calibration standard will be used as the standard added to each flask to generate the calibration standard concentrations. The recommended calibration concentrations to generate a curve are as follows: blank (0.00 mg/L), 0.03 mg/L, 0.10 mg/L and 0.50 mg/L. Table 1 demonstrates how these standards are prepared in 50 mL volumetric flasks.

Table 1: Calibration Standard Concentration Preparation

Standard Concentration	mL of 0.50 mg/L Phosphorous Calibration Standard Added to 50 mL Flask	Final Volume
Blank (0.0 mg/L)	0.0 mL	50 mL
0.03 mg/L	3.0 mL	50 mL
0.10 mg/L	10.0 mL	50 mL
0.50 mg/L	50.0 mL	50 mL

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review and must be available upon request.

- Phosphorous (Total) Ascorbic Acid/Spectrophotometer QC Sample Record

Phosphorous (Total) Ascorbic Acid/Spectrophotometer QC Sample Record

Laboratory

Analyst	Date	Blank (mg/L)	Reporting Limit (mg/L)		Midpoint (mg/L)		Curve Generation Date	Comments
			TV	Observed	TV	Observed		

Stability (Calcium Carbonate Saturation)

Quick Reference	**Standard/Reagent**	**Requirements**
Standard/Reagent Storage	Calcium Carbonate (Dry)	Room Temperature
Standard/Reagent Expiration	**Standard/Reagent**	**Expiration**
	Calcium Carbonate (Dry)	6 Years After Opening/ Manufacturer's Expiration Date
Required Quality Control	**QC Procedure**	**Frequency**
	pH & Alkalinity QC Apply	pH & Alkalinity QC Apply
Sample Collection	**Preservation**	**Maximum Hold Time**
	No Preservation Required	Prepare Samples Immediately

Method Reference

Standard Methods 22nd Edition (2330)

Survey Requirements

- One stability analysis per every three analysts must be prepared prior to the survey. The analysis of the prepared stability samples must be completed during the survey.
- All analysts will be required to participate in the analysis of a stability sample.
- Analysts will be expected to interpret results of the stability analysis.
- All reagents, standards and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

> **Note:** The change in sample alkalinity and pH after saturation with $CaCO_3$ is measured using approved methods for both alkalinity and pH. All certification requirements for the alkalinity and pH methods must be met to acquire certification for the stability method.

1.0) General Method Summary

A sample volume is collected into two identical BOD bottles. One of the bottles is supersaturated by adding calcium carbonate ($CaCO_3$); the other is left as collected. Both are stoppered with no headspace in the bottles. After filtration, samples from both bottles are analyzed for pH and alkalinity. The analytical results of this test are indicative of the corrosive properties of the water analyzed.

Interferences

Careful filtration of the $CaCO_3$ is of paramount importance. Any amount of undissolved $CaCO_3$ passing into the alkalinity/pH analysis beaker will render those results invalid and the analysis will need to be repeated.

If sequestering agents are naturally occurring or added as part of the water treatment process, test results may be unreliable.

2.0) Equipment

1. Two 300 mL glass BOD bottles with glass stoppers.
2. Magnetic stirring device and TFE-coated stir bars.
3. Filter funnel(s) and flasks.
4. Fine porosity fast flow glass fiber filters such as a Whatman Grade 934AH filter or equivalent.
5. All required for Alkalinity method analysis.
6. All required for pH method analysis.

3.0) Reagents

1. Calcium Carbonate ($CaCO_3$): Reagent grade.
2. All required for alkalinity method analysis.
3. All required for pH method analysis.
4. Reagent water.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Stability samples must be collected in duplicate, in two BOD bottles each stoppered with no headspace. Once collected begin procedural instructions in Section 5.0 immediately.
2. Preservation: No Preservative Required.
3. Maximum sample hold time: Sample preparation must begin immediately after collection.

5.0) Stability Analysis Procedure

A. Rapid Saturation

1. $CaCO_3$ Saturated Sample: Carefully add approximately 1.0 to 2.0 grams of $CaCO_3$ powder to one of the water samples collected in the 300 mL BOD bottles. Add a magnetic stirring bar and stopper with no headspace. If all of the $CaCO_3$ dissolves, begin the analysis from sample collection (collect both samples again). On the subsequent analysis add 4.0 grams $CaCO_3$ to the saturated sample.
2. Unsaturated Sample: To the second 300 mL BOD bottle filled with the water sample, add a magnetic stirring bar and stopper with no headspace.
3. Stir both the saturated and unsaturated bottles for a minimum of 30 minutes at moderate speed on a magnetic stirring device.
4. After stirring for 30 minutes, allow samples to settle for an additional 30 minutes.
5. Filter both samples separately using fine porosity fast flow filter paper. Do not use the same filter paper to filter both samples and do not collect the filtrate in the same container.

   > **Note:** Care should be taken when filtering the saturated sample to ensure no undissolved $CaCO_3$ is transferred into the collection container.

6. Discard the first 25 to 50 mL of filtrate, then collect enough sample volume to analyze pH and alkalinity for the saturated and unsaturated samples.
7. Analyze the $CaCO_3$ saturated sample filtrate for pH and alkalinity. Record the results.
8. Analyze the unsaturated sample filtrate for pH and alkalinity. Record the results.
9. Refer to Section 5.1 of this method for the instructions on interpreting the results.

B. Slow Saturation

1. $CaCO_3$ Saturated Sample: Carefully add approximately 1.0 to 2.0 g of $CaCO_3$ powder to one of the water samples collected in the 300 mL BOD bottles. Agitate this sample by shaking for 1 minute every hour for 8 hours. If all of the CaCO3 dissolves, begin the analysis from sample collection (collect both samples again). On the subsequent analysis add 4.0 g $CaCO_3$ to the $CaCO_3$ saturated sample.
2. Unsaturated Sample: The unsaturated bottle sample will remain as collected. Agitate this sample by shaking for 1 minute every hour for 8 hours.
3. Allow samples to settle overnight prior to proceeding to Step 4.
4. Filter both samples separately using fine porosity fast flow filter paper. Do not use the same filter paper to filter both samples and do not collect the filtrate in the same container.

> **Note:** Care should be taken when filtering the saturated sample to ensure no undissolved $CaCO_3$ is transferred into the collection container.

5. Discard the first 25 to 50 mL of filtrate, then collect enough sample volume to analyze pH and alkalinity for the saturated and unsaturated samples.
6. Analyze the $CaCO_3$ saturated sample filtrate for pH and alkalinity. Record the results.
7. Analyze the unsaturated sample filtrate for pH and alkalinity. Record the results.
8. Refer to Section 5.1 of this method for the instructions on interpreting the results.

5.1) Stability Interpretation

Stability analysis results determine whether water is interpreted as Stable, Corrosive or Scale Forming. This determination is based on the change of alkalinity and pH results between the $CaCO_3$ saturated sample and the unsaturated sample.

The interpretation is as follows:

Stable: There is no significant change of alkalinity and pH results between the $CaCO_3$ saturated sample and the unsaturated sample.

***Example**:* $CaCO_3$ saturated sample results: alkalinity – 84 mg/L, pH – 7.55,

Unsaturated sample results: alkalinity – 86 mg/L, pH – 7.60

> **Note:** Significant change may be defined as an increase/decrease in alkalinity of mg/L greater than 3% and in pH greater than 0.1 pH units of the $CaCO_3$ saturated sample result.

Corrosive: The alkalinity and pH results are higher for the $CaCO_3$ saturated sample than the alkalinity and pH results for the unsaturated sample.

***Example**:* $CaCO_3$ saturated sample results: alkalinity – 84 mg/L, pH – 7.45

Unsaturated sample results: alkalinity – 78 mg/L, pH – 7.25

Scale Forming: The alkalinity and pH results are lower for the $CaCO_3$ saturated sample than the alkalinity and pH results for the unsaturated sample.

***Example**:* $CaCO_3$ saturated sample results: alkalinity – 84 mg/L, pH – 7.55

Unsaturated sample results: alkalinity – 90 mg/L, pH – 7.75

Invalid: If the alkalinity and pH results are not both either higher or lower in the $CaCO_3$ saturated sample than they are in the unsaturated sample, the stability analysis is invalid and must be prepared and analyzed again.

Example: $CaCO_3$ saturated sample results: alkalinity – 84 mg/L, pH – 7.55

Unsaturated sample results: alkalinity – 90 mg/L, pH – 7.25

6.0) Analyst Requirements

Analysts must have laboratory certification for both pH and alkalinity to perform this method. All requirements for alkalinity and pH methods in this manual apply.

7.0) Quality Control Requirements

All titrant standardization and meter calibration requirements for alkalinity and pH methods in this manual apply.

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review and must be available upon request.

In addition to the following, all required documentation listed in both the pH method and the alkalinity method in this manual apply.

- Stability Method Interpretation Record

Stability Method Interpretation Record

Laboratory _____

Analyst	Date	Unsaturated Alkalinity	Unsaturated pH	$CaCO_3$ Saturated Alkalinity	$CaCO_3$ Saturated pH	Interpretation

Total Dissolved Solids Analysis

Quick Reference	**Standard/Reagent**	**Requirements**
Standard Storage	1000 mg/L KCl Standard	Manufacturer's Recommendation
Standard Expiration	**Standard/Reagent**	**Maximum Storage Time**
	1000 mg/L KCl Standard	1 Year After Preparation
Required Quality Control	**QC Procedure**	**Frequency**
	Blank Sample	Once Per Analysis/Every 10 Samples
	Duplicate Sample	Once Per Analysis/Every 10 Samples
	KCl QC Sample	Once Per Analysis/Every 10 Samples
	Balance Calibration Check	Prior to Use
	Oven Temperature	Prior to Use
Sample Collection	**Preservation**	**Maximum Hold Time**
	4°C	7 Days

Method Reference

Standard Methods 22nd Edition (2540 C)

Survey Requirements

- At least one total dissolved solids (TDS) analysis must be prepared prior to the survey so that it can be completed at the time of the survey.
- Procedural technique will be observed.
- All reagents, standards and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

A known volume of sample is filtered through a fine porosity glass fiber filter and placed into a weighed evaporating dish. The filtrate is then evaporated to dryness and dried to a constant weight at 180°C. The method measures the amount of minerals and other substances that are dissolved in the water sample.

Interferences

The evaporating dishes are prone to mineral deposits after prolonged use. Care should be taken to assure they are properly cleaned after analysis.

2.0) Equipment

1. Analytical balance capable of weighing to 0.1 mg.
2. Drying oven capable of maintaining a temperature of 180 ±2°C.
3. Drying oven capable of maintaining a temperature of 103 to 105°C.
4. Desiccator with a humidity indicator.
5. Evaporating dishes with a capacity of 50-100 mL.
6. 50 mL volumetric flask or pipet.
7. Filtering flask, holder, funnel and vacuum pump.
8. Fine porosity glass fiber filters, Whatman 934AH or equivalent.
9. Laboratory tongs.

> **Note:** All glassware must be cleaned and rinsed thoroughly with reagent water.

3.0) Reagents

1. 1000 mg/L Potassium Chloride (KCl) QC Solution: Commercially available. It may also be prepared as follows: dissolve 1.000 g potassium chloride, which has been heated and desiccated, in a 1 L Class A volumetric flask, bringing to a final volume of 1 L.
2. Reagent water.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Collect in a clean glass, plastic or fluoropolymer [e.g., polytetrafluoroethylene (PTFE)] screw top container (250 to 1000 mL).
2. Preservation: 4°C.
3. Maximum sample holding time: 7 Days. Ohio EPA recommends analyzing samples immediately after collection.

5.0) TDS Analysis Procedure

1. Oven-dry the evaporation dishes at 180°C ±2°C for one hour and allow them to cool in desiccator for one hour.
2. Immediately before use, weigh the dishes to 0.1 mg and record the weights. Balance should be monitored for drift and re-zeroed as necessary.
3. The dishes should always be handled with tongs after they have been dried.
4. Allow sample(s) to reach room temperature before filtration.
5. Assemble filter apparatus.

> **Note:** Use laboratory forceps when handling filters.

6. To prepare the filter, apply vacuum and wash with three successive 20 mL aliquots of reagent-grade. Continue suction to remove all traces of water and discard the washings.
7. Stir sample with a magnetic stirrer and then pipet 50 mL of sample onto a glass-fiber filter with applied vacuum.
8. Wash with three successive 10 mL aliquots of reagent-grade water, allowing complete drainage between washings. Continue suction for approximately three minutes after filtration is complete.
9. Transfer total filtrate (including washings) to a weighed evaporating dish.
10. Place evaporation dishes containing the samples in a 103 to 105°C oven or steam bath and allow the samples to evaporate to dryness.
11. Transfer the dry evaporation dishes to a 180°C oven and heat for at least one hour.
12. Transfer samples to a desiccator and allow to cool for 1 hour or until room temperature is reached.
13. Weigh the dishes and record weight.
14. Return the evaporation dishes to the 180°C oven for an additional hour.
15. Cool in a desiccator and re-weigh the dishes and record weight.
16. The consecutive weights must agree to less than 0.5 mg.
17. Repeat cycle of drying, cooling, desiccating and weighing until consecutive weights agree to less than 0.5 mg.
18. Subtract weight of dish from weight of dish and sample to determine the weight of the sample. Finally, divide the calculated weight by the sample volume. Record result as mg/L TDS.

6.0) Analyst Requirements

Certified Analyst Requirements

All certified analysts must perform the analysis once every three months.

Operationally Certified Analyst Requirements

Operational certification is not available for this method.

7.0) Quality Control Requirements

7.1) Balance Calibration

Balances must be checked prior to use with certified weights (ASTM type 1, 2 or 3 weights or NIST Class S or S1). A manufacturer's certificate for the certified weights must be available.

1. Balance checks must be done with at least three weights that bracket the range of weights normally used in the laboratory.

7.2) Drying Oven Temperature Records

Record thermometer temperatures of both drying ovens daily when in use.

7.3) QC Requirements with Each Analysis

With each sample batch analysis, the following QC samples must be prepared and analyzed:

1. Blank (0.0 mg/L): One per analysis and following every 10 samples. Acceptance: Results < 10 mg/L.
2. Duplicate sample: One per analysis and following every 10 samples. Acceptance: < 5% difference from average of two duplicate samples.
3. Potassium chloride QC sample at 10 to 200 mg/L: One per analysis and following every 10 samples. Acceptance: ±10% of true value.

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review and must be available upon request.

- Balance Calibration Record
- 180 ±2°C Drying Oven Temperature Record
- 103 to 105°C Drying Oven Temperature Record
- Total Dissolved Solids QC Analysis Record

Balance Calibration Record

Prior to each use, check each balance with certified weights. A minimum of three weights that bracket normal weighing needs are required. Record balance response to reference weight and sensitivity to reference weight plus test load (L). Analytical balance must be sensitive to a 0.1 mg test load.

Laboratory _____

Analyst	Date	Reference Weight and Test Load Readings in Grams											
		200	200 + L	100	100 + L	50	50 + L	10	10 + L	5	5 + L	1	1 + L

*Note action taken if calibration is unacceptable. Note: "L" refers to "Test Load"

180 ±2°C Drying Oven Temperature Record

Laboratory _____

Analyst	Date	Time	Temp (°C)	Analyst	Date	Time	Temp (°C)	Analyst	Date	Time	Temp (°C)

*Note action taken if temperature is out of range.

103 to 105°C Drying Oven Temperature Record

Laboratory _____

Analyst	Date	Time	Temp (°C)	Analyst	Date	Time	Temp (°C)	Analyst	Date	Time	Temp (°C)

*Note action taken if temperature is out of range.

Total Dissolved Solids QC Analysis Record

Laboratory _____

Analyst	Date	Blank Concentration (mg/L)	Duplicate #1 (mg/L)	Duplicate #2 (mg/L)	KCl QC Sample True Value (mg/L)	KCl QC Sample Actual (mg/L)

Turbidity Analysis by Nephelometric Method

Quick Reference	**Standard/Reagent**	**Requirements**
Standard/Reagent Storage	Formazin 4000 NTU	Manufacturer's Recommendations
	AMCO Standards	Manufacturer's Recommendations
	StablCal Standards	Manufacturer's Recommendations
	Secondary Standards	Manufacturer's Recommendations
Standard/Reagent Expiration	**Standard/Reagent**	**Maximum Storage Time**
	Formazin 4000 NTU	1 Year After Opening/ Manufacturer's Expiration Date
	AMCO Standards	1 Year After Opening/ Manufacturer's Expiration Date
	StablCal Standards	1 Year After Opening/ Manufacturer's Expiration Date
	Secondary Standards	Manufacturer's Expiration Date
	Diluted formazin	Discard after use
Required Quality Control	**QC Procedure**	**Frequency**
	Record Secondary Standard Verification	Once Per Shift/Every 8 hours
	Turbidimeter Calibration	Once Every Three Months
	Secondary Standard Value Assignment	Once Every Three Months, Following Calibration Procedure
Sample Collection	**Preservation**	**Maximum Hold Time**
	4°C	48 Hours

Method Reference

Standard Methods 22nd Edition (2130 B)

Survey Requirements

- Each certified analyst must be able to perform the calibration procedure.
- Each operationally certified analyst must be able to perform the calibration verification procedure.
- Procedural technique will be observed.
- All reagents, standards and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

Turbidity in water is caused by suspended matter such as clay, silt, organic matter, inorganic matter and microscopic organisms. The nephelometric turbidity method is based on light scattered at a right angle by the suspended matter contained in the sample. A volume of sample water is collected in an indexed vial and analyzed on a calibrated turbidimeter.

2.0) Equipment

1. Nephelometric Turbidimeter. Meter must be capable of operating in a non-ratio mode. Ratio only turbidimeters are not acceptable. Meters with a ratio mode may be used for drinking water analysis with the ratio mode on or off. The meter must have stable reliable reading below 0.050 NTU.
2. Class A volumetric pipet(s).
3. Sample Vials. Follow procedure detailed in Section 7.2 of this method to index the sample vials.

3.0) Reagents

1. Primary Standard: Commercially available in required concentrations. Acceptable calibration standards are as follows:
   - Formazin: 4000 NTU standard.
   - Hach StablCal: standard set for laboratory's meter and a 1.0 NTU standard.
   - AMCO Clear: standard set for laboratory's meter and a 1.0 NTU standard.
2. Secondary Standards: Commercially available. Two concentrations are required in the ranges of 0-2 NTU and 0-20 NTU. Discard secondary standards when they vary by more than 30% for 0-2 NTU standards, by 20% for 0-20 NTU standards and 10% for 0-200 NTU standards from the initial assigned value, or when manufacturer's expiration date is reached.
3. Low Turbidity Water (LTW) - Laboratory reagent water with less than 0.10 NTU or commercially available LTW.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Collect in a clean plastic or glass screw top container (250 to 1000 mL). Alternatively, samples may be collected in the analysis vial.
2. Preservation: 4°C.
3. Maximum sample holding time: 48 hours. Ohio EPA recommends analyzing samples immediately after collection.

5.0) Turbidity Sample Analysis

1. Fill test vial with sample and cover.
2. With a lint-free wipe, dry the outside of vial.
3. Coat vial with silicon oil and wipe off with lint free cloth.
4. Place vial in meter touching only the cap of the vial.
5. Line up index mark of vial and meter.
6. Record turbidity value after a stable reading is displayed.

> **Note:** Sample cells must be kept scrupulously clean both inside and out. Cold samples should be warmed, so that condensation is eliminated before the sample is analyzed. Discard the test cells when they become scratched or damaged.

6.0) Analyst Requirements

All certified and operationally certified analysts must perform sample analysis at a minimum of at least three days per month.

Certified Analyst Requirements

All certified analysts must perform the calibration procedure at least once every three months. (Refer to Section 7.0 of this method.) Calibration procedures must be dated and initialed by all certified analysts participating in each procedure.

Secondary standards must be analyzed, verified to be within acceptable range and recorded at least once per 8-hour shift. Certified analysts must participate in this procedure at least three times a month.

Operationally Certified Analyst Requirements

Secondary standards must be analyzed, verified to be within acceptable range and recorded at least once per 8-hour shift. Operationally certified analysts must participate in this procedure at least three times a month.

7.0) Quality Control Requirements

The turbidimeter calibration procedure must be performed prior to initial use for analyzing potable water and at least once every three months thereafter. Each calibration procedure must be dated and recorded.

The manufacturer's calibration procedures must be followed with the following exceptions: (1) prepare a 1.0 NTU formazin standard for the low level "calibration check" standard; (2) if AMCO or StablCal primary standards are used, purchase a 1.0 NTU standard in addition to the meter’s calibration kit; and (3) use only Class A volumetric glassware for formazin dilutions.

7.1) Air Reading

The turbidimeter must display a low NTU (e.g., <0.035) while empty and closed. A higher reading may indicate that the turbidimeter must be serviced or replaced.

7.2) Sample Vial Indexing Procedure

1. Fill all sample vials used for analysis with low turbidity/reagent water.
2. Place cells in the meter and rotate to determine lowest reading.
3. Mark cells at the position of the lowest reading.
4. Use only cells that read ±0.01 NTU of each other for the calibration.

7.3) Calibration of Meter

Refer to manufacturer’s calibration instructions for each meter.

7.4) 1.0 NTU Verification/LTW

1. Fill a clean sample vial with LTW.
2. Place the sample vial into the holder, close the cover and Press ENTER.
3. Record the LTW value.
4. Fill a clean sample vial with a well-mixed 1.0 NTU primary standard.
5. Place the sample vial into the holder, close the cover and Press ENTER.
6. Subtract the LTW value from the 1.0 NTU reading and record the result.
7. Confirm the result is ±10% of the 1.0 NTU. If it is not, begin the calibration procedure again (Section 7.3).

> **Note:** If using a purchased 1.0 NTU standard, analyze and record the reading for the 1.0 NTU standard. The LTW value is irrelevant.

7.5) Secondary Standard Calibration (AMCO/Hach GELEX sealed vials)

1. Place the 0-2 NTU secondary standard into the sample vial holder, close the cover and Press ENTER.
2. Assign this value to the 0-2 NTU secondary standard.
3. Place the 0-20 NTU secondary standard into the sample vial holder, close the cover and Press ENTER.
4. Assign this value to the 0-20 NTU secondary standard.
5. Each subsequent secondary standard analysis must fall within ±10% of these assigned values. These values will remain in effect until the next calibration procedure.
6. If, at any point, analysis results of secondary standards fall outside of the ±10% acceptable range, the meter may need to be calibrated.

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review and must be available upon request.

- Secondary Standard Record (SM 2130 B)
- Benchtop Turbidimeter Calibration Record (SM 2130 B)

Secondary Standard Record* (SM 2130 B)

*Required once per 8-hour shift

Analyst	Date	0 – 2 NTU Assigned Value _____ *±10% = _____To _____ Result	0 – 20 NTU Assigned Value _____ *±10% =_____To_____ Result	Comments

*Acceptable range = ±10% of the assigned value of the secondary standard.

Benchtop Turbidimeter Calibration Record* (SM 2130 B)

*Must be performed once every three months.

Date _____ Analyst(s) _____

	Result (NTU)
LTW Result (NTU)	
1.0 Result (NTU)	
1.0 NTU Acceptable Range, 0.9 to 1.1 NTU	Circle One: **Yes** or **No**
Corrected 1.0 NTU (1.0 NTU minus LTW NTU)[1]	
Air Display	

[1]Not applicable for AMCO Clear or Hach StablCal.

Secondary Standard Assigned Values

Secondary Standards	0 – 2.0 (NTU)	0 – 20 (NTU)
Assigned Value		
Acceptable Range (±10%)	To	To

Benchtop Turbidimeter Calibration Record* (SM 2130 B)

*Must be performed once every three months.

Date _____ Analyst(s) _____

	Result (NTU)
LTW Result (NTU)	
1.0 Result (NTU)	
1.0 NTU Acceptable Range, 0.9 to 1.1 NTU	Circle One: **Yes** or **No**
Corrected 1.0 NTU (1.0 NTU minus LTW NTU)[1]	
Air Display	

[1]Not applicable for AMCO Clear or Hach StablCal.

Secondary Standard Assigned Values

Secondary Standards	0 – 2.0 (NTU)	0 – 20 (NTU)
Assigned Value		
Acceptable Range (±10%)	To	To

Turbidity Analysis by Hach Method 10258

Quick Reference	**Standard/Reagent**	**Requirements**
Standard/Reagent Storage	AMCO Standards	Manufacturer's Recommendations
	StablCal Standards	Manufacturer's Recommendations
	Secondary Standards	Manufacturer's Recommendations
Standard/Reagent Expiration	**Standard/Reagent**	**Maximum Storage Time**
	AMCO Standards	1 Year After Opening/ Manufacturer's Expiration Date
	StablCal Standards	1 Year After Opening/ Manufacturer's Expiration Date
	Secondary Standards	Manufacturer's Expiration Date
Required Quality Control	**QC Procedure**	**Frequency**
	Record Secondary Standard Verification	Once Per Shift/ Every eight hours
	Turbidimeter Calibration	Once Every Three Months
Sample Collection	**Preservation**	**Maximum Hold Time**
	4°C	48 Hours

Method Reference

Hach Method 10258, Determination of Turbidity by 360° Nephelometry, January 2016

Survey Requirements

- Each certified analyst must be able to perform the calibration procedure.
- Each operationally certified analyst must be able to perform the calibration verification procedure.
- Procedural technique will be observed.
- All reagents, standards and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

Turbidity in water is caused by suspended matter such as clay, silt, organic matter, inorganic matter and microscopic organisms. The nephelometric turbidity method is based on light scattered at a right angle by the suspended matter contained in the sample. A volume of sample water is collected in a vial and analyzed on a calibrated turbidimeter.

2.0) Equipment

1. Laser 360° Nephelometric Turbidimeter.
2. Class A volumetric pipet(s).
3. Sample Vials.

3.0) Reagents

1. Primary Standard: Commercially available in required concentrations. Acceptable calibration standards are as follows:
    - Hach StablCal: standard set for laboratory's meter and a 1.0 NTU standard.
    - AMCO Clear: standard set for laboratory's meter and a 1.0 NTU standard.

2. Secondary Standards: Commercially available. Two concentrations are required in the ranges of 0-2 NTU and 0-20 NTU.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Collect in a clean plastic or glass screw top container (250 to 1000 mL). Alternatively, samples may be collected in the analysis vial.
2. Preservation: 4°C.
3. Maximum sample holding time: 48 hours. Ohio EPA recommends analyzing the samples immediately after collection.

5.0) Turbidity Sample Analysis

1. Fill test vial with sample and cover.
2. With a lint-free wipe, dry the outside and bottom of the vial.
3. Place vial in meter touching only the cap of the vial.
4. Record turbidity value after a stable reading is displayed. Two or three readings may be required to get a stable reading.

> **Note:** Sample cells must be kept scrupulously clean inside and out. They must be stored filled with reagent water when not in use. Cold samples should be warmed, so that condensation is eliminated before the sample is analyzed. Discard the test cells when they become scratched or damaged.

6.0) Analyst Requirements

All certified and operationally certified analysts must perform sample analysis at a minimum of at least three days per month.

Certified Analyst Requirements

All certified analysts must perform the calibration procedure at least once every three months. (Refer to Section 7.0 of this method.) Calibration procedures must be dated and initialed by all certified analysts participating in each procedure.

Secondary standards must be analyzed, verified to be within acceptable range and recorded at least once per 8-hour shift. Certified analysts must participate in this procedure at least three times a month.

Operationally Certified Analyst Requirements

Secondary standards must be analyzed, verified to be within acceptable range and recorded at least once per 8-hour shift. Operationally certified analysts must participate in this procedure at least three times a month.

7.0) Quality Control Requirements

The turbidimeter calibration procedure must be performed prior to initial use for analyzing potable water and at least once every three months thereafter. Each calibration procedure must be dated and recorded.

The manufacturer's calibration procedures must be followed. After calibration, a 1.0 NTU standard must be analyzed for verification, and then secondary standard values are analyzed, and the values entered onto the Daily Secondary Standard Record.

7.1) Calibration of Meter

Refer to manufacturer’s calibration instructions for each meter.

7.2) 1.0 NTU Verification

1. Fill a clean sample vial with a well-mixed 1.0 NTU primary standard.
2. Place the sample vial into the holder and close the cover; wait for reading to occur and/or Press READ.

3. Confirm the result is ±10% of the 1.0 NTU. If it is not, begin the calibration procedure again (Section 7.1).

7.3) Secondary Standard Calibration Verification (AMCO/Hach vials)

1. With a lint-free wipe, dry the outside and bottom of the vial.
2. Place the 0-2 NTU secondary standard into the sample vial holder, close the cover and Press ENTER.
3. Verify this value to the manufacturer's assigned value for the standard.
4. Place the 0-20 NTU secondary standard into the sample vial holder, close the cover and Press ENTER.
5. Verify this value to the manufacturer's assigned value for the standard.
6. Each subsequent secondary standard analysis must fall within ±10% of these values.
7. If analysis results of secondary standards fall outside of the ±10% acceptable range, fresh secondary standards must be verified, or the meter may need to be recalibrated.

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review and must be available upon request.

- Secondary Standard Record (Hach Method 10258)
- Benchtop Turbidimeter Calibration Record (Hach Method 10258)

Secondary Standard Record* (Hach Method 10258)

*Required once per 8-hour shift

Analyst	Date	0 – 2 NTU Assigned Value _____ *±10% = _____To _____ Result	0 – 20 NTU Assigned Value _____ *±10% =_____To_____ Result	Comments

*Acceptable range = ±10% of the assigned value of the secondary standard.

Benchtop Turbidimeter Calibration Record* (Hach Method 10258)

*Must be performed once every three months.

Date _____ Analyst(s) _____

	Result
LTR Result (Use glass rod or 0.10 NTU verification.)	NTU
1.0 Result (NTU)	NTU
1.0 NTU Acceptable Range, 0.9 to 1.1 NTU	Circle One: **Yes** or **No**

Secondary Standard Assigned Values

Secondary Standards	0 – 2.0 (NTU)	0 – 20 (NTU)
Assigned Value		
Acceptable Range (±10%)	To	To

Benchtop Turbidimeter Calibration Record* (Hach Method 10258)

*Must be performed once every three months.

Date _____ Analyst(s) _____

	Result
LTR Result (Use glass rod or 0.10 NTU verification.)	NTU
1.0 Result (NTU)	NTU
1.0 NTU Acceptable Range, 0.9 to 1.1 NTU	Circle One: **Yes** or **No**

Secondary Standard Assigned Values

Secondary Standards	0 – 2.0 (NTU)	0 – 20 (NTU)
Assigned Value		
Acceptable Range (±10%)	To	To

UV_{254} - Organic Constituent Analysis by UV Absorption/Spectrophotometric Method

Quick Reference	**Standard/Reagent**	**Requirements**
Standard/Reagent Storage	Liquid Reagents	Manufacturer's Recommendations
	Potassium Biphthalate (KHP)	Manufacturer's Recommendations
Standard/Reagent Expiration	**Standard/Reagent**	**Maximum Storage Time**
	Reagents	1 Year After Opening/ Manufacturer's Expiration Date
	Stock Standards	6 Months After Preparation
Required Quality Control	**QC Procedure**	**Frequency**
	Generate Calibration Curve	Once Every Three Months
	Blank Verification	With Each Analysis
	Reporting Limit Verification	With Each Analysis If Calibration Curve Is Not Generated
	Midpoint Calibration Verification	With Each Analysis If Calibration Curve Is Not Generated
Sample Collection	**Preservation**	**Maximum Hold Time**
	4°C	48 Hours

Method Reference

Standard Methods 22nd Edition (5910 B)

Survey Requirements

- Each certified analyst must be able to generate a calibration curve described in this method.
- Procedural technique will be observed.
- All reagents, standards and solutions used for this method will be audited for correct labeling and dating.
- All records will be audited.

1.0) General Method Summary

Some organic constituents commonly found in water, such as lignin, tannin, humic substances and aromatic compounds, strongly absorb ultraviolet (UV) radiation. The unique qualities of each water source will determine if there is a strong correlation between UV absorption and precursors of trihalomethanes (THMs) and other disinfection by-products.

A water sample is collected, and the pH of the sample is adjusted to maintain results between pH 4.0 and 10.0. The sample is filtered, collected and absorbance of the sample is analyzed on a spectrophotometer at a wavelength of 254 nanometers.

Interferences

The correlation between UV absorption, organic compounds that may be precursors of THMs, and other disinfection by-products is highly dependent on the unique characteristics of the water source. Turbidity, suspended solids and UV-absorbing qualities of the water may interfere with the analysis.

2.0) Equipment

1. A spectrophotometer capable of reading 254 nm with a cell light path width of at least 1 cm.
2. Spectrophotometer vials.
3. Computer with software capable of generating linear regressions.
4. Fine porosity fast flow glass fiber filters, such as Whatman 934AH filter or equivalent.
5. Gravity filter apparatus, including glass, TFE or stainless-steel funnel and collection flask.
6. Class A volumetric pipet(s).
7. Standard laboratory glassware.

> **Note:** All glassware must be cleaned and rinsed thoroughly with reagent water.

3.0) Reagents

1. 1000 mg/L Organic Carbon Stock Solution, Potassium Biphthalate (KHP): Commercially available.
2. 100 mg/L Organic Carbon Calibration Standard (KHP): To prepare: Add 100.0 mL of 1000 mg/L organic carbon stock solution to a 1000 mL Class A volumetric flask, half filled with reagent water. Bring to volume with reagent water.
3. Hydrochloric Acid (HCl) Solution (0.1 N): Commercially available.
4. Sodium Hydroxide (NaOH) Solution (0.1 N): Commercially available.
5. Reagent water.

4.0) Sample Collection/Preservation/Holding Time

1. Sample collection: Collect in a clean amber glass screw top container (250 to 1000 mL).
2. Preservation: <6°C.
3. Maximum sample holding time: 48 hours. Ohio EPA recommends analyzing samples immediately after collection.

5.0) UV_{254} Analysis Procedure

> **Note:** If analyzing for Specific Ultraviolet-visible Light (UV) Absorbance (SUVA), do not adjust pH.

1. Prepare a filter assembly.

   > **Note:** A new filter assembly must be used for each sample.

2. Wash filter assembly with at least 50 mL reagent water. Do not collect this wash in the sample collection flask.
3. If the pH of the sample is below 4.0 or above 10.0, adjust with 0.1 N NaOH solution or 0.1 N HCl solution so pH is between 4.0 and 10.0.
4. After pH adjustment, rinse filter with 25 mL of sample and discard filtrate.
5. Filter and collect at least 50 mL of the sample.

6. Measure UV absorbance of at least two filtered portions of the sample. Read the absorbance at wavelength 254 nanometers for each sample portion against the most recently generated calibration curve stored in the spectrophotometer. Alternatively, compare to a manually generated calibration curve on an Excel spreadsheet or graph paper.

> **Note:** Calculate using the following correlation equation:

$$UV = \left[\frac{\bar{A}}{b}\right] D$$

where:

b = cell path length, cm
Ā = mean absorbance measured
D = dilution factor resulting from pH adjustment and/or dilution with organic-free water

$$D = \frac{final\ sample\ volume}{initial\ sample\ volume}$$

6.0) Analyst Requirements

All certified analysts must perform sample analysis at a minimum of at least once per month.

Certified Analyst Requirements

All certified analysts must perform the calibration curve generation procedure at least once per three months. (Refer to Section 7.0 of this method.) Generations must be dated and initialed by all certified analysts participating in each procedure.

Operationally Certified Analyst Requirements

Operational certification is not available for this method.

7.0) Quality Control Requirements

The calibration curve generation procedure must be performed prior to initial use for analyzing potable water and at least once every three months thereafter. Each calibration curve generation procedure must be dated and recorded.

> **Note:** An Initial Demonstration of Capability (IDC) study and initial Method Detection Limit (MDL) study must be completed and documented for this method.

7.1) Calibration Standard Concentration Calculations

100.0 mg/L KHP calibration standard will be used as the standard added to each flask to generate the calibration standard concentrations. The recommended calibration concentrations to generate a curve are as follows: blank (0.00 mg/L), 1.0 mg/L, 5.0 mg/L and 10.0 mg/L. Table 1 demonstrates how these standards are prepared in 50 mL volumetric flasks.

Table 1: Calibration Standard Concentration Preparation

Standard Concentration	mL of 100.0 mg/L KHP Calibration Standard Added to 100 mL Flask	Final Volume
Blank (0.0 mg/L)	0.0 mL	100 mL
1.0 mg/L	1.0 mL	100 mL
5.0 mg/L	5.0 mL	100 mL
10.0 mg/L	10.0 mL	100 mL

A minimum of three calibration standard concentrations and a blank must be analyzed to generate a calibration curve. The lowest concentration point prepared should be at least the reporting limit for UV_{254} (1.0 mg/L KHP). Alternatively, a reporting limit verification sample may be prepared in addition to the three calibration standard concentrations if the curve generation does not include the reporting limit concentration (1.0 mg/L KHP).

1. Prepare three 100 mL volumetric flasks containing a known volume of 100.0 mg/L KHP calibration standard and reagent water per Table 1 (above). Label each flask with the concentration it contains.
2. Prepare a blank by adding 100 mL reagent water to a fourth volumetric flask.
3. Prepare a separate filter assembly for each standard.
4. Wash each filter assembly with at least 50 mL reagent water. Do not collect this wash in the standard collection flasks.
5. If the pH of the standard(s) is below 4.0 or above 10.0, adjust with 0.1 N NaOH solution or 0.1 N HCl solution so pH is between 4.0 and 10.0.
6. After pH adjustment, filter and collect at least 50 mL of each standard.
7. Read the absorbance of each calibration standard and blank at 254 nm. Follow the spectrophotometer manufacturer's instructions to generate and store a calibration curve using the blank and three prepared calibration standards.
8. If the spectrophotometer does not have the capability to store calibration curves, read absorbance for each calibration standard at 254 nm on spectrophotometer. Record absorbance.
9. Using the absorbance and concentration of each calibration standard, generate a calibration curve on an Excel spreadsheet or equivalent.

7.2) Correlation Coefficient (R)/Coefficient of Determination (R^2)

Once the calibration curve has been generated, acceptance of the curve is determined by the correlation coefficient (R) or the coefficient of determination (R^2). For the curve to be acceptable for sample analysis, the correlation coefficient (R) must be greater than 0.995 or the coefficient of determination (R^2) must be greater than 0.990. The spectrophotometer may display this value after the calibration curve has been stored. Alternatively, the calibration curve may be generated on an Excel spreadsheet or equivalent using the correlation coefficient function to determine the correlation coefficient (R) or the coefficient of determination (R^2).

> **Note:** Calculate using the following correlation equation: $UV_{254} = 0.0144X + 0.0018$ to determine the approximate UV_{254} absorbance, where X equals the samples known concentration in mg/L KHP. For example, a sample with a known concentration of 5.0 mg/L KHP should have a UV_{254} absorbance of approximately 0.0738 cm^{-1}.

7.3) QC Requirements with Each Analysis

With each sample batch analysis, the following QC samples must be digested and analyzed at the beginning and duplicating every 10th sample:

1. Baseline Absorbance (i.e., non-filtered organic-free reagent water): Acceptance: <0.00 cm^{-}
2. Filter Blank (0.0 mg/L): Acceptance: Results < ½ reporting limit.
3. Reporting limit verification (1.0 mg/L): Acceptance: ±30% of true value.
4. Midpoint calibration verification (5.0 mg/L): Acceptance: ±10% of true value.

> **Note:** A blank sample is required with each sample analysis. QC samples 2 and 3 are required only if an entire calibration curve is not analyzed with the sample batch.

8.0) Required Documentation

Each of the following records contain the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review and must be available upon request.

- UV_{254}-Organic Constituent/Spectrophotometer QC Sample Record

UV_{254} - Organic Constituent/Spectrophotometer QC Sample Record

Laboratory

Analyst	Date	Blank (mg/L)	Reporting Limit (mg/L)		Midpoint (mg/L)		Curve Generation Date	Comments
			TV	Observed	TV	Observed		

Inorganic Analytical Methods

Analysis of inorganic constituents in drinking water must be performed following Ohio EPA accepted analytical methods referenced in OAC rule 3745-81-27(A). Unless otherwise specified below, quality control (QC) acceptance limits listed in the individual method must be followed. In addition to individual method's QC requirements, **at a minimum**, the following program specific inorganic analysis QC must be met. Refer to Chapter 2, Section B of this manual for Quality Assurance Plan requirements.

- Laboratory analyte reporting limits must meet reporting limit concentrations referenced in the appendix to OAC rule 3745-89-03.
- An Initial Demonstration of Capability (IDC) study must be completed and documented for each analyst certified for drinking water method analysis. If not specified in the method, use a blank and four laboratory fortified blanks (LFBs) for the IDC study.
- For methods not included in this manual, certified analysts must generate a curve at least once annually for all analytical methods which they are certified.
- Curve generation is limited to 1st or 2nd order. Calibration curves must result in a Correlation Coefficient (R) greater than 0.995 or a Coefficient of Determination (R^2) greater than 0.990 to be acceptable for drinking water analysis. It is recommended that curves not be forced through zero. (Calibration curves must be at least 3 standards and a blank, unless otherwise specified in the method.)
- Any concentrations above the highest standard in the calibration curve must be diluted to fall within the calibration range.
- At least once every three months, a drinking water sample must be analyzed using the inorganic analytical methods for which each analyst is certified.
- An annual Method Detection Limit (MDL) study must be performed using the most recent version of U.S. EPA's "Definition and Procedure for the Determination of the Method Detection Limit" in accordance with the 40 Code of Federal Regulations (C.F.R.).
- A Reporting Limit Verification (RLV) sample must be analyzed with each analytical run. The RLV concentration is equal to the reporting limit concentration for each analyte of interest. If there is no regulatory reporting limit, use the lowest calibration concentration point as the RLV. The acceptance limits are ±30% of true value.
- A secondary source QC sample (QCS) must be digested and/or analyzed with each sample batch. The QCS must be at a concentration between the lowest calibration point and the highest calibration point of the calibration range. The acceptance limits are ±10% of true value.
- Control charts for all QC samples must be maintained and available during surveys.
- Method blank results must be less than reporting limits.

  > **Note:** It is recommended that results are less than ½ of the reporting limit concentration for individual analytes unless method requirements are stricter.

- Heating equipment used for digestion/preparation of samples must be verified to within ±2°C of method required temperature.

Metals Analytical Methods

Analysis of metal constituents in drinking water must be performed following Ohio EPA-accepted analytical methods referenced in OAC rule 3745-81-27. Unless otherwise specified below, quality control (QC) acceptance limits listed in the individual method must be followed. In addition to individual method's QC requirements, **at a minimum** the following program specific metals analysis QC must be met. Refer to Chapter 2, Section B of this manual for Quality Assurance Plan requirements.

- Laboratory analyte reporting limits must meet reporting limit concentrations referenced in the appendix to OAC rule 3745-89-03.
- An Initial Demonstration of Capability (IDC) study must be completed and documented for each analyst certified for drinking water method analysis. If not specified in the method, use a blank and four laboratory fortified blanks (LFBs) for the IDC study.
- For methods not included in this manual, certified analysts must generate a curve at least once annually for all analytical methods which they are certified.
- Curve generation is limited to 1st order. Calibration curves must result in a Correlation Coefficient (R) greater than 0.995 or a Coefficient of Determination (R^2) greater than 0.990 to be acceptable for drinking water analysis. It is recommended that curves not be forced through zero. (Calibration curves should be at least 3 standards and a blank, unless otherwise specified in the method.)
- Any concentrations above the highest standard in the calibration curve must be diluted to fall within the calibration range.
- At least once every three months, a drinking water sample must be analyzed using the analytical methods for which each analyst is certified.
- An annual Method Detection Limit (MDL) study must be performed using the most recent version of U.S. EPA's "Definition and Procedure for the Determination of the Method Detection Limit" in accordance with the 40 Code of Federal Regulations (C.F.R.).
- A Reporting Limit Verification (RLV) sample must be analyzed with each analytical run. The RLV concentration is equal to the reporting limit concentration for each analyte of interest. If there is no regulatory reporting limit, use the lowest calibration concentration point as the RLV. The acceptance limits are ±30% of true value.
- A secondary source QC sample (QCS) must be digested and/or analyzed with each sample batch.
- The QCS must be at a concentration between the lowest calibration point and the highest calibration point of the calibration range. The acceptance limits are ±10% of true value.
- Control charts for all QC samples must be maintained and available during surveys.
- Method blank results must be less than reporting limits.

  > **Note:** It is recommended that results are less than ½ of the reporting limit concentration for individual analytes unless method requirements are stricter (e.g., 200.7, 200.9, 245.1).

- Heating equipment used for digestion/preparation of samples must be verified to within ±2°C of method required temperature.

Organic Analytical Methods

Analysis of organic constituents in drinking water must be performed following Ohio EPA-accepted analytical methods referenced in OAC rule 3745-81-27(B). Unless otherwise specified below, quality control (QC) acceptance limits listed in the individual method must be followed. In addition to individual method's QC requirements, the following program specific organics analysis QC must be met **at a minimum**. Refer to Chapter 2, Section B of this manual for Quality Assurance Plan requirements.

- Laboratory analyte reporting limits must meet reporting limit concentrations referenced in the appendix to OAC rule 3745-89-03.
- An Initial Demonstration of Capability (IDC) study must be completed and documented for each analyst certified for drinking water method analysis. If not specified in the method, use a blank and four laboratory fortified blanks (LFBs) for the IDC study.
- For methods not included in this manual, certified analysts must generate a curve at least once annually for all analytical methods for which they are certified.
- Curves must be generated by 1st or 2nd order. 1st and 2nd order calibration curves must result in a Correlation Coefficient (R) greater than 0.995 or a Coefficient of Determination (R^2) greater than 0.990 to be acceptable for drinking water analysis. (Calibration curves should be at least 3 standards and a blank, unless otherwise specified in the method.) Response Factor may be used if cited in method.
- Any concentrations above the highest standard in the calibration curve must be diluted to fall within the calibration range.
- At least once every three months, a drinking water sample must be analyzed using the analytical methods for which each analyst is certified.
- An annual Method Detection Limit (MDL) study must be performed using the most recent version of U.S. EPA's "Definition and Procedure for the Determination of the Method Detection Limit" in accordance with the 40 Code of Federal Regulations (C.F.R.).
- A Reporting Limit Verification (RLV) sample must be analyzed with each analytical run. The RLV concentration is equal to the reporting limit concentration for each analyte of interest. If there is no regulatory reporting limit, use the lowest calibration concentration point as the RLV. The acceptance limits are ±50%.
- A secondary source QC sample (QCS) must be extracted and/or analyzed with each sample batch. The QCS must be at a concentration between the lowest calibration point and the highest calibration point of the calibration range. The acceptance limits are ±30% of true value.
- Control charts for all QC samples must be maintained and available during surveys.
- Method blank results must be less than reporting limits.

  > **Note:** It is recommended that results are less than ½ of the reporting limit concentration for individual analytes.

- Heating equipment used for extraction of samples must be verified to within ±2°C of method required temperature.

Appendix 1. Glossary

Analyte: The constituent or property of a sample to be measured.

Analytical Data: The qualitative or quantitative results from a chemical, physical, microbiological, toxicological, radiochemical or other scientific determination.

Analytical Result: A numerical estimate of the quantity of an analyte in a sample, obtained by carrying out the procedure specified in the analytical method once (unless the method calls for the result to be the average of two or more responses). The result also can be thought of as the final value reported to the user.

Batch: A set of samples analyzed together without interruption. Results are usually calculated from the same calibration curve or factor.

Blank: A synthetic sample, free of analytes of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. *Field blanks* are used to obtain information on contamination introduced during sample collection, transport or storage. *Method blanks* are used to reveal contamination introduced by laboratory.

Calibration Standard: Solution of a known analyte concentration, used in the calibration procedure to determine the relationship between concentration and analytical response.

Certification Officer: An Ohio EPA person who evaluates laboratories for the purpose of certification.

Check Standard: A solution of known concentration used to indicate bias and the precision of an analytical system. When used in conjunction with a control chart, it becomes a *control standard*. Check standards are prepared from different sources than standards used for calibration.

Acceptance Limits: Statistical warning and action limits calculated for control charts, used to make decisions on acceptability of QC results.

Drinking Water Certification Manual: U.S. EPA's *Manual for the Certification of Laboratories Analyzing Drinking Water.*

Environmental Laboratory: A facility in a specific geographic location, owned or managed by a single entity, where scientific determinations are performed on samples taken from the environment, including drinking water samples.

Holding Time: The allowed time from when a sample was taken or extracted until it must be analyzed. For composite samples, the holding time starts when the last composite aliquot is collected.

Inspection (a.k.a. Survey): An audit of laboratory capabilities, including but not limited to data review, SOP review, etc. May be scheduled or unannounced.

Laboratory certification section: Administers Ohio EPA's drinking water laboratory certification program.

Laboratory: (See *Environmental Laboratory.)*

Method: A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed.

Quality Assurance (QA): A set of activities designed to establish and document the reliability and usability of measurement data.

Quality Assurance Plan (QAP): A QA manual that contains documents, policies, organizational information, objectives, and specific QC and QA activities. Volume and scope of QA manuals vary with complexity of the laboratory mission.

Quality Control (QC): The routine application of statistically based procedures to assess the accuracy of measurement data.

Spike: A known amount of analyte added to a sample to reveal bias due to interference present in the sample. The magnitude of bias is estimated as percent recovery. If the spike is added to an environmental sample, the sample is called a *matrix spike*.

Standard: A solution of known and documented concentration, either a check or control standard, or a calibration standard that is used to prepare a calibration curve.

Standard Operating Procedure (SOP): A detailed written description of a procedure designed to systematize performance of the procedure.

Survey (a.k.a. Inspection): An audit of laboratory capabilities, including but not limited to data review, SOP review, etc. May be scheduled or unannounced.

Appendix 2. Acronyms

C.F.R.: Code of Federal Regulations

NELAP: National Environmental Laboratory Accreditation Program

NPDWR: National Primary Drinking Water Regulations

OAC: Ohio Administrative Code

Ohio EPA: Ohio Environmental Protection Agency

ORC: Ohio Revised Code

PT: Proficiency Test

QA: Quality Assurance

QAP: Quality Assurance Plan

QC: Quality Control

QCS: Quality Control Standard that is from a separate source than the standards used for calibration.

SOP: Standard Operating Procedure

SDWA: Safe Drinking Water Act

U.S. EPA: United States Environmental Protection Agency

Appendix 3. General Laboratory Bench Sheets

1. The **Reagent/Standard Receipt/Preparation Record** may be used to record the required information. The minimum requirements for documenting each verification procedure are as follows:
2. The **Calibration/Standardization Schedule** may be used to record the required information. The minimum requirements for documenting each verification procedure are as follows:
3. The **Annual Laboratory Manual Review Record** may be used to record the information required in Chapter 5 of this manual. The minimum requirements for documenting review of each method are as follows:

Reagent/Standard Receipt/Preparation Record

Laboratory _____

Supplier/ Analyst	Type of Reagent/Standard	Reagent/Standard Lot Number	Date Received/Prepared	Manufacturer Expiration Date	Open Date	Actual Expiration Date

Calibration/Standardization Schedule

Laboratory _____

Frequency	Month											
	1	2	3	4	5	6	7	8	9	10	11	12
Weekly												
Fluoride 1.0 Standard Verification												
pH 4 Buffer Verification*												
Monthly (standardization)												
Alkalinity												
Chloride												
Chlorine Dioxide FAS												
Chlorine FAS												
Chlorine PAO												
Fluoride QC												
Hardness												
Once Every Three Months												
Chlorine DPD Verification												
Turbidimeter Calibration												
UV_{254} Curve												

*Unless a three-point calibration is performed.

Annual Laboratory Manual Review Record

Laboratory _____

Analyst No.	Analyst Signature	Date of Review	Analyst No.	Analyst Signature	Date of Review

Appendix 4. Continuous Monitors

1.0) In-Line Chlorine Meter Verification

The results of the in-line chlorine meter must be verified with those recorded by the calibrated benchtop chlorine method at least once each day when producing water. The in-line verification sample must be collected as near the in-line chlorine meter as possible, analyzed by the calibrated benchtop chlorine method immediately, and compared to the in-line chlorine meter result at the time of sample collection.

The in-line chlorine meter's results must be within ±10% of results attained from the calibrated benchtop chlorine method. If results are not within ±10%, follow the manufacturer's instructions to adjust the in-line meter to coincide with the chlorine result from the calibrated benchtop chlorine method or contact the manufacturer for assistance. The in-line chlorine meter must be verified or adjusted by an analyst certified or operationally certified for chlorine analysis.

The daily verification between the in-line chlorine meter and the calibrated benchtop chlorine method must be recorded.

1.1) In-Line Chlorine Meter Calibration

In-line meters shall be calibrated once every 90 days or in accordance with the manufacturer's calibration requirements, whichever is more stringent.

2.0) In-Line pH Meters

In-line pH meter results must be verified with the results recorded by the calibrated benchtop pH meter and recorded at least once each day. The in-line verification sample must be collected as near the in-line pH meter as possible, analyzed by the calibrated benchtop pH meter immediately and compared to the in-line pH meter result at the time of sample collection.

The in-line pH meter's results must agree with a calibrated benchtop pH meter to within ±0.20 pH units. If the reading is not within ±0.20 pH units, follow manufacturer's instructions to adjust the in-line meter to coincide with the pH result from the calibrated benchtop pH meter or contact the manufacturer for assistance. The in-line pH meter must be verified or adjusted by an analyst certified or operationally certified for pH analysis.

The daily verification between the in-line pH meter and the calibrated benchtop pH meter must be recorded.

2.1) In-Line pH Meter Calibration

In-line meters shall be calibrated once every 90 days or in accordance with the manufacturer's calibration requirements, whichever is more stringent.

3.0) In-Line Turbidimeter Requirements

Combined Filter

Daily verification is required for all in-line filtered water turbidimeters used for monitoring representative samples of filtered water. In-line turbidimeter results must be verified with the results recorded by the calibrated benchtop turbidimeter at least once each day. The in-line verification sample must be collected as near the in-line turbidimeter as possible, analyzed by the calibrated benchtop turbidimeter immediately and compared to the in-line turbidimeter result at the time of sample collection.

The daily verification between the in-line turbidimeter(s) and the calibrated benchtop turbidimeter must be recorded.

Individual Filter

Monthly verification is required for all in-line individual filter turbidimeters. In-line turbidimeter results must be verified with the results recorded by the benchtop turbidimeter or have the calibration verified with a

secondary standard at least once per month. The in-line verification sample must be collected as near the in-line turbidimeter as possible, analyzed by the calibrated benchtop turbidimeter immediately and compared to the in-line turbidimeter result at the time of sample collection. If individual filter turbidity meters are being used for compliance with turbidity requirements, they should adhere to the combined filter/entry point criteria above.

Acceptance Limits for Drinking Water Results Equal to or Greater Than 0.3 NTU

The in-line turbidimeter(s) results must agree with a calibrated benchtop turbidimeter within ±10%. If the result is not within ±10%, follow manufacturer's instructions to adjust the in-line meter to coincide with the turbidity result from the calibrated benchtop turbidimeter or contact the manufacturer for assistance. The in-line turbidimeter(s) must be verified or adjusted by an analyst certified or operationally certified for turbidimeter analysis.

Acceptance Limits for Drinking Water Results Less Than 0.3 NTU

The in-line turbidimeter(s) results must agree with a calibrated benchtop turbidimeter within ±0.03 NTU. If the result is not within ±0.03 NTU, follow manufacturer's instructions to adjust the in-line meter to coincide with the turbidity result from the calibrated benchtop turbidimeter or contact the manufacturer for assistance. The in-line turbidimeter(s) must be verified or adjusted by an analyst certified or operationally certified for turbidimeter analysis.

3.1) In-Line Turbidity Meter Calibration

In-line meters shall be calibrated once every 90 days or in accordance with the manufacturer's calibration requirements, whichever is more stringent.

4.0) Documentation

Each of the following records contains the minimum requirements for documentation and must be retained by the laboratory per Chapter 2, Section E of this manual. All records are subject to review by Ohio EPA and must be available upon request.

- Daily In-Line Chlorine Meter Verification Record
- Daily In-Line pH Meter Verification Record
- Daily In-Line Turbidity Meter Verification Record (SM 2130 B)
- Daily In-Line Turbidity Meter Verification Record (Hach Method 10258)

5.0) Other Continuous Monitors

For any other continuous monitor being used for compliance, the public water system must consult with Ohio EPA for requirements regarding verification and calibration requirements.

Daily In-Line Chlorine Meter Verification Record

Laboratory _____

Analyst	Date	Benchtop Meter Result	*In-Line Meter Result ±10%	(Y/N)	Analyst	Date	Benchtop Meter Result	*In-Line Meter Result ±10%	(Y/N)

*Refer to Section 9.0 of this method for in-line chlorine meter acceptance limits.

Daily In-Line pH Meter Verification Record

Laboratory _____

Analyst	Date	Benchtop Meter Result	*In-Line Meter Result ±0.20 (Y/N)	Analyst	Date	Benchtop Meter Result	*In-Line Meter Result ±0.20 (Y/N)

*Refer to Section 9.0 of this method for in-line pH meter acceptance limits.

Daily In-Line Turbidity Meter Verification Record (SM 2130 B)

Laboratory _____ Turbidimeter ID/Location _____

Analyst	Date	Benchtop Meter Result	In-Line Meter Result	*Within Accept. Limits?	Analyst	Date	Benchtop Meter Result	In-Line Meter Result	*Within Accept. Limits?

*****Acceptance limits for drinking water results equal to or greater than 0.3 NTU:

The in-line turbidimeter(s) results must agree with a calibrated benchtop turbidimeter within ±10%.

*Acceptance limits for drinking water results less than 0.3 NTU:

The in-line turbidimeter(s) results must agree with a calibrated benchtop turbidimeter within ±0.03 NTU.

Comments/Issues:

Daily In-Line Turbidity Meter Verification Record (Hach Method 10258)

Laboratory _____ Turbidimeter ID/Location _____

Analyst	Date	Benchtop Meter Result	In-Line Meter Result	*Within Accept. Limits?	Analyst	Date	Benchtop Meter Result	In-Line Meter Result	*Within Accept. Limits?

*****Acceptance limits for drinking water results equal to or greater than 0.3 NTU:

The in-line turbidimeter(s) results must agree with a calibrated benchtop turbidimeter within ±10%.

*Acceptance limits for drinking water results less Than 0.3 NTU:

The in-line turbidimeter(s) results must agree with a calibrated benchtop turbidimeter within ±0.03 NTU.

Comments/Issues: