

Ohio EPA Laboratory Manual
for
Chemical Analyses
of
Public Drinking Water
2014

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Chapter 1 – Purpose and Introduction

A. Purpose of This Manual

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

The drinking water laboratory certification program requirements are found in Chapter 3745-89 of the OAC.

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 May 4, 2015.

This document replaces the “Ohio EPA Laboratory Manual for Chemical Analyses of Public Drinking Water 2000” and all previous versions.

B. Introduction

As authorized by the Safe Drinking Water Act (SDWA), the United States Environmental Protection Agency (USEPA) has set health-based standards in the form of the National Primary Drinking Water Regulations (NPDWR) to protect against contaminants 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 USEPA, 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 contaminants specified in the State primary drinking water regulations and parameters necessary for the operation of public water systems. Ohio EPA implements the drinking water laboratory certification program through the Laboratory Certification Section in the Division of Environmental Services (DES). The program is implemented in conjunction with Ohio EPA’s Division of Drinking and Ground Waters.

Following rules in Chapters 3745-81, 3745-82 and 3745-89 of the OAC, the Laboratory Certification Section recommends to the Director of Ohio EPA whether to grant or deny certification to laboratories and laboratory personnel.

The “Ohio EPA Laboratory Manual for Chemical Analyses of Public Drinking Water 2014” and the “Ohio EPA Laboratory Manual for Microbiological Analyses of Public Drinking Water 2014” outline requirements for obtaining and maintaining certification for the analysis of drinking water in the State. 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

Plans for any type of laboratory construction or remodeling must be submitted to the Laboratory Certification Section for review and approval. Laboratory plan approval is covered under rule 3745-89-03 of the OAC. In addition, Ohio EPA has developed a “Laboratory Construction and Remodeling Checklist” located at: <http://www.epa.ohio.gov/ddagw/labcert.aspx>.

All items listed below may not be applicable to a particular laboratory. If you have questions or need assistance, contact the Laboratory Certification Section. Laboratories are encouraged to contact the Laboratory Certification Section staff early in the planning stages for construction or remodeling of a laboratory.

1. 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 every six feet along the work benches. Adequate gas and vacuum outlets must be provided for microbiological testing.
- Acid and alkaline resistant sinks are required. All sinks must be of double bowl construction unless written exemption is issued by the Laboratory Certification Section.
- 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 area must be isolated from and not allow direct entry into bathrooms or shower areas.
- Physical isolation of a microbiological section of the laboratory from chemical analytical sections is not mandatory, with the exception of 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

- A minimum of six linear feet of work bench must be provided per certified method for each chemical analytical group.
- A minimum of five feet per analyst is required for microbiological testing.

3. Equipment

- A list of all analytical equipment to be used for drinking water analyses must be submitted to the Laboratory Certification Section. The list must include manufacturer and model number so each piece of equipment can be evaluated and approved for use.
- In a microbiological laboratory a horizontal steam operated autoclave must be provided, and must be vented to the outside of the building or be equipped with a condenser to allow steam discharge to enter the sanitary sewer.
- 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. An exhaust hood must be equipped with explosion-proof motors and switches if it is to be used in conjunction with solvents, 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 in-line turbidimeters, pH meters, or chlorine analyzers are to be installed, a bench model is required for calibrations and reference samples.
- All bench tops 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. However, this bench area cannot detract from the six linear feet of work bench area per certified method.
- 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 rule 3745-89-03(A)(2) of the OAC, must include the following information:

- Table of laboratory organization delineating responsibilities of all laboratory personnel.
- Standard operating procedures including identification of the reference methods used to perform the drinking water analysis. These standard operating procedures must be reviewed and/or revised at least annually.
- Sample handling procedures, including:
 - Directions for maintaining sample integrity from collection to receipt to 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 rejecting samples not meeting method requirements.
- Routine practices to maintain the precision and accuracy of data.
- Corrective analytical action procedures.
- Preventative instrument maintenance procedures.
- Documentation of standard preparation and reagent expiration dates.
- Reporting procedures.

This manual may be used by public water system laboratories seeking certification for plant control tests and microbiological tests as their QAP. In addition, these laboratories may use the Analytical Methods Standard Operating Procedures (SOPs) located in Chapter 7 of these manuals 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 must develop a QAP as described in USEPA'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 <http://water.epa.gov/scitech/drinkingwater/labcert/index.cfm>

C. Laboratory Contingency Plan

Ohio EPA strongly recommends each certified laboratory 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. Public water systems should include this information in the contingency plan required by rule 3745-85-01 of the OAC.

D. Reporting of Analytical Results

Results of drinking water samples are reported to Ohio EPA by public water systems and certified laboratories to demonstrate that drinking water meets health based standards. Rule 3745-89-08 of the OAC 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) are required to be submitted to Ohio EPA through eDWR. For additional information about eDWR, please go to Ohio EPA's website at: <http://www.epa.ohio.gov/ddagw/reporting.aspx>.

E. Data Management

1. Document Management

Public water supply laboratories are required to record standardizations and calibrations on a standardized record form or bench sheet. 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.

Entries or data results must be recorded in ink or an electronic version approved by the Laboratory Certification Section. Incorrect entries are common in laboratory work and the incorrect entry should be crossed using one line through the entire row or column; this method should leave the crossed out entry still 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.

2. Record Retention

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

- 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. For the remainder of the retention period the records may be kept off-site.

F. Proficiency Test (PT) Samples

In accordance with rule 3745-89-03 of the OAC, 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 for 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.

Arrangements must be made with the PT provider to order a make-up PT sample for any regulated analyte(s) resulting in a "Not Acceptable" evaluation.

A Laboratory receiving a “Not Acceptable” evaluation for the scheduled PT sample and the make-up PT sample for any regulated analyte(s) for which it is certified, is advised to immediately attempt to determine the cause of the “Not Acceptable” evaluation, submit a corrective actions report to the Laboratory Certification Section and obtain a second make-up PT sample for the analyte(s) in question.

Arrangements must be made with the PT provider to submit all PT sample results to the Laboratory Certification Section either by e-mail or mail.

A provider of PT samples must be accredited by a Proficiency Testing Provider Accreditor that meets the National Environmental Laboratory Accreditation Conference requirements.

Fluoride QC Sample:

Requirements for the fluoride QC sample are detailed in Section 7.2 of the **Fluoride Analysis by Ion-Selective Electrode Method**, located Chapter 8 of this manual.

G. Interim Authorization for New Contaminants and New Methods

Interim authorization for new contaminants and new methods, as defined in rule 3745-89-01 of the OAC, may be granted for certified laboratories following these procedures:

- Interim authorization shall only be available to laboratories which currently have valid certification for the same type of drinking water analysis (microbiological contaminants, inorganic, trace metals, etc.) as the drinking water analyses to be included in the interim authorization.
- In order to be considered for interim authorization, the laboratory must submit an application for interim authorization which includes the following information:
 - The name, address and telephone number of the laboratory and of the individual(s) responsible for the laboratory.
 - Statement of the drinking water analyses and methods for which interim authorization is sought and the analysts to be included in the interim authorization to perform the analyses. The analysts must be individuals already identified on a valid certificate for the laboratory for performing similar analyses or for analyzing the same type of contaminant.
 - Documentation that the laboratory obtained acceptable results within the past twelve months for at least one proficiency test (PT), in accordance with Chapter 2, Section F of this manual, for each drinking water analysis to be included in the interim authorization.
 - Documentation that a method detection limit study has been completed by the laboratory for each drinking water chemistry analysis to be included in the interim authorization, with the studies indicating the laboratory is capable of meeting any specified analytical reporting requirements.
 - Documentation that the laboratory has successfully passed one microbiological PT set, in accordance with Chapter 2, Section F of this manual, with the method not approved by Ohio EPA. The test data must be sent directly to the Laboratory Certification Section from the PT provider. The laboratory must pass the PT study with the method for which interim authorization is being sought.
- When granted, the interim authorization must state the individual(s) and drinking water analyses

included in the interim authorization and the length of time the interim authorization will remain in effect.

- An on-site survey must be scheduled to verify acceptable performance by the laboratory granted interim authorization. Interim authorization will remain in effect until the on-site survey is completed and certification is granted.

H. Laboratory Safety

The Laboratory Certification Section strongly recommends each laboratory seeking certification have in place a safety program developed to meet the specific requirements of the laboratory. The laboratory safety plan should focus on the methods for which it is seeking certification and the requirements needed to safely conduct those analyses.

While safety criteria are not part of the laboratory certification survey, the safety equipment identified in **Laboratory Construction and Remodeling Requirements, Chapter 2, Section A** of this manual, are required in order for a laboratory to be considered for certification.

The Laboratory Certification Section recommends reviewing “Standard Methods for the Examination of Water and Wastewater,” Part 1090 “Laboratory Occupational Health and Safety” for a detailed reference on the requirements of a laboratory safety plan.

Chapter 3 - Requirements for Participating in the Laboratory Certification Program

A. Applying for Certification and Paying Fees

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

Applications can be acquired at the Laboratory Certification Section website:
<http://www.epa.ohio.gov/ddagw/labcert.aspx>

1. Initial Certification

An application for initial certification must be submitted in writing to the Laboratory Certification Section indicating which analysis methods are requested for certification.

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

- Obtain Ohio EPA Director's approval of a detailed laboratory floor plan.
- Submit a complete application and pay the appropriate fee.
- Submit with the application a method detection limit study and an initial demonstration of capability (IDC) study (required for laboratories applying for the following base certifications: Standard Chemistry, Limited Chemistry, THMs/Haloacetic Acids/VOC, SOC/Pesticides, Inorganic Chemistry (Metals) and (Radionuclides).
- Submit an acceptable quality assurance plan.
- Submit documentation of initial QC procedures required by the methods.
- Successfully analyze required proficiency test samples.
- Pass an on-site survey.

2. Certification Renewal and Maintenance

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

- Maintain a valid and unexpired laboratory certification.
- Submit results of proficiency test sample analyses.
- Make required improvements in its quality assurance plan.
- Report significant changes in facility, equipment, personnel or quality assurance plan.
- Submit a renewal application and pay the appropriate fee.
- Submit to required audits and implement any required corrective actions.

An application for certification renewal 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 rule 3745-89-04 of the OAC and are deemed complete, the laboratory certification will be extended until such time as an on-site survey is completed. Should failure to follow guidelines result in loss of certification for a period of time, it will be the laboratory's responsibility to have required water analysis completed by a certified lab during that time.

3. Fees

Fees are detailed in Section 3745.11 of the Ohio Revised Code (ORC) and shall be paid at the time of survey request.

Survey fees are detailed on the website at: <http://www.epa.ohio.gov/portals/47/facts/feeschedule.pdf>

Chapter 4 - On-Site Surveys

The Laboratory Certification Section conducts two types of on-site surveys: announced (scheduled with laboratory) and unannounced (not scheduled with laboratory). The surveys are to confirm the information provided to the Laboratory Certification Section by the laboratory on its application, review and evaluate each analyst and review records maintained by the laboratory.

The following personnel are required to be available during an announced on-site 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 certification cycle.

Surveys are conducted between 8:00 a.m. – 5:00 p.m. Required laboratory records must be located in the laboratory, clearly labeled and easily accessible. Copies of the records must be made available upon request by the certification officer.

It is recommended that at least two people 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 on-site 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 on-site survey.
- Analysis of proficiency test samples.
- For laboratories seeking initial certification, maintenance of laboratory records for at least thirty (30) days prior to the on-site survey, with the records documenting:
 - All appropriate laboratory equipment and auxiliary equipment is operational within prescribed limits.
 - Sufficient practice analyses have been conducted by each analyst participating in the on-site 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 each analyst participating in the on-site survey, except for analysts to be designated for operational certification.

- Acceptable method detection limit studies have been completed for each method and instrument.
- Conformance to the laboratory plan as approved by the Director.
- Conformance by the laboratory to the analytical reporting limits identified in rule 3745-89-03 of the OAC.
- Correction of deviations noted in previous survey reports.

B. Review of Survey Findings

At the completion of the on-site survey the certification officer will meet with the appropriate laboratory representatives to review the findings of the survey. A copy of the deviations noted during the survey will be provided within 45 days of the survey.

C. Survey Report

A survey report will be issued to the applicant by the Laboratory Certification Section within forty-five (45) days of an on-site survey. The survey report will indicate the acceptability of the applicant's performance during the on-site survey and will state deviations required to be corrected prior to certification of the laboratory. If the survey report includes deviations, the Director of Ohio EPA may deny, suspend or revoke certification in accordance with rule 3745-89-06 of the OAC.

In accordance with rule 3745-89-01 of the OAC, a deviation 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 deviations identified during the survey.

Chapter 5 - Requirements for Analyst Certification

A. Certification/Operational Certification for Plant Control Tests

There are two types of drinking water certification available for laboratories and personnel.

1. Certified

Each certified analyst is required to perform all QC requirements, including calibrations, standardizations and verifications as detailed in Chapter 7.0 of in 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.

2. Operational Certification

Operational certification is defined in rule 3745-89-01 of the OAC as certification granted by the Director for an analyst to perform one or more of the plant control tests for alkalinity, alkalinity stability, chloride, chlorine, chlorite, chlorine dioxide, fluoride, hardness, pH, or turbidity, including daily calibration and standardization but neither including the preparation of standards or reagents, nor the required monthly or quarterly calibration and standardization. Operationally certified analysts may not perform calibrations, standardizations and other QC activities unless otherwise noted in Chapter 8, Section 6.2 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.

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 the 20-day parallel testing period. "Acceptable performance" is defined as obtaining results within plus or minus ten per cent of the certified analyst for the plant control test.
- The number of individuals requested for interim authorization by the laboratory may not be more than two.
- A laboratory must submit an application 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 twenty days of analytical results generated in parallel testing with an analyst included on a certificate for those same plant control tests. The previous certification of an individual to perform plant control tests may be considered for satisfying this requirement.

An on-site survey will be scheduled within six months of an interim authorization. Interim authorization shall remain in effect for a period not to exceed six months unless an extension is granted.

Chapter 6 - Issuance of Laboratory Certification

Based on the results of the on-site survey Laboratory Certification Section staff provides a recommendation to the Director concerning the certification status of the laboratory. Categories are as follows:

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 time period not to exceed three years from the date of issue.

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

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 deviations noted on the survey report. The provisional certification will remain in effect during the period of time between the completion of the on-site survey and the deadline allotted for the lab to respond to the deviations listed on the survey report. The laboratory will be certified for the analytical method(s) by the Laboratory Certification Section if the laboratory provides an acceptable response addressing the deviations 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 Chapter 3745-89 of the OAC.

Certificates

Certificates are nontransferable. It is the laboratory's responsibility to notify the Laboratory Certification Section of all personnel changes. All certificates of approval remain the property of Ohio EPA and must be returned to the Laboratory Certification Section 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 rule 3745-89-06 of the OAC, 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 rules 3745-89-03 to 3745-89-05 of the OAC.

- The laboratory fails to meet the reporting requirements in rule 3745-89-08 of the OAC.
- 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.
- A person not named on a valid laboratory certificate performed analysis of a water PT sample for purposes of retaining a valid laboratory certification.
- 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 deviations.

In addition to the items listed above, examples of when the Director of Ohio EPA may take an action to deny, suspend or revoke a laboratory's certification are:

- 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 guidelines result in loss of certification for a period of time, 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

A. Standard Operating Procedures (SOPs)

All approved methods for the analysis of drinking water in the State of Ohio are located in rule 3745-81-27 of the OAC.

Public water system laboratories may use the methods in Chapter 8 of this manual as the SOP of record for each method for 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. Quality Control Requirements.
7. Calibration, Standardization or Verification Procedure.
- 8.-10. 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 author or 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 ₂ SO ₄)	Room Temperature
	Indicator (Bromcresol Green/Methyl Red)	Room Temperature
	Sodium Thiosulfate	Room Temperature
	0.020 N Sodium Carbonate (Na ₂ CO ₃) Standard	Room Temperature
Standard/Reagent Expiration	Standard/Reagent	Expiration
	0.020 N Sulfuric Acid (H ₂ SO ₄)	1 Year After Opening/Manufacturer's Expiration Date
	Indicator (Bromcresol Green/Methyl Red)	1 Year After Opening/Manufacturer's Expiration Date
	Sodium Thiosulfate	1 Year After Opening/Manufacturer's Expiration Date
	0.020 N Sodium Carbonate (Na ₂ CO ₃) Standard	1 Year After Opening/Manufacturer's Expiration Date
Required Quality Control	QC Procedure	Frequency
	Standardize Titrant / 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)

On-Site Survey Requirements

- Each certified analyst must be able to perform the alkalinity titrant standardization described in Section 7.0 of 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 0.020 N sulfuric acid 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-bromocresol 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

- a. 25 to 50 mL digital or self-leveling automatic burette.
- b. Burette with sufficient capacity so that all tests and standardizations can be performed without refilling the burette.
- c. 20.0 mL Class A volumetric pipet(s).
- d. Titration vessels of appropriate volume.
- e. Graduated cylinders (50 to 100 mL).
- f. Magnetic stirring device & stir bars.
- g. Balance.

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 2-35, Section 3. Reagents)

- a. Sulfuric Acid Titrant (0.020 N): Commercially available.
- b. Mixed Bromocresol Green-Methyl Red Indicator: Commercially available. Prepare with alcoholic solution.
- c. Phenolphthalein Alcoholic Solution.
- d. Reagent Water.
- e. 0.1 N Sodium Thiosulfate Solution: Commercially available.
- f. 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 4 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

- a. Sample collection: Alkalinity sample may be collected in a clean plastic or glass screw top container (250 to 1000 mL). Alternatively, the sample may be collected directly into a graduated cylinder if the sample is analyzed immediately.
- b. Preservation: 4°C.
- c. Maximum sample holding time: 14 Days. The Laboratory Certification Section recommends analyzing samples immediately after collection.

5.0 Alkalinity Analysis Procedure

A. Colorimetric Titration

1. Fill the burette with 0.020 N H₂SO₄ titrant. Zero the burette reading if digital burette is used.
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 CaCO₃.
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 CaCO₃.

B. Potentiometric Titration

1. Standardize the pH meter (Section 7.0 pH method).
2. Fill the burette with 0.020 N H₂SO₄ titrant. Zero the burette reading if digital burette is used.
3. Rinse out the titrating vessel with sample and discard.
4. Measure the sample with an appropriately sized graduated cylinder.
5. Place the pH probe 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 is reached.
8. Record the volume of titrant used for phenol alkalinity determination.
9. Slowly add titrant to the sample, mixing with a magnetic stir bar.
10. Stop adding titrant when a stable pH of 4.5 is reached.
11. Record the volume of titrant used for total alkalinity determination.
12. 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.
13. Record the phenol alkalinity value and total alkalinity value in mg/L as CaCO₃.

6.0 Quality Control Requirements

6.1 Titrant Standardizations

Titrant standardization procedure must be completed initially upon opening or preparation of titrant and at least once per month thereafter. (Refer to Section 7.0.) Each standardization procedure must be dated and recorded.

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the titrant standardization procedure at least once per quarter. (Refer to Section 7.0.) 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 . The **Alkalinity pH 4.5 Endpoint Verification Record** on page 29 may be used to document the required information. The pH must be 4.5 ± 0.2 .

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. The **Alkalinity pH 4.5 Endpoint Verification Record** on page 29 of this manual may be used to document the required information. The pH must be 4.5 ± 0.2 .

7.0 Titrant Standardization Procedure

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 H_2SO_4 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 Titrant Standardization Procedure (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.
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 (Na_2CO_3) 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 (Na_2CO_3) 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 ± 0.1 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 $\pm 5\%$ 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 to 21.0 mL.

If the amount of the laboratory prepared titrant used is outside of the acceptable range replace the titrant or calculate a correction factor.

7.4 Correction Factor (Used only for laboratory prepared titrant.)

The correction factor adjusts the alkalinity calculation for the concentration of titrant used.

Three titrant checks must be performed for the calculation as follows:

$$\frac{20 \text{ mL}}{\text{Average of Three Titrations (mL)}} = \text{Correction Factor}$$

Multiply all titration volumes performed with titrant associated with its correction factor.

Note: Do not use correction factors on purchased titrants. They must be within range or replaced.

7.4 Required Standardization Documentation

The **Monthly Alkalinity Titrant Standardization Record** on page 28 of this manual may be used to document each standardization procedure. The minimum requirements for documenting each verification procedure are as follows:

- a. Analyst(s) initials.
- b. Date standardization performed.
- c. Volume of reagent water used (mL).
- d. Volume of acid titrant used for the blank (mL).
- e. Volume of standard used (mL).
- f. Volume of acid titrant used for titrations 1 and 2 (mL).
- g. The third titration value and correction factor if used.
- h. Comments.

Chloride Analysis by Silver Nitrate Titration Method

Quick Reference	Standard/Reagent	Requirements
Standard/Reagent Storage	0.0141 N Silver Nitrate Titrant	Room Temperature, Away From Light
	Potassium Chromate Indicator	Room Temperature
	0.0141 N Sodium Chloride Standard	Refrigeration
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
	4°C	28 Days

Method Reference

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

On-Site Survey Requirements

- Each certified analyst must be able to perform the chloride titrant standardization described in Section 7.0 of 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

After collecting a known volume of sample, approximately 0.5 ml of potassium chromate indicator is added. A titration is performed with 0.0141 N silver nitrate. When the sample solution color changes from yellow to red/orange, the titration is complete. 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 to it 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

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

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 4-72 & 73, Section 3. Reagents)

- a. Silver Nitrate Titrant (0.0141 N): Commercially available. This titrant is light sensitive and should be stored away from light.
- b. Potassium Chromate Indicator: Commercially available.
- c. Sodium Chloride Standard (0.0141 N): Commercially available.
- d. Reagent Water.

4.0 Sample Collection/Preservation/Holding Time

- a. Sample collection: Collect in a clean plastic or glass screw top container (250 to 1000 mL). Alternatively, samples may be collected in the analysis container if they are analyzed immediately.
- b. Preservation: 4°C.
- c. Maximum sample holding time: 28 Days. The Laboratory Certification Section recommends analyzing samples immediately after collection.

5.0 Chloride Analysis Procedure

1. Fill/zero burette with silver nitrate titrant.
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 sample/indicator changes color from yellow to red/orange.
7. Record the amount (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 10.
9. Record this value as chloride concentration in mg/L.

Example:

Amount (mL) of silver nitrate titrant needed to change color from yellow to red/orange: 7.2 mL
Multiplier factor for 50 mL of sample volume: 10

Chloride Concentration (mg/L): $7.2 \times 10 = 72$ mg/L

Note: If 100 mL of sample volume is analyzed, the multiplier factor is 5.

6.0 Quality Control Requirements

6.1 Titrant Standardizations

The titrant standardization procedure must be performed prior to initial use for analyzing potable water and at least once per month thereafter. (Refer to Section 7.0.) Each standardization procedure must be dated and recorded.

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the titrant standardization procedure at least once per quarter. (Refer to Sections 7.0.) 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 Titrant Standardization Procedure

7.1 Blank (Verification of chloride free reagent water)

1. Add 45 mL of reagent water using a graduated cylinder, then add sufficient potassium chromate indicator to the vessel to produce a distinctive color.
2. Slowly add 0.0141 N silver nitrate titrant to the sample, mixing with a magnetic stir bar, until color endpoint 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. If more than 0.6 mL (approximately 12 drops) of titrant is needed to reach the endpoint, obtain acceptable reagent water.
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 to 1.0 mL of potassium dichromate indicator.
2. Using a class A volumetric pipet, add 5.0 mL of the (0.0141 N) sodium chloride standard solution.
3. Titrate with 0.0141 N silver nitrate titrant to the red/orange color.
4. Record the volume of titrant used.
5. Repeat Steps 1 through 5 for the second titrant standardization.
6. If blank results indicate there is chloride in the reagent water (Section 7.1), subtract the blank value (in mL) from each of the standard titration values.

7.3 Titrant Standardization Acceptance Limits

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

When using 5.0 mL of 0.0141 N sodium chloride (NaCl) standardizing solution, the acceptable range is 4.75 to 5.25 mL.

If the amount of the laboratory prepared titrant used is outside of the acceptable range, replace the titrant or calculate a correction factor.

7.4 Correction Factor

The correction factor must be used if the titrant is prepared in the laboratory. Three titrant standardizations must be performed for the calculation as follows:

$$\frac{5.0 \text{ mL}}{\text{Average of three titrations (mL)}} = \text{Correction Factor}$$

Multiply all titration analyses with the correction factor associated with each new titrant preparation.

Note: Do not use correction factors on purchased titrants. They must be within acceptance limits or replaced.

7.5 Required Standardization Documentation

The **Monthly Chloride Titrant Standardization Record** on page 35 of this manual may be used to document each standardization procedure. The minimum requirements for documenting each standardization procedure are as follows:

- a. Analyst(s) initials.
- b. Date standardization performed.
- c. Volume of reagent water used (mL).
- d. Volume of titrant used for the blank (mL).
- e. Volume of standard used (mL).
- f. Volume of titrant used for the titrations 1 and 2 (mL).
- g. The third titration value and correction factor, if used.
- h. Comments.

Chlorine Analysis by Amperometric (POA) Titration Method

Quick Reference	Standard/Reagent	Requirements
Standard/Reagent Storage	Liquid Reagents	Room Temperature
	Standards	Refrigerated
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 Immediately

Method Reference

Standard Methods 22nd Edition (4500-Cl D)

On-Site Survey Requirements

- Each certified analyst must be able to perform the PAO titrant standardization described in Section 7.0 of 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 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

A known volume of potable water is collected and titrated on an amperometric titrator to deflection end point, 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 by using the volume of titrant needed to reach endpoint. Potassium iodide solution and acetate buffer are then added to the sample, adjusting it 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

- a. Amperometric titrator equipped with the following:
 - Platinum electrode: Follow manufacturer's recommendations for maintenance.
 - Salt bridge: Follow manufacturer's recommendations for maintenance.
 - Silver-Silver chloride reference electrode.
 - Agitator: Follow manufacturer's recommendations for maintenance.
 - Titrant burette (1.00 mL to 5.00 mL).
 - Sample container with 200 mL graduation.
- b. 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

Reference: Standard Methods, 22nd Edition, (Page 4-65, Section 3. Reagents)

- a. Phenylarsine Oxide (PAO) Titrant (0.00564 N): Commercially available.
- b. Potassium Iodide (KI) Solution: Commercially available.
- c. Acetate Buffer Solution: Commercially available.
- d. Potassium Biiodate, Commercially Prepared Solution (0.025 N). Expires 1 year after opening or at manufacturer's expiration date.
- e. 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.

- f. 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 to 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 1 year after preparation.
- g. 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.
- h. Sulfuric Acid Solution (10% or 4 N): Commercially available. It may also be prepared as follows: Slowly add 20 mL of concentrated H₂SO₄ (49-51%) 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: H₂SO₄ is highly acidic. Safety glasses, lab coat and acid resistant gloves must be worn when handling H₂SO₄.
- i. Reagent water.

4.0 Sample Collection/Preservation/Holding Time

- a. Sample collection: Samples may be collected in a clean plastic or glass screw top container dedicated to chlorine sample collection. Alternatively, the sample may be collected directly into the analysis container if the sample is analyzed immediately.
- b. Preservation: No Preservation Required.
- c. 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 5 minutes to maintain a constant concentration of chlorine 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. 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 that has been 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 + 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

$$(1.8 \text{ mg/L Total chlorine} - 1.2 \text{ mg/L Free chlorine}) = 0.6 \text{ mg/L Combined chlorine}$$

6.0 Quality Control Requirements

6.1 Titrant Standardizations

Titrant standardization procedure must be completed initially upon opening or preparation of titrant and at least once per month thereafter. (Refer to Section 7.0.) Each standardization procedure must be dated and recorded.

6.2 Analyst Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the titrant standardization procedure at least once per quarter. (Refer to Section 7.0.) 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 Titrant Standardization Procedure

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 amount of PAO titrant. If the needle does not move, the reagent water is free of chlorine. Record 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, e or d). 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. Use the formula in Section 7.3 to calculate normality of PAO titrant.
9. This procedure must be done twice.

7.3 PAO Titrant Normality Calculation

**Normality of potassium biiodate x Volume (mL) potassium biiodate = Normality of PAO titrant
Volume (mL) PAO titrant needed to reach standardization endpoint**

Example:

Normality of potassium biiodate: 0.0025 N

Volume (mL) potassium biiodate: 5.0 mL

Volume (mL) PAO titrant needed to reach standardization endpoint: 2.20 mL

$$\frac{0.0025 \text{ N} \times 5.0 \text{ mL}}{2.2 \text{ mL}} = 0.00568 \text{ N}$$

7.4 Titrant Standardization Acceptance Limits

The true value of the PAO titrant is 0.00564 N. The acceptance range is $\pm 5\%$ of the true value (0.00564 N) which is (0.005358 N to 0.005922 N). If the PAO titrant normality is outside of the acceptable range, replace the PAO titrant.

7.5 Required Standardization Documentation

The **Monthly Chlorine Amperometric (PAO) Titrant Standardization Record** on page 42 of this manual may be used to document each standardization procedure. The minimum requirements for documenting each verification procedure are as follows:

- a. Analyst(s) initials.
- b. Date standardization procedure was performed.
- c. Reagent water verification, free of chlorine.
- d. Volume of standard used (mL).
- e. Volume of PAO titrant used for the titrations (mL).
- f. Calculated normality (N) of PAO titrant.
- g. Comments.

Chlorine Analysis by Colorimetric/DPD Method

Quick Reference	Standard/Reagent	Requirements
Standard/Reagent/Equipment Storage	Commercially Available Ampules	Refrigerated
	Potassium Permanganate (KMnO ₄) 891.0 mg/L Standard	Refrigerated
	Potassium Permanganate (KMnO ₄) 89.1 mg/L Standard	NA
	Sealed DPD Powder Pillows	Room Temperature
	DPD Single Dose Dispensers	Room Temperature
	Liquid DPD Indicator	Room Temperature
Standard/Reagent Expiration	Standard/Reagent	Expiration
	Commercially Available Ampules	Manufacturer's Expiration Date
	Potassium Permanganate (KMnO ₄) 891.0 mg/L Standard	1 Year After Opening or Preparation
	Potassium Permanganate (KMnO ₄) 89.1 mg/L Standard	1 Day After Preparation
	Sealed DPD Powder Pillows	Manufacturer's Expiration Date
	DPD Single Dose Dispensers	6 Months After Opening
	Liquid DPD Indicator	6 Months After Opening
Required Quality Control	QC Procedure	Frequency
	Colorimeter Calibration Verification	Once Per Three Months
	Chlorine Free Reagent Water Verification	Once Per Three Months
Sample Collection	Preservation	Maximum Hold Time
	No Preservation Required	Analyze Immediately

Method Reference

Standard Methods 22nd Edition (4500-Cl G)

On-Site Survey Requirements

- Each certified analyst must be able to perform the calibration verification procedure described in Section 7.0 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 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

The DPD/Colorimetric method is the most frequently used method for the analysis of free and total chlorine concentrations in potable water. A sample of potable water is collected and a measured amount of chlorine indicator reagent (DPD) is added to the sample. The sample is then analyzed. Free chlorine is analyzed immediately after DPD is added, while total chlorine is analyzed 3-5 minutes after DPD is added.

Interferences

Bubbles introduced during the shaking of the sample 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 is rarely a factor in finished potable water.

Note: If free chlorine concentration is greater 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

- a. Electronic filter colorimeter or Spectrophotometer. The functional range of the colorimeter must accommodate the highest and lowest concentrations of chlorine observed throughout the distribution system.
- b. An adjustable microliter pipettor.
- c. Dedicated plastic or glass screw top container (250 to 1000 mL).
- d. Class A volumetric pipets.
- e. Class A volumetric flasks.
- f. Balance.

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 4-69, Section 3. Reagents)

- a. N,N-Diethyl-p-phenylenediamine Indicator (DPD): Commercially available in both powder and liquid.

Note: Liquid DPD indicators are suspected to be less stable than the solid DPD indicators. Replace liquid DPD indicator six months after opening or if the calibration verification results are not within the $\pm 10\%$ acceptance range.

- b. Reagent water.

- c. Ampule Chlorine Standard Solution: Commercially available from Hach Chemical Co. The concentration will vary with each lot. Opened ampules are stable for $\frac{1}{2}$ hour after opening. Discard unopened ampules on the manufacturer's expiration date.

- d. Optional: 891.0 mg/L Potassium Permanganate (KMnO₄) Stock Standard: Commercially available as 891.0 mg/L KMnO₄. This may be prepared in the laboratory as follows: Weigh 0.891 g of desiccated reagent grade KMnO₄ using an analytical balance. Add this to a 1 liter Class A volumetric flask, half filled with reagent water. Bring to volume with reagent water.

Note: This solution is equivalent to 1000 mg/L as chlorine. Discard one year after preparation.

- e. 89.1 mg/L Potassium Permanganate Working Standard: With a Class A volumetric pipet add 10.0 mL of the 891.0 mg/L KMnO₄ stock standard to a 100 mL volumetric flask, half filled with reagent water. Bring to volume with reagent water. This solution is equivalent to 100 mg/L of chlorine. (This solution must be prepared prior to each calibration verification procedure).

4.0 Sample Collection/Preservation/Holding Time

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

5.0 Chlorine Analysis Procedure (Hach Pocket Colorimeter)

This procedure is written for the Hach Pocket Colorimeter. Other chlorine analyzers may have unique procedures. Please consult the manufacturer's instructions for procedural details.

A. Free Chlorine

1. Run the sample tap for at least 5 minutes to maintain a constant concentration of chlorine 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 confirming that the index mark faces to the front of 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 shake for 10 seconds.
9. Place the vial in the colorimeter. Cover the vial.
10. Analyze the sample by pressing "READ".
11. Record the displayed result (in mg/L) as free chlorine.

B. Total Chlorine

1. Run the sample tap for at least 5 minutes to maintain a constant concentration of chlorine 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 confirming that the index mark faces to the front of 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 shake for 10 seconds.
9. Place the vial in the colorimeter. Cover the vial.
10. **Wait at least 3 minutes, but no more than 5 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

$$(2.2 \text{ mg/L Total Chlorine} - 1.6 \text{ mg/L Free Chlorine}) = 0.6 \text{ mg/L Combined Chlorine}$$

6.0 Quality Control Requirements

6.1 DPD Colorimeter Calibration Verification.

The verification must be completed prior to initial use for analyzing potable water and at least once every three months thereafter. (Refer to Section 7.0.) 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 ampules of free chlorine standards; and, (2) Prepared potassium permanganate (KMnO_4) solution at a concentration of 89.1 mg/L. (This is equivalent to 100 mg/L as chlorine.)

The spike concentrations prepared for the calibration verification must span the range of chlorine concentrations observed throughout the entire distribution system. For example: If the lowest concentration of chlorine 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 must be higher than 2.0 mg/L. The three additional spikes will be prepared at concentrations between the lowest and highest spike concentrations.

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

All certified analysts are required to participate in the calibration verification procedure at least once every three months. (Refer to Sections 7.0 -7.3.) Calibration verifications must be dated and initialed by all participating certified analysts.

Operationally Certified Analyst Requirements

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

7.0 DPD Colorimeter Calibration Verification Procedure

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 one total chlorine DPD indicator to the reagent water.

4. Wait three minutes.
5. Read the reagent water result displayed by colorimeter.
6. If the total chlorine is less than 0.1 mg/L, then proceed to the next step. If it is greater than or equal to 0.1 mg/L, then 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 sample blank with a known volume of standard. Add a free chlorine DPD indicator to the ampule standard or a total DPD indicator to the KMnO₄ standard.
9. Mix thoroughly. Analyze immediately if standardizing with ampule standards (free chlorine DPD). Analyze the sample after 3 minutes if standardizing with KMnO₄ (total chlorine DPD). 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.)
10. Adjust the microliter pipettor to the next spike volume.
11. Repeat Steps 7 through 10 using five different standard concentrations which must span the range of chlorine concentrations observed throughout the distribution system.

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.

7.1 Expected Calculations for Calibration Verification

A. Calibration Verification with Ampule Chlorine Standard

Concentrations are unique to each Lot number. Calculations will need to 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:

$$\frac{(\text{Standard Concentration mg/L}) \times (\text{Volume of Spike Added in microliters})}{(\text{Volume of Water in microliters}) + (\text{Volume of Spike Added in microliters})} = \text{Expected Concentration}$$

Note: 10 mL = 10000 µL (mL= milliliter, µL= microliter)

Examples: (The following examples assume the ampule standard concentration is 65.35 mg/L)

$$\text{Spike with 50 } \mu\text{L} \quad \frac{(65.35 \text{ mg/L}) \times (50 \text{ } \mu\text{L})}{(10000 \text{ } \mu\text{L}) + (50 \text{ } \mu\text{L})} = 0.32 \text{ mg/L}$$

$$\text{Spike with 150 } \mu\text{L} \quad \frac{(65.35 \text{ mg/L}) \times (150 \text{ } \mu\text{L})}{(10000 \text{ } \mu\text{L}) + (150 \text{ } \mu\text{L})} = 0.97 \text{ mg/L}$$

$$\text{Spike with 250 } \mu\text{L} \quad \frac{(65.35 \text{ mg/L}) \times (250 \text{ } \mu\text{L})}{(10000 \text{ } \mu\text{L}) + (250 \text{ } \mu\text{L})} = 1.59 \text{ mg/L}$$

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

Example: (The following example assumes a sample vial volume of 25 mL and a dilution factor of 2.5)

$$\text{Spike with 150 } \mu\text{L} \quad \frac{(65.35 \text{ mg/L}) \times (150 \text{ } \mu\text{L})}{(25000 \text{ } \mu\text{L}) + (150 \text{ } \mu\text{L})} = 0.39 \text{ mg/L}$$

Multiply by the dilution factor: $0.39 \text{ mg/L} \times 2.5 = 0.97 \text{ mg/L}$

B. Calibration Verification with 89.1 mg/L KMnO₄ (Equivalent to 100 mg/L as chlorine)

The chart below provides examples of some spike volume/expected concentrations for the 89.1 mg/L KMnO₄ standard. Verification spike volumes should be adjusted to bracket the chlorine concentrations observed in the distribution system.

89.1 mg/L KMnO ₄ (Equivalent to 100 mg/L as chlorine)							
Spike Vol (μl)	Expected Concentration:			Spike Vol (μl)	Expected Concentration:		
	5 mL Vial	10 mL Vial	25 mL Vial		5 mL Vial	10 mL Vial	25 mL Vial
20	0.40 mg/L	0.20 mg/L	NA	110	2.15 mg/L	1.09 mg/L	NA
25	0.50 mg/L	0.25 mg/L	0.10 mg/L	125	2.44 mg/L	1.23 mg/L	0.50 mg/L
30	0.60 mg/L	0.30 mg/L	NA	140	2.72 mg/L	1.38 mg/L	NA
40	0.79 mg/L	0.40 mg/L	NA	150	2.91 mg/L	1.48 mg/L	0.60 mg/L
50	0.99 mg/L	0.50 mg/L	0.20 mg/L	160	3.10 mg/L	1.57 mg/L	NA
60	1.18 mg/L	0.60 mg/L	NA	170	3.29 mg/L	1.67 mg/L	NA
70	1.38 mg/L	0.70 mg/L	NA	175	3.38 mg/L	1.72 mg/L	0.70 mg/L
75	1.48 mg/L	0.74 mg/L	0.30 mg/L	180	3.47 mg/L	1.77 mg/L	NA
80	1.57 mg/L	0.79 mg/L	NA	190	3.66 mg/L	1.86 mg/L	NA
90	1.77 mg/L	0.89 mg/L	NA	200	3.85 mg/L	1.96 mg/L	0.79 mg/L
100	1.96 mg/L	0.99 mg/L	0.40 mg/L				

Note: Refer to Section 7.2 of this method for acceptance limit calculations.

7.2 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. If the observed concentration results are outside the acceptable range, the colorimeter must be serviced or replaced.

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

Then: **-10% of 0.97 mg/L: $0.97 \text{ mg/L} \times 0.9 = 0.87 \text{ mg/L}$ (Lowest Acceptable Observed Conc.)**

+10% of 0.97 mg/L: $0.97 \text{ mg/L} \times 1.1 = 1.07 \text{ mg/L}$ (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.**

7.3 Required Verification Documentation

The **Three Month DPD Colorimeter Calibration Verification Record** page 51 of this manual may be used to document each verification procedure. The minimum requirements for documenting each

verification procedure are as follows:

- a. Analyst(s) initials.
- b. Date verification procedure was performed.
- c. Stock standard concentration (mg/L).
- d. Stock standard expiration date.
- e. Spike volume (Volume in μL of stock standard added to 10.0 mL reagent water).
- f. Calculated concentration (mg/L).
- g. Observed concentration (mg/L).
- h. Comments.
- i. Reagent Water Result.

8.0 In-line Chlorine Meter Verification

In-line chlorine meter results must be verified with the results recorded by the bench top chlorine meter 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 bench top chlorine meter 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 $\pm 10\%$ of results attained from a calibrated bench top chlorine meter. If results are not within $\pm 10\%$, follow manufacturer's instructions to adjust the in-line meter to coincide with the chlorine result from the calibrated bench top chlorine meter 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 bench top chlorine meter must be recorded. The **Daily In-line Chlorine Meter Verification Record** on page 52 of this manual may be used to document the required information.

8.1 In-Line Chlorine Meter Calibration

The Laboratory Certification Section recommends in-line meters be calibrated once every 90 days not to exceed manufacturer's calibration requirements.

9.0 Certification of Field Personnel for Chlorine Analysis

Field personnel limited to conducting chlorine analysis in the distribution system or in accordance with sampling water for microbiological testing are exempt from the need to be certified for chlorine analysis as long as the chlorine analysis is conducted via the colorimetric/DPD method. However, these personnel are required to undergo a five day training in chlorine sample collection and analysis with an analyst certified in chlorine sampling and analysis. This training must be completed prior to reporting chlorine results and documented using the **Distribution System Training Record** for Chlorine Analysis located on page 53 of this manual.

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		

Chlorine Analysis by DPD/FAS Titration Method

Quick Reference	Standard/Reagent	Requirements
Standard/Reagent Storage	Liquid Reagents	Room Temperature
	Standards	Refrigerated
Standard/Reagent Expiration	Standard/Reagent	Maximum Storage Time
	Reagents	1 Year After Opening/Manufacturer's Expiration Date
	Standards	1 Year After Opening/Manufacturer's Expiration Date
Required Quality Control	QC Procedure	Frequency
	FAS Titrant Standardization	Once Per Month
	Blank Color Reference	Once Per Month
Sample Collection	Preservation	Maximum Hold Time
	No Preservation Required	Analyze Immediately

Method Reference

Standard Methods 22nd Edition (4500-Cl F)

On-Site Survey Requirements

- Each certified analyst must be able to perform the FAS titrant standardization described in Section 7.0 of 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

The DPD/FAS (ferrous ammonium sulfate) titration is completed where complete differentiation of chlorine species is not required. The procedure may be simplified to give only free and combined chlorine or total chlorine.

Note: In the DPD/FAS titration, the endpoint for each analyte is reached when the pink color created by the addition of DPD dissipates, leaving the sample colorless.

Interferences

Suspended solids, precipitates and dirty glassware may affect results.

2.0 Equipment

- a. 25 to 50 mL digital or self-zeroing automatic burette.

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

- b. 2.0 mL and 10.0 mL Class A volumetric pipet(s).
- c. Titration vessels of appropriate volume.
- d. Graduated cylinders (50 to 100 mL).
- e. Magnetic stirring device & stirring bars.
- f. Balance.

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 4-67 & 68, Section 2. Reagents)

- a. Phosphate Buffer Solution: Commercially available.
- b. N,N-Diethyl-p-phenylenediamine (DPD) Indicator Solution: Commercially available.
- c. Ferrous Ammonium Sulfate (FAS) Titrant (0.00282N): Commercially available.
- d. Potassium Iodide (KI) crystals.
- e. Potassium Iodide (KI) Solution: Commercially available.
- f. Glycine Solution: Commercially available.
- g. Barium Diphenylaminesulfonate: Commercially available.
- h. Sodium Arsenite Solution: Commercially available.
- i. Thioacetamide Solution: Commercially available. CAUTION: Cancer suspect agent. Take care to avoid skin contact or ingestion.
- j. Barium Chloride crystals.

- k. Sulfuric Acid Solution (10%).
- l. Reagent water.

4.0 Sample Collection/Preservation/Holding Time

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

5.0 Free Chlorine, Monochloramine, Dichloramine and Total Chlorine Analysis Procedure

Note: Free chlorine, monochloramine, dichloramine and total chlorine analysis will use the same 100 mL volume of sample collected. Procedures must be followed consecutively

Free Chlorine Analysis Procedure

1. Measure a 100 mL sample in a beaker.
2. Add 5.0 mL DPD indicator solution and 5.0 mL phosphate buffer solution to this titration flask.
3. Titrate this solution rapidly with FAS titrant until red/pink color dissipates leaving the sample colorless.
4. Record the volume of FAS titrant needed to reach endpoint (record this as Reading **A**).
5. Keep this solution for total chlorine analysis, go to Step 6.

Total Chlorine Analysis Procedure

6. To the titration flask from Step 5 add 1 g KI crystals to the solution and mix.
7. Let stand for 2 minutes.
8. Do not refill the burette. Titrate this solution rapidly with FAS titrant until red/pink color dissipates leaving the sample colorless.
9. Record the volume of FAS titrant needed to reach endpoint (record this as Reading **C**).

5.1 Calculations

Note: For a 100 mL sample, 1.00 mL FAS titrant needed to reach endpoint of titration = 1.0 mg available chlorine (Example: 1.20 mL FAS titrant needed to reach endpoint = 1.20 mg available chlorine).

Free Chlorine Calculation: Free chlorine mg/L = Reading **A**

Example

Reading **A** = 0.60 mL (This equals 0.6 mg)

0.60 mg/L = 0.60 mg/L Free chlorine

Total Available Chlorine Calculation: Total available chlorine mg/L = Reading **C**

Example

Reading **C** = 1.00 mL (This equals 1.00 mg)

1.0 mg/L = 1.00 mg/L Total chlorine

6.0 Quality Control Requirements

6.1 Titrant Standardizations

The titrant standardization procedure must be performed prior to initial use for analyzing potable water and at least once per month thereafter. (Refer to Section 7.0.) Each standardization procedure must be dated and recorded.

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the titrant standardization procedure at least once per month. (Refer to Section 7.0.) 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 Titrant Standardization Procedure

7.1 Blank (Verification of Endpoint Color)

1. Add 100 mL of reagent water to a titrating flask.
2. Slowly add 15 mL of sulfuric acid solution (10%) to the flask.
3. Add 2 to 3 drops of ferroin indicator solution to the flask and mix.
4. Titrate to orange endpoint color with FAS titrant.
5. Keep this flask as a reference color for the titrant standardization procedure.

7.2 Titrant Standardization Procedure

1. Add 100 mL of reagent water to a titrating flask.
2. Slowly add 15 mL of sulfuric acid solution (10%) to the flask.
3. Add 2 to 3 drops of ferroin indicator solution to the flask and mix.
4. Using a volumetric pipet, add 2.0 mL of potassium dichromate solution (0.0025 N) to the flask.

Note: If using a 10 mL burette for daily analysis, add 10 mL and standardize to 10 mL potassium dichromate solution (0.0025 N).

5. Titrate to orange endpoint color with FAS titrant, using the blank titrated in Section 7.1 as reference for the endpoint color.
6. Repeat Steps 1 through 5 for the second titrant standardization.

7.3 Titrant Standardization Acceptance Limits

The acceptable range for the adjusted amount of titrant used is $\pm 5\%$ of true value.

The true value of FAS titrant needed to reach endpoint for 2.0 mL potassium dichromate solution (0.0025 N) equals 1.77 mL. The acceptable range is (1.68 to 1.86 mL).

The true value of FAS titrant needed to reach endpoint for 10.0 mL potassium dichromate solution (0.0025 N) equals 8.86 mL. The acceptable range is (8.42 to 9.30 mL).

If the amount of the laboratory prepared FAS titrant needed to reach endpoint is outside of the acceptable range replace the titrant or calculate a correction factor.

7.4 Correction Factor (Used only for laboratory prepared titrant.)

The correction factor adjusts the calculation for the concentration of titrant used, either 2 mL or 10 mL.

Three titrant checks must be performed for one of the two calculations as follows:

Endpoint of 2 mL

$$\frac{2.0 \text{ mL}}{\text{Average of Three Titrations (mL)}} = \text{Correction Factor}$$

Endpoint of 10 mL

$$\frac{10.0 \text{ mL}}{\text{Average of Three Titrations (mL)}} = \text{Correction Factor}$$

Multiply all titration volumes performed with titrant associated with its correction factor.

Note: Do not use correction factors on purchased titrants. They must be within range or replaced.

7.5 Required Standardization Documentation

The **Monthly Chlorine DPD/FAS Titrant Standardization Record** on page 60 of this manual may be used to document each standardization procedure. The minimum requirements for documenting each standardization procedure are as follows:

- a. Analyst(s) initials.
- b. Date standardization procedure was performed.
- c. Identify if a blank reference was used (yes/no).
- d. Volume of reagent water used (mL).
- e. Volume of standard used (mL).
- f. Volume of FAS titrant used for titrations 1 and 2 (mL).
- g. The third titration value and correction factor if used.
- h. Comments.

Chlorine Dioxide Analysis by DPD/Spectrophotometric Method

Quick Reference	Standard/Reagent	Requirements
Standard/Reagent Storage	Liquid Reagents	Room Temperature
	Standards	Refrigerated
Standard/Reagent Expiration	Standard/Reagent	Maximum Storage Time
	Reagents	1 Year After Opening/Manufacturer's Expiration Date
	Standards	1 Year After Opening/Manufacturer's Expiration Date
Required Quality Control	QC Procedure	Frequency
	Generate Calibration Curve	Once Per 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
	No Preservation Required	Analyze Immediately

Method Reference

Standard Methods 19th and 20th Editions (4500-ClO₂ D), Reserved - 22nd Edition

On-Site Survey Requirements

- Each certified analyst must be able to generate a calibration curve described in Section 7.0 of 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 is an extension of the DPD method for determining free chlorine and chloramine in water. Chlorine dioxide reacts to one fifth of its concentration with DPD to produce a red color which can be read on a spectrophotometer and compared to a standard curve. Glycine is used to suppress the free available chlorine. Based on the DPD reaction with chlorine, the values of other forms of available residual chlorine can be determined. Free, combined, total, monochloramine, dichloramine and chlorite can all be determined through this method, if needed.

Interferences

Turbidity and water color may interfere with the determination of the absorbance contribution from DPD. Oxidized manganese is the most significant source of interference, but this is typically not a problem in finished drinking water. Interference of copper levels up to approximately 10 mg/L is overcome by the EDTA in the DPD solution. The EDTA also helps the stability the DPD solution.

2.0 Equipment

- a. A spectrophotometer capable of reading 515 nm with a cell light path width of at least 1 cm.
- b. Spectrophotometer vials.
- c. Computer with software capable of generating linear regressions.
- d. Class A volumetric pipet(s) or microliter pipettor.
- e. Titration vessels of appropriate volume.
- f. Standard laboratory glassware.

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 4-81)

- a. Phosphate Buffer Solution: Add 24.0 g anhydrous Na_2HPO_4 and 46.0 g anhydrous KH_2PO_4 in a 1 liter Class A volumetric flask, half filled with reagent water. Add 0.8 g disodium EDTA to the 1 liter volumetric flask. Bring to volume with reagent water. Add 0.0020 g HgCl_2 as a preservative. Store in an amber glass container.
- b. N,N-Diethyl-p-phenylenediamine (DPD) Indicator Solution: Commercially available. Alternatively, prepare as follows: Dissolve 1.0 g DPD oxalate, or 1.5 g DPD sulfate pentahydrate, or 1.1 g anhydrous DPD sulfate in chlorine free reagent water containing 8 mL of 1 + 3 H_2SO_4 (2 mL water + 6 mL H_2SO_4) and 0.2 g disodium EDTA. Dilute to 1 liter and store in an amber glass container.
- c. 891.0 mg/L Potassium Permanganate (KMnO_4) Stock Standard: Commercially available. This may be prepared in the laboratory as follows: Weigh 0.891g of desiccated reagent grade KMnO_4 using an analytical balance. Add this to a 1 liter Class A volumetric flask, half filled with reagent water. Bring to volume with reagent water.

Note: This solution is equivalent to 1000 mg/L as chlorine. Discard one year after preparation.

- d. 89.1 mg/L Potassium Permanganate (KMnO_4) Calibration Standard: With a class A volumetric pipet add 10.0 mL of the 891.0 mg/L KMnO_4 stock standard to a 100 mL volumetric flask, half

filled with reagent water. Bring to volume with reagent water. This solution is equivalent to 100 mg/L of chlorine. (This solution must be prepared prior to each calibration curve construction.)

- e. Potassium Iodide (KI) crystals.
- f. Glycine Solution: Add 10 g glycine (amino acetic acid) in a 100 mL volumetric flask, half filled with reagent water. Bring to volume with reagent water.
- g. 5% Sulfuric Acid Solution: Add 5 mL concentrated H₂SO₄ to a 100 mL volumetric flask, half filled with reagent water. Bring to volume with reagent water.
- h. Sodium Bicarbonate Solution: Dissolve 27.5 g Na₂HCO₃ in a 100 mL volumetric flask, half filled with reagent water. Bring to volume with reagent water.
- i. Sodium Arsenite (NaAsO₂) Solution (Recommended for Interference suppression if needed): Add 0.5 g NaAsO₂ to a 100 mL volumetric flask, half filled with reagent water. Bring to volume with reagent water. CAUTION: Toxic. Take care to avoid ingestion.
- j. Thioacetamide Solution: Add 0.250 g CH₃CSNH₂ to a 100 mL volumetric flask, half filled with reagent water. CAUTION: Suspected carcinogen. Take care to avoid skin contact or ingestion.
- k. Reagent water.

4.0 Sample Collection/Preservation/Holding Time

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

5.0 Chlorine Dioxide, Free Chlorine, Monochloramine, Dichloramine and Total Chlorine Analysis Procedure

Chlorine Dioxide (ClO₂) Analysis Procedure

1. Measure a 100 mL sample into an Erlenmeyer flask.
2. Add 2 mL glycine solution, put this flask aside.
3. In a separate flask add 5.0 mL of phosphate buffer solution and 5.0 mL DPD indicator solution.
4. Add the flask containing the 100 mL sample/2 mL glycine solution to the flask from Step 3 and mix. Analyze immediately.
5. Read the absorbance and concentration at 515 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.
6. Record this as Reading **G**. The **Chlorine Dioxide DPD/Spectrophotometer Analysis Record**

on page 69 of this manual may be used to document the required information.

7. Discard solution.

Note: Free chlorine, monochloramine, dichloramine and total chlorine analysis will use the same 100 mL volume of sample collected. Procedures must be followed consecutively.

Free Chlorine Analysis Procedure

1. Measure a 100 mL sample in a flask.
2. Add 5.0 mL phosphate buffer and 5.0 mL DPD indicator solution to this flask.
3. Pour into the spectrophotometer vial and read absorbance at 515 nm.
4. Record this as reading **A**.
5. Pour contents of spectrophotometer vial back into flask. Keep this solution for the monochloramine analysis in Step 6.

Monochloramine (NH₂Cl) Analysis Procedure

6. To the flask from Step 5 add 1 crystal of KI (solid) or 2 drops of KI solution and mix.
7. Pour into the spectrophotometer vial and read absorbance at 515 nm.
8. Record this as reading **B**.
9. Pour contents of spectrophotometer vial back into flask. Keep this solution for the dichloramine analysis in Step 10.

Dichloramine (NHCl₂) Analysis Procedure

10. To the flask in Step 9 add 1 g KI crystals (solid) to the solution and mix.
11. Let stand for 2 minutes.
12. Pour into the spectrophotometer vial and read absorbance at 515 nm.
13. Record this as Reading **C**.
14. Pour contents of spectrophotometer vial back into flask. Keep this solution for the total available chlorine including chlorite analysis in Step 15.

Total Available Chlorine Including Chlorite (ClO₂⁻) Analysis Procedure

15. To the flask from Step 14 add 1 mL (10%) H₂SO₄ solution.
16. Let stand for 2 minutes.
17. Add 5.0 mL NaHCO₃, mix this solution.
18. Pour into the spectrophotometer vial and read absorbance at 515 nm.
19. Record this as Reading **D**.

Plot Sample Concentration

Read the absorbance at 515 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.

5.1 Calculations

Chlorine Dioxide Calculation (ClO₂): Chlorine dioxide mg/L = 5 x Reading **G** (or 1.9 x Reading **G**, expressed as ClO₂)

Example

Reading **G** = 0.20 mg/L

$$5 \times 0.20 \text{ mg/L} = 1.0 \text{ mg/L Chlorine dioxide}$$

Free Chlorine Calculation: Free chlorine mg/L = Reading **A** – Reading **G**

Example

Reading **A** = 0.60 mg/L

Reading **G** = 0.20 mg/L

$$0.60 \text{ mg/L} - 0.20 \text{ mg/L} = 0.40 \text{ mg/L Free chlorine}$$

Monochloramine Calculation (NH₂Cl): Monochloramine mg/L = Reading **B** – Reading **A**

Example

Reading **A** = 0.60 mg/L

Reading **B** = 0.80 mg/L

$$0.80 \text{ mg/L} - 0.60 \text{ mg/L} = 0.20 \text{ mg/L Monochloramine}$$

Dichloramine Calculation (NHCl₂): Dichloramine mg/L = Reading **C** – Reading **B**

Example

Reading **B** = 0.80 mg/L

Reading **C** = 1.00 mg/L

$$1.00 \text{ mg/L} - 0.80 \text{ mg/L} = 0.20 \text{ mg/L Dichloramine}$$

Total Available Chlorine Calculation: Total available chlorine mg/L = Reading **C** + 4 x Reading **G**

Example

Reading **C** = 1.00 mg/L

Reading **G** = 0.20 mg/L

$$1.0 \text{ mg/L} + (4 \times 0.20 \text{ mg/L}) = 1.80 \text{ mg/L Total chlorine}$$

Chlorite Calculation (ClO_2^-): mg/L (D) = Chlorite mg/L = Reading D – [Reading C + (4 x Reading G)]

Example

Reading D = 2.00 mg/L

Reading C = 1.00 mg/L

Reading G = 0.20 mg/L

$$2.0 \text{ mg/L} - [1.00 \text{ mg/L} + (4 \times 0.20 \text{ mg/L})] = 0.20 \text{ mg/L Chlorite}$$

6.0 Quality Control Requirements

6.1 Calibration Curve Generation

The calibration curve generation procedure must be performed prior to initial use for analyzing potable water and at least once per three months thereafter. (Refer to Section 7.0.) Each calibration curve generation procedure must be dated and recorded.

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

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the calibration curve generation procedure at least once per 3 months. (Refer to Section 7.0.) 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.

6.3 QC Requirements with Each Analysis

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

- a. Blank (0.0 mg/L). Acceptance: Results < reporting limit.
- b. Reporting limit verification (0.50 mg/L). Acceptance: $\pm 30\%$ of true value.
- c. Midpoint calibration verification (0.99 mg/L). Acceptance: $\pm 10\%$ of true value.

Note: A blank sample is required with each sample analysis. QC samples b and c are required only if an entire calibration curve is not analyzed/digested and generated with the sample batch.

7.0 Calibration Curve Generation Procedure

A minimum of four 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 chlorine dioxide (0.50 mg/L). Alternatively, a reporting limit verification sample must be prepared in

addition to the four calibration standard concentrations if the curve generation does not include the reporting limit concentration (0.50 mg/L). The reporting limit verification sample results must be within \pm 30% of the true value.

1. Prepare four 100 mL volumetric flasks containing a known volume of 89.1 mg/L KMnO_4 Calibration Standard Solution and reagent water according to the table in Section 7.2. Label each flask with the calibration standard it contains.
2. Prepare a blank by adding 100 mL reagent water to a volumetric flask.
3. Pour standards and blank into labeled Erlenmeyer flasks.
4. Add 2.0 mL glycine solution to each of the flasks, then put these flasks aside.
5. In separate flasks labeled to correspond with the calibration standards, add 5.0 mL of phosphate buffer solution and 5.0 mL DPD indicator solution to each.
6. Add each of the flasks containing the blank and 100 mL calibration standard/2 mL glycine solution to their corresponding flasks from Step 5 and mix.
7. Read absorbance of each calibration standard and blank at 515 nm on a spectrophotometer. Follow the spectrophotometer manufacturer's instructions to generate and store a calibration curve using the blank and prepared calibration concentration points.
8. If the spectrophotometer does not have the capability to store calibration curves, read absorbance for each calibration standard at 515 nm on spectrophotometer. Record absorbance.
9. Using absorbance and concentration of each calibration curve point, generate a calibration curve manually on an Excel spreadsheet.

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). In order 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

89.1 mg/L KMnO_4 calibration standard will be used as the standard added to each flask to generate the calibration standards. The recommended calibration concentrations to generate a curve are as follows: blank (0.0 mg/L), 0.10 mg/L, 0.50 mg/L, 0.99 mg/L and 1.48 mg/L. The table in Section 7.2 demonstrates how these standards are prepared in 100 mL volumetric flasks.

7.2 Calibration Standard Concentration Preparation Table

Calibration Standard Concentration	mL of 89.1 mg/L KMnO ₄ Calibration Standard Added to 100 mL Flask	Final Volume
Blank (0.0 mg/L)	0.00 mL	100 mL
0.10 mg/L	0.10 mL	100 mL
0.50 mg/L	0.50 mL	100 mL
1.00 mg/L	1.00 mL	100 mL
1.50 mg/L	1.50 mL	100 mL

7.3 Required Calibration Curve Generation Documentation

The **Chlorine Dioxide DPD/Spectrophotometer QC Sample Record** on page 70 of this manual may be used to document the required information. The minimum requirements for documenting each calibration curve generation procedure are as follows:

- a. Analyst(s) initials.
- b. Analysis date.
- c. Blank concentration (mg/L).
- d. Reporting limit concentration (mg/L).
- e. Midpoint concentration (mg/L).
- f. Date calibration curve generated.
- g. Comments.

Chlorine Dioxide Analysis by DPD/FAS Titration Method

<i>Quick Reference</i>	Standard/Reagent	Requirements
Standard/Reagent Storage	Liquid Reagents	Room Temperature
	Standards	Refrigerated
Standard/Reagent Expiration	Standard/Reagent	Maximum Storage Time
	Reagents	1 Year After Opening/Manufacturer's Expiration Date
	Standards	1 Year After Opening/Manufacturer's Expiration Date
Required Quality Control	QC Procedure	Frequency
	FAS Titrant Standardization	Once Per Month
	Blank Color Reference	Once Per Month
Sample Collection	Preservation	Maximum Hold Time
	No Preservation Required	Analyze Immediately

Method Reference

Standard Methods 19th and 20th Editions (4500-ClO₂ D), Reserved - 22nd Edition

On-Site Survey Requirements

- Each certified analyst must be able to perform the FAS titrant standardization described in Section 7.0 of 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

The DPD/FAS (ferrous ammonium sulfate) titration is completed in several successive steps to determine chlorine dioxide, free chlorine, monochloramine, dichloramine and total chlorine.

Note: In the DPD/FAS titration, the endpoint for each analyte is reached when the pink color created by the addition of DPD dissipates, leaving the sample colorless.

Interferences

Suspended solids, precipitates and dirty glassware may affect results.

2.0 Equipment

- a. 25-50 mL digital or self-zeroing automatic burette.

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

- b. 2.0 mL and 10.0 mL Class A volumetric pipet(s).
- c. Titration vessels of appropriate volume.
- d. Graduated cylinders (50 to 100 mL).
- e. Magnetic stirring device & stirring bars.
- f. Balance.

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 4-81)

- a. Phosphate Buffer Solution: Commercially available.
- b. DPD Indicator Solution: Commercially available.
- c. Ferrous Ammonium Sulfate (FAS) Titrant (0.00282 N): Commercially available.
- d. Potassium Iodide, KI crystals.
- e. Potassium Iodide Solution: Commercially available.
- f. Glycine Solution: Commercially available.
- g. Sulfuric Acid Solution (10% or 4N): Commercially available.
- h. Sodium Bicarbonate Solution: Commercially available.
- i. Disodium Salt of Ethylenediamine Tetracetic Acid (EDTA): Commercially available as a solid.
- j. Potassium Dichromate ($K_2Cr_2O_7$) Solution (0.100 N): Add 4.904 g potassium dichromate to a 1 liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.

- k. Potassium Dichromate ($K_2Cr_2O_7$) Solution (0.0025 N): Add 25.0 mL potassium dichromate solution (0.100 N) to a 1 liter volumetric flask, half filled with reagent water. Bring to volume with reagent water.

Note: This solution must be newly prepared for each standardization.

- l. Ferroin Indicator Solution: Add 1.485 g 1,10-phenanthroline monohydrate and 0.695 g ferrous sulfate ($FeSO_4 \cdot 7H_2O$) to a 100 mL volumetric flask, half filled with reagent water. Bring to volume with reagent water.
- m. Reagent water.

4.0 Sample Collection/Preservation/Holding Time

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

5.0 Chlorine Dioxide, Free Chlorine, Monochloramine, Dichloramine and Total Chlorine Analysis Procedure

Chlorine Dioxide (ClO_2) Analysis Procedure

1. Measure a 100 mL sample in a beaker.
2. Add 2 mL glycine solution, put this beaker aside.
3. In a separate titration flask add 5 mL of phosphate buffer solution, 5 mL DPD indicator solution and approximately 200 mg EDTA crystals.
4. Add the beaker containing the 100 mL sample/2 mL glycine solution to the titration flask.
5. Titrate this solution rapidly with FAS titrant until red/pink color dissipates leaving the sample colorless.
6. Record the volume of FAS titrant (record this as Reading **G**). The **Chlorine Dioxide DPD/FAS Analysis Record** on page 78 may be used to document the required information.
7. Discard solution.

Note: Free chlorine, monochloramine, dichloramine and total chlorine analysis will use the same 100 mL volume of sample collected. Procedures must be followed consecutively.

Free Chlorine Analysis Procedure

1. Measure a 100 mL sample in a beaker.
2. Add about 200 mg EDTA crystals and 5 mL DPD indicator solution to this titration flask.

3. Titrate this solution rapidly with FAS titrant until red/pink color dissipates leaving the sample colorless.
4. Record the volume of FAS titrant (record this as Reading **A**).
5. Keep this solution for the monochloramine analysis in Step 6.

Monochloramine (NH₂Cl) Analysis Procedure

6. To the titration flask from Step 5 add 1 crystal of KI (solid) or 2 drops of KI solution and mix.
7. Titrate this solution rapidly with FAS titrant until red/pink color is dissipates leaving the sample colorless.
8. Record the volume of FAS titrant (record this as Reading **B**).
9. Keep this solution for the dichloramine analysis in Step 10.

Dichloramine (NHCl₂) Analysis Procedure

10. To the titration flask from Step 9 add 1 g KI crystals (solid) to the solution and mix.
11. Let stand for 2 minutes.
12. Titrate this solution rapidly with FAS titrant until red/pink color dissipates leaving the sample colorless.
13. Record the volume of FAS titrant (record this as Reading **C**).
14. Keep this solution for the total chlorine analysis in Step 15.

Total Available Chlorine Including Chlorite (ClO₂⁻) Analysis Procedure

15. To the titration flask from Step 14 add 1 mL (10%) H₂SO₄ solution.
16. Let stand for 2 minutes.
17. Add 5.0 mL NaHCO₃, mix this solution.
18. Titrate this solution rapidly with FAS titrant until red/pink color dissipates leaving the sample colorless.
19. Record the volume of FAS titrant (record this as Reading **D**).

5.1 Calculations

Note: For a 100 mL sample, 1.00 mL FAS titrant needed to reach endpoint of titration = 1.0 mg available chlorine (Example: 1.20 mL FAS titrant needed to reach endpoint = 1.20 mg available chlorine).

Chlorine Dioxide Calculation (ClO_2): Chlorine dioxide mg/L = 5 x Reading **G** (or 1.9 x Reading **G** expressed as ClO_2)

Example

Reading **G** = 0.20 mL (This equals 0.2 mg)

$$5 \times 0.20 \text{ mg/L} = 1.0 \text{ mg/L Chlorine dioxide}$$

Free Chlorine Calculation: Free chlorine mg/L = Reading **A** – Reading **G**

Example

Reading **A** = 0.60 mL (This equals 0.6 mg)

Reading **G** = 0.20 mL (This equals 0.2 mg)

$$0.60 \text{ mg/L} - 0.20 \text{ mg/L} = 0.40 \text{ mg/L Free chlorine}$$

Monochloramine Calculation (NH_2Cl): Monochloramine mg/L = Reading **B** – Reading **A**

Example

Reading **A** = 0.60 mL (This equals 0.60 mg)

Reading **B** = 0.80 mL (This equals 0.80 mg)

$$0.80 \text{ mg/L} - 0.60 \text{ mg/L} = 0.20 \text{ mg/L Monochloramine}$$

Dichloramine Calculation (NHCl_2): Dichloramine mg/L = Reading **C** – Reading **B**

Example

Reading **B** = 0.80 mL (This equals 0.80 mg)

Reading **C** = 1.00 mL (This equals 1.00 mg)

$$1.00 \text{ mg/L} - 0.80 \text{ mg/L} = 0.20 \text{ mg/L Dichloramine}$$

Total Available Chlorine Calculation: Total available chlorine mg/L = Reading **C** + 4 x Reading **G**

Example

Reading **C** = 1.00 mL (This equals 1.00 mg)

Reading **G** = 0.20 mL (This equals 0.20 mg)

$$1.0 \text{ mg/L} + (4 \times 0.20 \text{ mg/L}) = 1.80 \text{ mg/L Total chlorine}$$

Chlorite Calculation (ClO_2^-): mg/L (**D**) = Chlorite mg/L = Reading **D** – [Reading **C** + (4 x Reading **G**)]

Example

Reading **D** = 2.00 mL (This equals 2.0 mg)

Reading **C** = 1.00 mL (This equals 1.00 mg)

Reading **G** = 0.20 mL (This equals 0.20 mg)

$$2.0 \text{ mg/L} - (1.00 \text{ mg/L} + (4 \times 0.20 \text{ mg/L})) = 0.20 \text{ mg/L Chlorite}$$

6.0 Quality Control Requirements

6.1 Titrant Standardizations

The titrant standardization procedure must be performed prior to initial use for analyzing potable water and at least once per month thereafter. (Refer to Section 7.0.) Each standardization procedure must be dated and recorded.

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the titrant standardization procedure at least once per month. (Refer to Section 7.0.) 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 Titrant Standardization Procedure

7.1 Blank (Verification of Endpoint Color)

1. Add 100 mL of reagent water to a titrating flask.
2. Slowly add 15 mL of 10% sulfuric acid solution to the flask.
3. Add 2 to 3 drops of ferroin indicator solution to the flask and mix.
4. Titrate to orange endpoint color with FAS titrant.
5. Keep this flask as a reference color for the titrant standardization procedure.

7.2 Titrant Standardization Procedure

1. Add 100 mL of reagent water to a titrating flask.
2. Slowly add 15 mL of 10% sulfuric acid solution to the flask.
3. Add 2 to 3 drops of ferroin indicator solution to the flask and mix.
4. Using a volumetric pipet, add 2.0 mL of potassium dichromate solution (0.0025 N) to the flask.

Note: If using a 10 mL burette for daily analysis, add 10.0 mL and standardize to 10 mL potassium dichromate solution (0.0025 N).

5. Titrate to orange endpoint color with FAS titrant using the blank titrated in Section 7.1 as reference for the endpoint color.
6. Repeat Steps 1 through 5 for the second titrant standardization.

7.3 Titrant Standardization Acceptance Limits

The acceptable range for the adjusted amount of titrant used is $\pm 5\%$ of true value.

The true value of FAS titrant needed to reach endpoint for 2.0 mL potassium dichromate solution (0.0025 N) equals 1.77 mL. The acceptable range is 1.68 to 1.86 mL.

The true value of FAS titrant needed to reach endpoint for 10.0 mL potassium dichromate solution (0.0025 N) equals 8.86 mL. The acceptable range is 8.42 to 9.30 mL.

If the amount of the laboratory prepared FAS titrant needed to reach endpoint is outside of the acceptable range replace the titrant or calculate a correction factor.

7.4 Correction Factor (Used only for laboratory prepared titrant.)

The correction factor adjusts the calculation for the concentration of titrant used, either 2 mL or 10 mL.

Three titrant checks must be performed for one of the two calculations as follows:

Endpoint of 2 mL

$$\frac{2.0 \text{ mL}}{\text{Average of Three Titrations (mL)}} = \text{Correction Factor}$$

Endpoint of 10 mL

$$\frac{10.0 \text{ mL}}{\text{Average of Three Titrations (mL)}} = \text{Correction Factor}$$

Multiply all titration volumes performed with titrant associated with its correction factor.

Note: Do not use correction factors on purchased titrants. They must be within range or replaced.

7.5 Required Standardization Documentation

The **Monthly Chlorine Dioxide DPD/FAS Titrant Standardization Record** on page 79 of this manual may be used to document each standardization procedure. The minimum requirements for documenting each standardization procedure are as follows:

- a. Analyst(s) initials.
- b. Date standardization procedure was performed.
- c. Identify if a blank reference was used (yes/no).
- d. Volume of reagent water used (mL).
- e. Volume of standard used (mL).
- f. Volume of FAS titrant used for titrations 1 and 2 (mL).
- g. The third titration value and correction factor if used.
- h. Comments.

Copper Analysis by Bathocuproine/Spectrophotometric Method

Quick Reference	Standard/Reagent	Requirements
Standard/Reagent Storage	Liquid Reagents	Room Temperature
	Standards	Room Temperature
Standard/Reagent Expiration	Standard/Reagent	Maximum Storage Time
	Reagents	1 Year After Opening/Manufacturer's Expiration Date
	Standards	1 Year After Preparation/Manufacturer's Expiration Date
Required Quality Control	QC Procedure	Frequency
	Generate Calibration Curve	Once Per 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
	Adjust Sample pH < 2.0 With HNO ₃	6 Months

Method Reference

Standard Methods 22nd Edition (3500-Cu C)

On-Site Survey Requirements

- Each certified analyst must be able to generate a calibration curve described in Section 7.0 of 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 is intended only for use by water treatment plants that use copper sulfate in the treatment process and is not to be used for the lead and copper rule. Copper ions in solution are reduced to the cuprous state with hydroxylamine hydrochloride. The cuprous ions then form an orange colored chelate with the bathocuproine reagent in the pH buffered reaction solution. The absorbance of the sample is analyzed on a spectrophotometer at a wavelength of 484 nanometers.

Interferences

Color differences in potable water should not be present in sufficient concentrations to interfere with the analysis. Total residual chlorine concentrations up to 1.0 mg/L can be tolerated. If chlorine levels are ≥ 1.0 mg/L, allow the sample to stand in an open-top container for about fifteen minutes to reduce the chlorine level or add an additional milliliter of hydroxylamine hydrochloride to all standards and samples.

2.0 Equipment

- a. A spectrophotometer capable of reading 484 nm with a cell light path width of at least 1 cm.
- b. Spectrophotometer vials.
- c. Computer with software capable of generating linear regressions.
- d. Class A volumetric pipet(s).
- e. Standard laboratory glassware.
- f. Balance.

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 manganese contamination.

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 3-76, Section 3. Reagents)

- a. 1000 mg/L Copper Stock Standard: Commercially available.
- b. 10.0 mg/L Copper Calibration Standard: Prepare as follows: Add 10.0 mL of 1000 mg/L copper stock standard to a 1 liter Class A volumetric flask, half filled with reagent water. Add 2 mL of concentrated HNO_3 . Bring to volume with reagent water.
- c. Hydrochloric Acid Solution (50%): Commercially available.
- d. Hydroxylamine Hydrochloride Solution ($\text{NH}_2\text{OH}\cdot\text{HCl}$): Commercially available.
- e. Sodium Citrate Solution: Commercially available.
- f. Disodium Bathocuproine Solution: Commercially available.
- g. Reagent water.

4.0 Sample Collection/Preservation/Holding Time

- a. Sample collection: Collect in a clean plastic or glass screw top container (250 to 1000 mL).
- b. Preservation: Adjust to pH less than 2.0 with HNO₃. No preservation needed if samples are analyzed/digested immediately after collection.
- c. Maximum sample holding time: 6 months. The Laboratory Certification Section recommends analyzing samples immediately after collection.

5.0 Copper Analysis Procedure

1. Measure 100 mL of sample(s) into an Erlenmeyer flask(s).
2. Add 2.0 mL of hydrochloric acid solution (50%) to the sample(s). Mix sample(s).
3. Add 10.0 mL of hydroxylamine hydrochloride solution (NH₂OH·HCl) to the sample(s). Mix sample(s).
4. Add 10.0 mL of sodium citrate solution to the sample(s). Mix sample(s).
5. Add 10.0 mL of disodium bathocuproine solution to the sample(s). Mix sample(s).
6. Read the absorbance and concentration at 484 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.

6.0 Quality Control Requirements

6.1 Calibration Curve Generation

The calibration curve generation procedure must be performed prior to initial use for analyzing potable water and at least once per three months thereafter. (Refer to Section 7.0.) Each calibration curve generation procedure must be dated and recorded.

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

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the calibration curve generation procedure at least once per 3 months. (Refer to Section 7.0.) 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.

6.3 QC Requirements with Each Analysis

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

- a. Blank (0.0 mg/L). Acceptance: Results < Reporting limit.
- b. Reporting limit verification (0.050 mg/L). Acceptance: $\pm 30\%$ of true value.
- c. Midpoint calibration verification (0.10 mg/L). Acceptance: $\pm 10\%$ of true value.

Note: A blank sample is required with each sample analysis. QC samples b and c are required only if an entire calibration curve is not analyzed and generated with the sample batch.

7.0 Calibration Curve Generation Procedure

A minimum of four calibration standard concentrations and a blank must be analyzed to generate a calibration curve. The lowest calibration standard prepared should be at least the reporting limit for copper (0.050 mg/L). Alternatively, a reporting limit verification sample must be prepared in addition to the four calibration standard concentrations if the curve generation does not include the reporting limit concentration (0.050 mg/L). The reporting limit verification sample results must be within $\pm 30\%$ of the true value.

1. Prepare four 100 mL volumetric flasks containing a known volume of 10.0 mg/L copper calibration standard and reagent water according to the table in Section 7.2. Label each flask with the calibration concentration it contains.
2. Prepare a blank by adding 100 mL reagent water to a fifth volumetric flask.
3. Pour each calibration standard into an Erlenmeyer flask. Label each Erlenmeyer flask with the calibration concentration it contains.
4. Add 2.0 mL of hydrochloric acid solution (50%) to the standards. Mix standards.
5. Add 10.0 mL of hydroxylamine hydrochloride solution ($\text{NH}_2\text{OH}\cdot\text{HCl}$) to the standards. Mix standards.
6. Add 10.0 mL of sodium citrate solution to the standards. Mix standards.
7. Add 10.0 mL of disodium bathocuproine solution to the standards. Mix standards.
8. Read absorbance of each calibration standard and blank at 484 nm. Follow the spectrophotometer manufacturer's instructions to generate and store a calibration curve using the blank and prepared calibration standards.
9. If the spectrophotometer does not have the capability to store calibration curves, read absorbance for each calibration standard at 484 nm on spectrophotometer. Record absorbance.
10. Using the absorbance and concentration for each calibration standard, generate a calibration curve manually on an Excel spreadsheet.

Correlation Coefficient (R)/Coefficient of Determination (R²)

Once the calibration curve has been generated, acceptance of the curve is determined by the correlation coefficient (R) or the coefficient of determination (R²). In order for the curve to be acceptable for sample analysis, the correlation coefficient (R) must be greater than 0.995 or the coefficient of determination (R²) 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 (R²).

7.1 Calibration Standard Concentration Calculations

10.0 mg/L copper 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 (0.0 mg/L), 0.020 mg/L, 0.050 mg/L, 0.10 mg/L and 0.30 mg/L. The table in Section 7.2 demonstrates how these standards are prepared in 100 mL volumetric flasks.

7.2 Calibration Standard Concentration Preparation Table

Calibration Standard Concentration	mL of 10.0 mg/L Copper Calibration Standard Added to 100 mL Flask	Final Volume
Blank (0.0 mg/L)	0.0 mL	100 mL
0.02 mg/L	0.2 mL	100 mL
0.05 mg/L	0.5 mL	100 mL
0.10 mg/L	1.0 mL	100 mL
0.30 mg/L	3.0 mL	100 mL

7.3 Required Calibration Curve Generation Documentation

The **Copper Bathocuproine/Spectrophotometer QC Sample Record** on page 85 of this manual may be used to document the required information. The minimum requirements for documenting each calibration curve generation procedure are as follows:

- a. Analyst(s) initials.
- b. Analysis date.
- c. Blank concentration (mg/L).
- d. Reporting limit concentration (mg/L).
- e. Midpoint concentration (mg/L).
- f. Date calibration curve generated.
- g. Comments.

Fluoride Analysis by Ion-Selective Electrode Method

<i>Quick Reference</i>	Standard/Reagent/Equipment	Requirements
Standard/Reagent Storage	Reference Probe	Reagent Water
	Fluoride Probe	Dry
	TISAB	Room Temperature
	0.5/5.0/1.0 mg/L Standards	Room Temperature
	100 mg/L Standard	Refrigerated
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
	Linearity (1.0 mg/L Check)	Once Per Week
	QC Sample Analysis	Once Per Month
Sample Collection	Preservation	Maximum Hold Time
	4°C	48 Hours

Method Reference

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

On-Site Survey Requirements

- Each certified analyst must be able to perform the calibration procedure described in Section 7.0 of this method.
- Each operationally certified analyst must be able to perform the calibration procedure described in Section 7.0 of 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 sample drinking water is collected in a clean ion-free container and mixed with an equal volume of fluoride buffer (TISAB). The fluoride meter probe 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, crystalline buildup and/or improper storage) will cause unacceptable linearity or increase in stabilization time. Care should be taken to maintain electrodes following manufacturer's directions.

2.0 Equipment

- a. A specific ion meter capable of being calibrated with a minimum of two standards and equipped with a slope display. Analog ion meters are not recommended.
- b. A fluoride selective ion electrode.
- c. A sieve type reference electrode.
- d. A magnetic stirring device and a least three TFE-coated (Teflon) stirring bars.
- e. Class A volumetric pipets.
- f. Class A volumetric flasks.
- g. (2) 25 mL graduated cylinders.
- h. Plastic beakers (50 - 100 mL).

2.1 General Probe Maintenance

- a. Follow manufacturer's instruction for storing and maintaining electrodes/probes. Alternatively, follow b through f below.
- b. Probes should be kept clean and free from crystalline buildup.
- c. The sensing electrode should be cleaned periodically (on the bottom only) using fluoride toothpaste to improve response time.
- d. The sensing probe can be stored dry in air when not in use.
- e. Store probes as they are received until they are put into use.
- f. Probes taking longer than 3 minutes stabilize in calibration solution may need service or replacement.

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 4-86, Section 3. Reagents)

- a. Reagent water.
- b. 100 mg/L Stock Fluoride Solution: Commercially available.
- c. 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.
- d. 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.
- e. 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.

- f. Buffer Solution (TISAB): Commercially available.

4.0 Sample Collection/Preservation/Holding Time

- a. Sample collection: Collect in a clean plastic or glass screw top container (250 to 1000 mL). Alternatively, samples may be collected in the analysis container if they are analyzed immediately.
- b. Sample preservation: 4°C.
- c. Maximum sample holding time: 28 days. The Laboratory Certification Section 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. 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, measure and pour equal amounts of sample water and TISAB (25 mL sample water/25 mL TISAB is common) into 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 meter probe in the sample mixture and allow meter to stabilize while stirring.
5. Record the result as fluoride in mg/L.

Note: Probe(s) must be rinsed with reagent water before and between all analyses of samples/standards. The samples/standards must be stirred during analysis.

6.0 Quality Control Requirements

6.1 Fluoride Meter Calibration

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.

6.2 Analyst QC Requirements

All certified and operationally certified analysts are required to 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 are required to perform the calibration procedure at least three times per month. (Refer to Section 7.0.) 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. The results of the 1.0 mg/L verification standard must be within $\pm 10\%$ of the true value. The acceptance limits are 0.9 to 1.10 mg/L.

Operationally Certified Analyst Requirements

All operationally certified analysts are required to 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 Fluoride Meter Calibration Procedure

Note: Calibrations must be performed once per shift, 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. (Refer to Section 6.2 for 1.0 mg/L requirements.) This is required of certified analysts.

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

5. 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.
6. Record the slope value (-54.0 to - 60.0 mV). (Refer to Section 7.1 in this method for detailed acceptance limits.)
7. 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 7.1 for corrective measures.)

Note: Probe(s) must be rinsed with reagent water before and between all analyses of samples/standards. The samples/standards must be stirred during analyses.

7.1 Calibration Acceptance Limits

The slope/linearity value must fall in the acceptable range of 95% to 105% (slope value displayed in %) or -54.0 to -60.0 mV (value displayed in millivolts).

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

7.2 Monthly Fluoride QC Sample Analysis

All laboratories certified for fluoride analysis are required to successfully analyze and record one QC sample in a range of 0.5 to 1.5 mg/L prior 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.

The acceptance limits for the QC sample are $\pm 10\%$ of the certified value. The **Monthly Fluoride QC Sample Record** on page 93 of this manual may be used to document the QC sample results.

7.3 Required Calibration Documentation

The **Fluoride Slope/Weekly Linearity Verification (1.0 mg/L Standard) Record** on page 92 of this manual may be used to document each calibration procedure. The minimum requirements for documenting each verification procedure are as follows:

- a. Analyst(s) initials.
- b. Date calibration procedure was performed, required to be recorded at a minimum of once per shift.
- c. Linearity value percent (%) or millivolts (mV).
- d. Confirmation value of 1.0 mg/L \pm 10% verification standard, required to be recorded at a minimum of once per week.
- e. Comments.

Monthly Fluoride QC Sample Record

Laboratory _____

Analyst	Date	Results (mg/L)	Certified Value (mg/L)	Within $\pm 10\%$ (Y/N)	QC Sample Suppliers Name	Sample Lot #

Hardness Analysis by EDTA Titration Method

Quick Reference	Standard/Reagent	Requirements
Standard/Reagent Storage	EDTA	Room Temperature
	Indicator	Room Temperature
	Buffer	Room Temperature
	1000 mg/L Calcium Chloride (CaCO ₃) Standard	Refrigerated
	Commercial Dry Reagents	Room Temperature
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 (CaCO ₃) Standard	1 Year After Opening/Manufacturer's Expiration Date
	Commercial Dry Reagents	1 Year 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)

On-Site Survey Requirements

- All certified analyst must be able to perform the hardness titrant standardization described in Section 7.0 of 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 0.020 N EDTA to specified color in the presence of the endpoint indicator eriochrome black-T at a pH of 10.0. 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.

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.

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 5 minutes from the time the buffer is added to the sample.

2.0 Equipment

- a. 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.

- b. 20.0 mL Class A volumetric pipet(s).
- c. Titration vessels of appropriate volume.
- d. Graduated cylinders (50 to 100 mL).
- e. Magnetic stirring device & stirring bars.
- f. Balance.

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 2-45 & 46, Section 2. Reagents)

- a. Standard EDTA titrant (0.01 M): Commercially available.
- b. Buffer Solution: Commercially available.
- c. Mixed Eriochrome Black T Indicator: Commercially available. Prepare with calcium or magnesium ions.
- d. Calmagite: Commercially available.

- e. Calcium Standard (0.020 N): Commercially available Calcium Chloride, 1000 mg/L as CaCO₃.
- f. Reagent water.

4.0 Sample Collection/Preservative /Storage

- a. 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.
- b. Preservation: Adjust to pH less than 2.0 with HNO₃, 4°C. Preservation is not required if sample is analyzed immediately.
- c. Maximum sample holding time: 28 days. The Laboratory Certification Section 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 CaCO₃.

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

CaCO₃ Concentration (mg/L): $7.2 \times 10 = 72$ mg/L

Note: If 50 mL of sample volume is analyzed the multiplier factor is 20.

6.0 Quality Control Requirements

6.1 Titrant Standardization

Titration standardization procedure must be completed initially upon opening or preparation of titrant and at least once per month thereafter. (Refer to Section 7.0.) Each standardization procedure must be dated and recorded.

6.2 Analyst Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the titration standardization procedure at least once per quarter. (Refer to Section 7.0.) 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 Titrant Standardization Procedure

7.1 Blank (Verification of hardness free reagent water)

1. Add 30 mL of reagent water using a graduated cylinder add sufficient buffer and indicator to the vessel to produce a distinctive color change.
2. Slowly add 0.010 M EDTA titrant to the sample, mixing with a magnetic stir bar, until color endpoint is reached.
3. 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).
4. If more than 0.1 mL (approximately 2 drops) of titrant is needed to reach the endpoint, obtain acceptable reagent water.
5. 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 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 1 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 $\pm 5\%$ of theoretical value.

When using 20.0 mL of 0.020 N calcium chloride (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 the titrant or calculate a correction factor.

7.4 Correction Factor

The correction factor adjusts the hardness calculation for the concentration of titrant used.

Three titrant checks must be performed for the calculation as follows:

$$\frac{20.0 \text{ mL}}{\text{Average of three titrations (mL)}} = \text{Correction Factor}$$

Multiply all titration volumes performed with titrant associated with its correction factor.

Note: Do not use correction factors on purchased titrants. They must be within range or replaced.

7.5 Required Documentation

The **Monthly Hardness Titrant Standardization Record** on page 99 of this manual may be used to document each standardization procedure. The minimum requirements for documenting each standardization procedure are as follows:

- a. Analyst(s) initials.
- b. Date standardization procedure was performed.
- c. Volume of reagent water used (mL).
- d. Volume of titrant used for the blank (mL).
- e. Volume of standard used (mL).
- f. Volume of titrant used for titrations 1 and 2 (mL).
- g. The third titration value and correction factor if used.
- h. Comments.

Iron Analysis by Phenanthroline/Spectrophotometric Method

Quick Reference	Standard/Reagent	Requirements
Standard/Reagent Storage	Liquid Reagents	Room Temperature
	Standards	Room Temperature
Standard/Reagent Expiration	Standard/Reagent	Maximum Storage Time
	Reagents	1 Year After Opening/Manufacturer's Expiration Date
	Standards	1 Year After Preparation/Manufacturer's Expiration Date
Required Quality Control	QC Procedure	Frequency
	Generate Calibration Curve	Once Per 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 HNO ₃	6 Months

Method Reference

Standard Methods 22nd Edition (3500-Fe B)

On-Site Survey Requirements

- Each certified analyst must be able to generate a calibration curve described in Section 7.0 of 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 is intended only for use by those water plants where iron removal treatment is used. A volume of sample is collected and the iron in the water is reduced to the ferrous state by digesting (boiling) with hydrochloric acid and hydroxylamine hydrochloride before treatment with 1, 10-phenanthroline at a pH of 3.2 or 3.3. A fume hood must be used for this type of digestion to exhaust caustic fumes and to contain samples. After digestion (boiling), the absorbance of the sample is analyzed on a spectrophotometer at a wavelength of 510 nanometers (nm).

Interferences

Zinc and polyphosphate interferences are eliminated by the acid digestion. During 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

- a. A spectrophotometer capable of reading 510 nm with a cell light path width of at least 1 cm.
- b. Spectrophotometer vials.
- c. Computer with software capable of generating linear regressions.
- d. Class A volumetric pipet(s).
- e. Standard laboratory glassware.
- f. A hot plate large enough to hold all the standards and samples at the same time for digestion.
- g. Heating blocks may be used as long as reagent proportions are not changed.
- h. A fume hood for use with the hot plate digestion.
- i. Balance.

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 iron contamination.

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 3-78, Section 3. Reagents)

- a. 1000 mg/L Iron Standard: Commercially available.
- b. 100 mg/L Intermediate Iron Standard: Prepare as follows: Add 100.0 mL of 1000 mg/L manganese stock standard to a 1 liter Class A volumetric flask, half filled with reagent water. Add 2 mL of concentrated HNO₃. Bring to volume with reagent water.
- c. 10.0 mg/L Iron Calibration Standard: Prepare as follows: Add 100.0 mL of 100 mg/L iron standard to 1 liter volumetric flask, half filled with reagent water. Add 2 mL of concentrated HNO₃. Bring to volume with reagent water.
- d. Concentrated Hydrochloric Acid: Commercially available.

- e. Hydroxylamine Solution: Commercially available.
- f. Ammonium Acetate Buffer Solution: Commercially available.
- g. Phenanthroline Color Solution: Commercially available. Store in an amber glass container. Expires 1 month after preparation.
- h. Reagent water.

4.0 Sample Collection/Preservation/Holding Time

- a. Sample collection: Collect in a clean plastic or glass screw top container (250 to 1000 mL).
- b. Preservation: Adjust to pH less than 2.0 with HNO₃. No preservation needed if samples are analyzed/digested immediately after collection.
- c. Maximum sample holding time: 6 months. The Laboratory Certification Section recommends analyzing samples immediately after collection.

5.0 Iron Analysis Procedure

1. Measure 100 mL of sample(s) into an Erlenmeyer flask or beaker.
2. Add 2.0 mL of concentrated HCl to the sample(s).
3. Add 2.0 mL of hydroxylamine hydrochloride to the sample(s).
4. Digest (Boil) the sample(s) to a volume of 15 to 20 mL on a hot plate. The hot plate 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 for this procedure.
5. Remove the flask(s) from the hot plate and cool. Carefully, transfer the sample(s) to 100 mL Class A volumetric flask(s).
6. Add 10.0 mL of ammonium acetate buffer to the volumetric sample(s).
7. Add 2.0 mL of phenanthroline color reagent to the sample(s) and dilute to a final volume of 100 mL with reagent water. Allow 15 minutes for color development.
8. Read the absorbance at 510 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.

6.0 Quality Control Requirements

6.1 Calibration Curve Generation

The calibration curve generation procedure must be performed prior to initial use for analyzing potable water and at least once per three months thereafter. (Refer to Section 7.0.) Each calibration curve generation procedure must be dated and recorded.

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

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the calibration curve generation procedure at least once per 3 months. (Refer to Section 7.0.) 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.

6.3 QC Requirements with Each Analysis

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

- a. Blank (0.0 mg/L).
- b. Reporting limit verification (0.10 mg/L). Acceptance: $\pm 30\%$ of true value.
- c. Midpoint calibration verification (0.50 mg/L). Acceptance: $\pm 10\%$ of true value.

Note: A blank sample is required with each sample analysis. QC samples b and c are required only if an entire calibration curve is not analyzed/digested and generated with the sample batch.

7.0 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 iron (0.10 mg/L). Alternatively, a reporting limit verification sample must be prepared in addition to the three calibration standard concentrations, if the curve generation does not include the reporting limit concentration (0.10 mg/L). This reporting limit verification sample results must be within $\pm 30\%$ of the true value.

1. Prepare three 100 mL volumetric flasks containing a known volume of 10.0 mg/L iron calibration standard and reagent water according to the table in Section 7.2. Label each flask with the calibration concentration it contains.
2. Prepare a blank by adding 100 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 2.0 mL of concentrated HCl to each of the standards.
5. Add 2.0 mL of hydroxylamine hydrochloride to each of the standards.

6. Digest (Boil) the standards to a volume of 15 to 20 mL on a hot plate. The hot plate must be large enough to digest all samples and standards simultaneously. A fume hood is required for this procedure.
7. Remove the Erlenmeyer flasks from the hot plate and cool to room temperature.
8. Carefully, transfer each of the calibration standards into 100 mL Class A volumetric flasks. Label each volumetric flask with the calibration concentration it contains.
9. Add 10.0 mL of ammonium acetate buffer to each standard.
10. Add 2.0 mL of phenanthroline color reagent to each standard and bring to a final volume of 100 mL with reagent water. Allow 15 minutes for color development.
11. Read absorbance of each calibration standard and blank at 510 nm. Follow the spectrophotometer manufacturer's instructions to generate and store a calibration curve using the blank and prepared calibration standards.
12. If the spectrophotometer does not have the capability to store calibration curves, read absorbance for each calibration standard at 510 nm on spectrophotometer. Record absorbance.
13. Using the absorbance and concentration of each calibration standard, generate a calibration curve manually on an Excel spreadsheet.

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). In order 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

10.0 mg/L iron calibration standard will be used as the standard added to each flask to generate the calibration curve concentration points. The recommended calibration concentrations to generate a curve are as follows: blank (0.0 mg/L), 0.1 mg/L, 0.5 mg/L and 1.0 mg/L. The table in Section 7.2 demonstrates how these standards are prepared in 100 mL volumetric flasks.

7.2 Calibration Standard Concentration Preparation Table

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

7.3 Required Calibration Curve Generation Documentation

The **Iron Phenanthroline/Spectrophotometer QC Sample Record** on page 106 of this manual may be used to document the required information. The minimum requirements for documenting each calibration curve generation procedure are as follows:

- a. Analyst(s) initials.
- b. Analysis date.
- c. Blank concentration (mg/L).
- d. Reporting limit concentration (mg/L).
- e. Midpoint concentration (mg/L).
- f. Date calibration curve generated.
- g. Comments.

Manganese Analysis by Persulfate/Spectrophotometric Method

Quick Reference	Standard/Reagent	Requirements
Standard/Reagent Storage	Liquid Reagents	Room Temperature
	Standards	Room Temperature
Standard/Reagent Expiration	Standard/Reagent	Maximum Storage Time
	Reagents	1 Year After Opening/Manufacturer's Expiration Date
	Standards	1 Year After Preparation/Manufacturer's Expiration Date
Required Quality Control	QC Procedure	Frequency
	Generate Calibration Curve	Once Per 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 HNO ₃	6 Months

Method Reference

Standard Methods 22nd Edition (3500-Mn B)

On-Site Survey Requirements

- Each certified analyst must be able to generate a calibration curve described in Section 7.0 of 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 is intended only for use by those water plants where manganese removal treatment is used. Analysis of manganese by the persulfate method is the only colorimetric method which is acceptable for total manganese determination. A volume of sample is collected and persulfate oxidation of soluble manganous compounds to form permanganate is carried out in the presence of silver nitrate. The absorbance of the sample is then analyzed on a spectrophotometer at a wavelength of 525 nanometers (nm).

Interferences

Sample loss may occur due to bumping during the hot plate digestion.

2.0 Equipment

- a. A spectrophotometer capable of reading 525 nm with a cell light path width of at least 1 cm.
- b. Spectrophotometer vials.
- c. Computer with software capable of generating linear regressions.
- d. Class A volumetric pipet(s).
- e. Standard laboratory glassware.
- f. A hot plate large enough to hold all the standards and samples at the same time for digestion.
- g. Heating blocks may be used as long as reagent proportions are not changed.
- h. A fume hood for use with the hot plate digestion.
- i. Balance.

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 manganese contamination.

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 3-86, Section 3. Reagents)

- a. 1000 mg/L Manganese Stock Standard: Commercially available.
- b. 100 mg/L Intermediate Manganese Standard: Prepare as follows: Add 100.0 mL of 1000 mg/L manganese stock standard to a 1 liter Class A volumetric flask, half filled with reagent water. Add 2 mL of concentrated HNO₃. Bring to volume with reagent water.
- c. 1.0 mg/L Manganese Calibration Standard: Prepare as follows: Add 10.0 mL of 100 mg/L manganese stock standard to a 1 liter Class A volumetric flask, half filled with reagent water. Add 2 mL of concentrated HNO₃. Bring to volume with reagent water.
- d. Special Reagent (Persulfate Method): Commercially available.
- e. Ammonium Persulfate (NH₄)₂S₂O₈: Commercially available.

- f. Reagent water.

4.0 Sample Collection/Preservation/Holding Time

- a. Sample collection: Collect in a clean plastic or glass screw top container (250 to 1000 mL).
- b. Preservation: Adjust to pH less than 2.0 with HNO₃. No preservation needed if samples are analyzed/digested immediately after collection.
- c. Maximum sample holding time: 6 months. The Laboratory Certification Section recommends analyzing samples immediately after collection.

5.0 Manganese Analysis Procedure

1. Measure 100 mL of sample(s) into an Erlenmeyer flask.
2. Add 4.0 mL of Special Reagent to the Erlenmeyer sample(s). Mix flask and special reagent.
3. Digest (boil) the sample(s) to a volume of about 50 mL on a hot plate. The hot plate 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 for this procedure.
4. Remove the flask(s) from the hot plate and add 1 g of ammonium persulfate to each. Bring the sample(s) to a boil for one minute, remove from heat and cool on the bench top for one minute.
5. Cool the flask(s) to room temperature.
6. Carefully, transfer the sample(s) to a Class A 100 mL volumetric flask(s) and bring to volume with reagent water.
7. Read the absorbance at 525 nm 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.

6.0 Quality Control Requirements

6.1 Calibration Curve Generation

The calibration curve generation procedure must be performed prior to initial use for analyzing potable water and at least once per three months thereafter. (Refer to Section 7.0.) Each calibration curve generation procedure must be dated and recorded.

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

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the calibration curve generation procedure at least once per 3 months. (Refer to Section 7.0.) 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.

6.3 QC Requirements with Each Analysis

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

- a. Blank (0.0 mg/L). Acceptance: Results < reporting limit.
- b. Reporting limit verification (0.02 mg/L). Acceptance: $\pm 30\%$ of true value.
- c. Midpoint calibration verification (0.10 mg/L). Acceptance: $\pm 10\%$ of true value.

Note: A blank sample is required with each sample analysis. QC samples b and c are required only if an entire calibration curve is not analyzed/digested and generated with the sample batch.

7.0 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 the reporting limit for manganese (0.02 mg/L). Alternatively, a reporting limit verification sample must be prepared in addition to the three calibration standard concentrations, if the curve generation does not include the reporting limit concentration (0.02 mg/L). The reporting limit verification sample results must be within $\pm 30\%$ of the true value.

1. Prepare three 100 mL volumetric flasks containing a known volume of 1.0 mg/L manganese calibration standard and reagent water according to the table in Section 7.2. Label each flask with the calibration concentration it contains.
2. Prepare a blank by adding 100 mL reagent water to a sixth volumetric flask.
3. Pour each calibration standard into an Erlenmeyer flask. Label each Erlenmeyer flask with the calibration concentration it contains.
4. Add 4.0 mL of Special Reagent to the volumetric flask. Mix standard and special reagent.
5. Digest (boil) the standards to a volume of about 50 mL on a hot plate. The hot plate 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 for this procedure.
6. Remove the standards from the hot plate and add 1 g of ammonium persulfate to each. Bring the flasks to a boil for one minute, remove from heat.
7. Cool the Erlenmeyer flasks to room temperature.
8. Carefully, transfer the standards to Class A 100 mL volumetric flasks and bring to volume with reagent water.

9. Read absorbance of each calibration standard and blank at 525 nm. Follow the spectrophotometer manufacturer's instructions to generate and store a calibration curve using the blank and prepared calibration standards.
10. If the spectrophotometer does not have the capability to store calibration curves, read absorbance for each calibration standard at 525 nm on spectrophotometer. Record absorbance.
11. Using the absorbance and concentration of each calibration curve point, generate a calibration curve manually on an Excel spreadsheet.

Correlation Coefficient (R)/Coefficient of Determination (R²)

Once the calibration curve has been generated, acceptance of the curve is determined by the correlation coefficient (R) or the coefficient of determination (R²). In order for the curve to be acceptable for sample analysis, the correlation coefficient (R) must be greater than 0.995 or the coefficient of determination (R²) 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 (R²).

7.1 Calibration Standard Concentration Calculations

1.0 mg/L manganese 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 (0.0 mg/L), 0.02 mg/L, 0.10 mg/L and 0.30 mg/L. The table in Section 7.2 demonstrates how these standards are prepared in 100 mL volumetric flasks.

7.2 Calibration Standard Concentration Preparation Table

Standard Concentration	mL of 1.0 mg/L Manganese Calibration Standard Added to 150 mL Flask	Final Volume
Blank (0.0 mg/L)	0.0 mL	100 mL
0.02 mg/L	2.0 mL	100 mL
0.10 mg/L	10.0 mL	100 mL
0.30 mg/L	30.0 mL	100 mL

7.3 Required Calibration Curve Generation Documentation

The **Manganese Persulfate/Spectrophotometer QC Sample Record** on page 113 of this manual may be used to document the required information. The minimum requirements for documenting each calibration curve generation procedure are as follows:

- a. Analyst(s) initials.
- b. Analysis date.
- c. Blank concentration (mg/L).
- d. Reporting limit concentration (mg/L).
- e. Midpoint concentration (mg/L).
- f. Date calibration curve generated.
- g. Comments.

Nitrate Analysis by Cadmium Reduction/Spectrophotometric Method

<i>Quick Reference</i>	Standard/Reagent	Requirements
Standard/Reagent Storage	Liquid Reagents	Room Temperature
	Standards	Refrigerated
Standard/Reagent Expiration	Standard/Reagent	Maximum Storage Time
	Reagents	1 Year After Opening/Manufacturer's Expiration Date
	Standards	1 Year After Opening/Manufacturer's Expiration Date
Required Quality Control	QC Procedure	Frequency
	Generate Calibration Curve	Once Per Three Months
	Blank Verification	With Each Analysis/Reduction
	Reporting Limit Verification	With Each Analysis/Reduction If Calibration Curve Is Not Generated
	Midpoint Calibration Verification	With Each Analysis/Reduction If Calibration Curve Is Not Generated
Sample Collection	Preservation	Maximum Hold Time
	4°C	48 Hours

Method Reference

Standard Methods 22nd Edition (4500 - NO₃⁻ E)

On-Site Survey Requirements

- Each certified analyst must be able to generate a calibration curve described in Section 7.0 of 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

Nitrate is reduced to nitrite in the presence of cadmium granules that are treated with copper sulfate. This reduction occurs in a packed glass column. The nitrite produced is quantitated by absorbance on a spectrophotometer after the addition of a color reagent. The cadmium reduction method is limited to samples containing nitrate concentrations less than 1.0 mg/L. Samples with nitrate concentrations greater than 1.0 mg/L must be diluted to less than 1.0 mg/L prior to beginning this procedure. Any nitrite present in the sample will cause a positive bias. Compensate for this by analyzing the sample without passing it through the reduction column and subtracting the resulting concentration from the combined nitrate/nitrite result of the reduced sample.

Interferences

Suspended solids, precipitates and dirty glassware may affect results. Excessive amounts of heavy metals can interfere. This is usually overcome by adding EDTA when metals are in the mg/L range.

2.0 Equipment

- a. A spectrophotometer capable of reading 543 nm with a cell light path width of at least 1 cm.
- b. Spectrophotometer vials.
- c. Computer with software capable of generating linear regressions.
- d. Class A volumetric pipet(s).
- e. Standard laboratory glassware.
- f. Reduction column: Purchased or constructed from 100 mL pipet as described in Standard Methods, 22nd Edition, Figure 4500-NO₃⁻: 1. Page 4-126.
- g. Balance.

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

Reference: Standard Methods, 22nd Edition, (Pages 4-126, Section 3. Reagents)

- a. 100 mg/L Nitrate-Nitrogen Stock Solution: Commercially available or prepare as follows: Dissolve 0.7218 g of anhydrous potassium nitrate (KNO₃) in a 1 liter Class A volumetric flask, half filled with reagent water. Bring to volume with reagent water. This solution is stable for 6 months, kept under refrigeration when not in use.
- b. 10.0 mg/L Nitrate-Nitrogen Calibration Standard Solution: Prepare as follows: Add 10.0 mL of 100 mg/L Nitrate-Nitrogen Stock Solution in a 100 mL Class A volumetric flask, half filled with reagent water. Bring to volume with reagent water. Standard and intermediate solutions should be prepared fresh daily and discarded after their initial use.
- c. 100 mg/L Sodium Nitrite Stock Solution: Commercially available or prepare as follows: Dissolve 0.4929 g of Sodium Nitrite (NaNO₂) in a 1 liter Class A volumetric flask, half filled with reagent water. Bring to volume with reagent water. This solution is stable for 3 months if preserved with

2.0 mL chloroform per liter and kept under refrigeration when not in use.

- d. 10 mg/L Nitrite-Nitrogen Calibration Standard Solution: Add 10.0 mL of 100 mg/L Sodium Nitrite-Nitrogen Stock Solution in a 100 mL Class A volumetric flask, half filled with reagent water. Bring to volume with reagent water. This solution should be prepared fresh daily.
- e. 100 mg/L as Potassium Nitrite-Nitrogen Stock Solution: Commercially available or prepare as follows: Dissolve 0.607 g potassium nitrite (KNO_2) in a 1 liter Class A volumetric flask, half filled with reagent water. Bring to volume with reagent water. This solution is stable for 3 months if preserved with 2.0 mL chloroform per liter and kept under refrigeration when not in use.
- f. Cadmium: granulated 40-60 mesh: Commercially available.
- g. Copper Sulfate: (2% W/V): Dissolve 2 g of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in a 100 mL Class A volumetric flask, half filled with reagent water. Bring to volume with reagent water.
- h. Copper-cadmium granules (Cu-Cd): Clean about 25 g of cadmium granules with 4 N HCl by swirling in an Erlenmeyer flask or large beaker. Rinse the acid cleaned cadmium with reagent water to remove all trace of the acid. Add enough 2% copper sulfate to cover the cadmium granules. Swirl occasionally for at least 5 minutes until a fine brown precipitate is formed. If blue color fades or no precipitate is formed, carefully decant the liquid portion and repeat with another portion of 2% copper sulfate. Rinse the excess copper (the fine, brown precipitate) from the copperized cadmium with reagent water.
- i. Ammonium Chloride/EDTA: Dissolve 13 g of ammonium chloride (NH_4Cl) and 1.7 g disodium ethylene-diamine-tetraacetate ($\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2\text{Na}_2 \cdot 2\text{H}_2\text{O}$) in 900 mL of reagent water. Adjust the pH to 8.5-8.6 with concentrated ammonium hydroxide (NH_4OH). Dilute to 1 liter.
- j. Dilute ammonium chloride/EDTA: Dilute 300 mL of the ammonium chloride/EDTA with reagent water to 500 mL final volume.
- k. Color Reagent: In a class A volumetric flask dissolve 1.0 gram sulfanilamide ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$) and 0.1 gram N (1 naphthyl)-ethylenediamine dihydrochloride in a mixture of 10 mL concentrate phosphoric acid (H_3PO_4 , 85%) and dilute to 100 mL with reagent water. Keep in a dark glass container, refrigerate when not in use and discard after 1 month.
- l. Activation Standard: Combine 25 mL of the 1.0 mg/L NO_3^- and 75 mL of the full strength ammonium chloride - EDTA and mix well.

4.0 Sample collection/preservation/Storage/hold time

- a. Sample collection: Collect in a clean plastic or glass screw top container (250 to 1000 mL).
- b. Preservation: 4°C.
- c. Maximum sample holding time: 48 Hours. The Laboratory Certification Section recommends analyzing samples immediately after collection.

5.0 Reduction Column Preparation/Regeneration Procedure

1. Assemble cadmium column apparatus as detailed in Standard Methods, 22nd Edition, Figure 4500-NO₃ : 1. Page 4-126.
2. Fill the empty glass column with reagent water and clamp off the rubber hose. Pour sufficient cadmium granules into the column. Remove clamp and drain most of the reagent water leaving only enough to cover the Cu-Cd granules. Glass wool may be used to ensure the Cu-Cd granules do not escape the column during the process.
3. When the column is packed, measure the flow rate of the column with reagent water and a graduated cylinder. Adjust the rate to between 7 and 10 mL per minute.
4. Remove any excess reagent water from the column and rinse column by passing 200 mL dilute ammonium chloride - EDTA through it.
5. Activate the column by passing 100 mL of the activation standard through the column.
6. The column is now ready for sample/standard reduction.
7. Once all of the samples have been reduced, wash the column with 50 mL of dilute ammonium chloride - EDTA. Pour enough reagent water to wash this solution through and leave enough reagent water to cover the granules during storage.

Note: Air must not be introduced into the Cu-Cd granules once the column has been packed and the granules have been added to the reagent water (Step 1).

Note: The Cu-Cd reduction column should be regenerated periodically. Sample number and type will determine the frequency of regeneration needed.

5.1 Column Efficiency Verification Procedure

Each time the analysis is performed, the column efficiency must be verified. To determine column efficiency, run the highest curve concentration for nitrite followed by the same nitrate concentration. The reduction column efficiency must be greater than 90%. The reduction efficiency is calculated as follows:

$$\frac{\text{mg/L NO}_3}{\text{mg/L NO}_2} \times 100 = \% \text{ Reduction Efficiency}$$

5.2 Procedure for Sample/Standard Column Reduction

1. Using pH paper or a meter, verify sample pH is between 7.0 and 9.0. If needed, adjust sample pH with dilute HCl or NaOH to the appropriate pH range.

Note: Samples preserved with H₂SO₄ will need to be pH adjusted with NaOH.

2. Combine 25 mL of sample/standard with 75 mL of dilute ammonium chloride - EDTA solution and mix.
3. Prepare the activated column for use by dripping approximately 30 mL of dilute ammonium chloride - EDTA buffer through it.
4. Allow the column to flow until there is just enough solution left in the column to cover the Cu-Cd granules.

5. Pour 25 mL of the dilute ammonium chloride - EDTA prepared sample/standard.
6. Allow the column to flow until there is just enough solution left to cover the Cu-Cd granules. Do not collect this eluate.
7. Pour 30 to 50 mL of standard or sample onto the column.
Note: The same volume of sample/standard should be added onto the column for each reduction.
8. Allow the column to flow and collect the eluate into a flask.
Note: The same volume of sample/standard should be collected from the column for each reduction.
9. Add approximately 25 mL of dilute ammonium chloride - EDTA onto the column and allow this portion to flow through until there is just enough solution left to cover the Cu-Cd granules. Do not collect this eluate.
10. Repeat Steps 1 through 9 for each sample/standard.
11. Add 1.0 mL of the color reagent to 25 mL of reduced sample, cap and mix. Allow at least 10 minutes for full color development. After full development, the color will remain stable for up to two hours.
Note: Reduced samples and standards should not be allowed to stand for longer than 15 minutes prior to the addition of the color reagent.
12. Measure and record the absorbance of each sample and standard with a spectrophotometer set at a wavelength of 543 nm. Matched cuvettes or a single cuvette which is rinsed with a small amount of sample between measurements may be used.

Note: During the entire procedure the liquid in the column must not fall below the level of Cu-Cd granules in between sample/standard reductions. Should this occur, the column will need to be packed again and prepared following Section 5.0.

Note: Samples exceeding 1.0 mg/L must be diluted into the working range of the column (0.10 mg/L - 1.0 mg/L nitrate). Do this by diluting sample with reagent water. Buffer this solution as in Step 2 above. The final value will then be multiplied by a dilution factor.

5.3 Nitrite Check

Combine 25 mL sample with 75 mL of ammonium chloride - EDTA solution and mix. Add 1.0 mL of color reagent to a 25 mL of sample to check for the presence of nitrite; this sample is not passed through the column. Read absorbance and subtract any significant nitrite results for nitrate results.

6.0 Quality Control Requirements

6.1 Calibration Curve Generation

The calibration curve generation procedure must be performed prior to initial use for analyzing potable water and at least once per three months thereafter. (Refer to Section 7.0.) Each calibration curve generation procedure must be dated and recorded.

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

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the calibration curve generation procedure at least once per 3 months. (Refer to Section 7.0.) 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.

6.3 QC Requirements with Each Analysis

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

- a. Blank (0.0 mg/L). Acceptance: Results < 0.10 mg/L.
- b. Reporting limit verification (0.50 mg/L). Acceptance: $\pm 30\%$ of true value.
- c. Midpoint calibration verification (1.0 mg/L). Acceptance: $\pm 10\%$ of true value.

Note: A blank sample is required with each sample analysis. QC samples b and c are required only if an entire calibration curve is not reduced/analyzed and generated with the sample batch.

7.0 Calibration Curve Generation Procedure

A minimum of four 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 nitrate (0.50 mg/L). Alternatively, a reporting limit verification sample must be prepared in addition to the four calibration standard concentrations if the curve generation does not include the reporting limit concentration (0.50 mg/L). The reporting limit verification sample results must be within $\pm 30\%$ of the true value.

1. Prepare four 100 mL volumetric flasks containing a known volume of 10.0 mg/L nitrate calibration standard solution and reagent water according to the table in Section 7.2. Label each flask with the calibration standard it contains.
2. Prepare a blank by adding 100 mL reagent water to a volumetric flask.
3. Follow the reduction procedure (Section 5.2, Steps 1 through 11) for each standard.
4. At absorbance 543 nm. Follow the spectrophotometer manufacturer's instructions to generate and store a calibration curve using the blank and the prepared calibration standards.
5. If the spectrophotometer does not have the capability to store calibration curves, go to Step 6.
6. Read absorbance of each calibration standard and blank at 543 nm on spectrophotometer.

Follow the spectrophotometer manufacturer's instructions to generate and store a calibration curve using the blank and prepared calibration standards.

7. If the spectrophotometer does not have the capability to store calibration curves, read absorbance for each calibration standard at 543 nm on spectrophotometer. Record absorbance.
8. Using the absorbance and concentration of each calibration standard, generate a calibration curve manually on an Excel spreadsheet.

Correlation Coefficient (R)/Coefficient of Determination (R²)

Once the calibration curve has been generated, acceptance of the curve is determined by the correlation coefficient (R) or the coefficient of determination (R²). In order for the curve to be acceptable for sample analysis, the correlation coefficient (R) must be greater than 0.995 or the coefficient of determination (R²) 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 (R²).

7.1 Calibration Standard Concentration Calculations

10.0 mg/L nitrate 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 (0.0 mg/L), 0.10 mg/L, 0.50 mg/L, 1.00 mg/L and 1.50 mg/L. The table in Section 7.2 demonstrates how these standards are prepared in 100 mL volumetric flasks.

7.2 Calibration Standard Concentration Preparation Table

Standard Concentration	mL of 10.0 mg/L Nitrate Calibration Standard Solution Added to 100 mL Flask	Final Volume
Blank (0.0 mg/L)	0.0 mL	100 mL
0.10 mg/L	1.0 mL	100 mL
0.50 mg/L	5.0 mL	100 mL
1.0 mg/L	10.0 mL	100 mL
1.5 mg/L	15.0 mL	100 mL

7.3 Required Calibration Curve Generation Documentation

The **Nitrate Cadmium Reduction/Spectrophotometer QC Sample Record** on page 122 of this manual may be used to document the required information. The minimum requirements for documenting each calibration curve generation procedure are as follows:

- a. Analyst(s) initials.
- b. Analysis date.
- c. Blank concentration (mg/L).
- d. Reporting limit concentration (mg/L).
- e. Midpoint concentration (mg/L).
- f. Date calibration curve generated.
- g. Column efficiency.
- h. Comments.

Nitrate Analysis by Electrode Method

<i>Quick Reference</i>	Standard/Reagent/Equipment	Requirements
Standard/Reagent Storage	Reference Probe	Drained/ Dry
	Nitrate Probe	Dry
	ISA	Room Temperature
	Standards	Refrigerated
	100 mg/L Nitrate Standard	Refrigerated
Standard/Reagent Expiration	Standard/Reagent	Expiration
	ISA	1 Year After Opening/Manufacturer's Expiration Date
	Standards	48 Hours
	100 mg/L Nitrate Standard	1 Year After Opening/Manufacturer's Expiration Date
Required Quality Control	QC Procedure	Frequency
	Calibrate Meter	With Each Analysis
	Linearity (1.0 mg/L Check)	With Each Analysis
	QC Sample Analysis	With Each Analysis
Sample Collection	Preservation	Maximum Hold Time
	4°C	48 hours

Method Reference

Standard Methods 22nd Edition (4500-NO₃⁻ D)

On-Site Survey Requirements

- Each certified analyst must be able to perform the calibration procedure described in Section 7.0 of this method.
- Instrument and electrode performance will be audited.
- 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 multi-parameter meter is used with ion-specific probes to relate nitrate concentration to millivolt readings. The Specific Ion Electrode Method for nitrate determination works well for drinking water samples with nitrate concentrations greater than 1.0 mg/L. An expected non-linear area will be observed in the 0.1 to 0.5 mg/L concentration range. Bracketing during standardization must be used.

Interferences

The method is pH and temperature dependent. The pH of the standards and samples must remain constant during the analysis. Temperature bias can be eliminated by allowing all standards reagents and samples to stabilize at room temperature (approximately 20 - 25°C) before starting the procedure.

Chloride concentrations greater than 20 times the sampled NO₃ concentration may cause a significant bias (10%) in the electrode method. Silver sulfate solution should be added to all standards and samples when samples have significantly high chloride concentrations (add 10 mL per 50 mL of sample). Alternatively, silver sulfate may be added to all samples and standards prior to analysis.

2.0 Equipment

- a. A Digital specific ion meter capable of being calibrated with a minimum of three standards and equipped with a slope display.
- b. A nitrate selective ion electrode.
- c. A Double-junction reference electrode.
- d. A magnetic stirring device and a least three TFE-coated (Teflon) stirring bars.
- e. Class A volumetric pipets.
- f. Class A volumetric flasks.
- g. 25 mL graduated cylinders.
- h. Plastic beakers (50 - 100 mL).

2.1 General Probe Maintenance

- a. Follow manufacturer's instruction for storing and maintaining electrodes/probes. Alternatively, follow b through f below.
- b. Probes should be kept clean and free from crystalline build-up.
- c. The sensing electrode should be replaced periodically.
- d. The sensing probe can be stored dry in air when not in use.
- e. Store probes as they are received until they are put into use.
- f. Probes taking longer than 3 minutes stabilize in calibration solution may need service or replacement.

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 4-125, Section 3. Reagents)

- a. 100 mg/L Potassium Nitrate Stock Solution: Commercially available or prepared as follows: dissolve 0.7218 grams of desiccated anhydrous potassium nitrate (KNO_3) in reagent water and dilute to 1 liter in a Class A volumetric flask. This solution is stable for 6 months under refrigeration.
- b. 20.0 mg/L Potassium Nitrate Standard Solution: Add 20.0 mL of 100 mg/L Potassium Nitrate Stock Solution to a 100 mL volumetric flask. Bring to volume with reagent water.
- c. 10.0 mg/L Potassium Nitrate Standard Solution: Add 10.0 mL of 100 mg/L Potassium Nitrate Stock Solution to a 100 mL volumetric flask. Bring to volume with reagent water.
- d. 5.0 mg/L Potassium Nitrate Standard Solution: Add 5.0 mL of 100 mg/L Potassium Nitrate Stock Solution to a 100 mL volumetric flask. Bring to volume with reagent water.
- e. 1.0 mg/L Potassium Nitrate Standard Solution: Add 1.0 mL of 100 mg/L Potassium Nitrate Stock Solution to a 100 mL volumetric flask. Bring to volume with reagent water.
- f. 0.75 mg/L Potassium Nitrate Standard Solution: Add 15.0 mL of 5.0 mg/L Potassium Nitrate Standard Solution to a 100 mL volumetric flask. Bring to volume with reagent water.
- g. 0.50 mg/L Potassium Nitrate Standard Solution: Add 5.0 mL of 10 mg/L Potassium Nitrate Standard Solution to a 100 mL volumetric flask. Bring to volume with reagent water.
- h. 0.40 mg/L Potassium Nitrate Standard Solution: Add 4.0 mL of 10 mg/L Potassium Nitrate Standard Solution to a 100 mL volumetric flask. Bring to volume with reagent water.
- i. 0.30 mg/L Potassium Nitrate Standard Solution: Add 3.0 mL of 10 mg/L Potassium Nitrate Standard Solution to a 100 mL volumetric flask. Bring to volume with reagent water.
- j. 0.20 mg/L Potassium Nitrate Standard Solution: Add 2.0 mL of 10 mg/L Potassium Nitrate Standard Solution to a 100 mL volumetric flask. Bring to volume with reagent water.
- k. Ionic Strength Adjuster (ISA): Commercially available or prepare as follows: Add 17.32 g $\text{Al}_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$, 3.43 g Ag_2SO_4 , 1.28 g H_3BO_3 , and 2.52 g Sulfamic acid ($\text{H}_2\text{NSO}_3\text{H}$) to 800 mL reagent water in a 1000 mL volumetric flask. Adjust to pH 3.0 by slowly adding 0.10N NaOH. Bring to volume with reagent water. This solution must be stored in a dark glass bottle.
- l. Outer Filling Solution (reference electrode), Ammonium Sulfate Solution: Add 0.53 g $(\text{NH}_4)_2\text{SO}_4$ to 80 mL reagent water in a 100 mL in volumetric flask. Bring to volume with reagent water.
- m. Dilute Sulfuric Acid Solution: Add 3.00 mL of concentrated H_2SO_4 to 80 mL of reagent water in a 100 mL volumetric flask, cool and bring to volume with reagent water.
- n. Silver Sulfate Solution (0.01 M): Add 0.31 g Ag_2SO_4 to 80 mL of reagent water in a 100 mL volumetric flask. Lightly heat until dissolved, cool and bring to volume with reagent water.

4.0 Sample Collection/Preservation/Holding Time

- a. Sample collection: Collect in a clean plastic or glass screw top container (250 to 1000 mL). Alternatively, samples may be collected in the analysis container if they are analyzed immediately.
- b. Sample preservation: 4°C.
- c. Maximum sample holding time: 48 hours. The Laboratory Certification Section recommends analyzing samples immediately after collection.

5.0 Nitrate Sample Analysis Procedure

This is a general procedure. Each Ion-Selective meter may have a unique procedure. Please reference the manufacturer's instructions for procedural details.

1. Calibrate nitrate meter following procedure detailed in Section 7.0.
2. Using a graduated cylinder, pour 80 mL of sample water and 20 mL ISA into 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. If needed, adjust pH of each sample to between 3.5 and 4.0 by slowly adding 0.1 N H₂SO₄ or 0.1 N NaOH. pH paper is used for verification.
4. Add a stir bar to the beaker containing the mixture and place on magnetic stirrer.
5. While stirring the sample, immerse nitrate meter probe in sample mixture and allow meter to stabilize.
6. Record the result as nitrate in mg/L directly; alternatively graph the concentration vs. millivolts.

Note: Probe(s) must be rinsed with reagent water before and between all analyses of samples/standards. The samples/standards must be stirred during analysis.

6.0 Quality Control Requirements

6.1 Nitrate Meter Calibration.

The calibration procedure must be performed resulting in an acceptable slope/linearity value in millivolt (mV) prior to each use for analyzing potable water (Section 7.0). The slope value must be recorded each time the meter is calibrated.

6.2 Analyst QC Requirements

Certified Analyst Requirements

All certified analysts are required to perform the calibration procedure and perform sample analysis at least once every three months. (Refer to Section 7.0.) Calibrations must be dated and initialed by all certified analysts participating in each calibration procedure.

Operationally Certified Analyst Requirements

Operational certification is not available for this method.

7.0 Nitrate Meter Calibration Procedure

Standard Curve (mV vs. Conc.): The concentrations of standards used to prepare the standard curve should be representative of the working range anticipated.

Meters Limited to a Two Point Standard Calibration

Samples Containing Nitrate Concentrations Greater than or equal to 1.0 mg/L:

Calibrate with nitrate standard solutions 1.0 mg/L and 10.0 mg/L. The subsequent slope result must fall within the acceptance range (-54 mV to -60 mV). A midrange verification standard (2.0 mg/L or 5.0 mg/L) must then be analyzed. The secondary source QC sample may be used for the midrange verification. The midrange standard must be within $\pm 10\%$ of its true value to accept the calibration. Samples with nitrate concentrations greater than the calibration range must be diluted into this range.

Samples with Nitrate Concentrations Less Than 1.0 mg/L

Calibrate with nitrate standard solutions 1.0 mg/L and 10.0 mg/L. The subsequent slope result must fall within the acceptance range (-54 mV to -60 mV). A midrange verification standard (2.0 mg/L or 5.0 mg/L) must then be analyzed. The secondary source QC sample may be used for the midrange verification. The midrange standard must be within $\pm 10\%$ of its true value to accept the calibration. The meter must then be used in millivolt mode to generate a curve with at least three nitrate standard concentrations between 0.2 mg/L and 1.0 mg/L. The curve is generated using standard millivolt response vs. standard concentration, and then plotting sample millivolt response along the generated curve.

Meters Capable of a Three Point Standard Calibration

Samples with Nitrate Concentrations Greater than or equal to 1.0 mg/L:

Calibrate with three nitrate standard solutions including the 1.0 mg/L and 10.0 mg/L. The third calibration standard must be in the midrange of the curve (2.0 mg/L or 5.0 mg/L). The subsequent slope result must fall within the acceptance range (-54 mV to -60 mV).

Samples with Nitrate Concentrations Less Than 1.0 mg/L

Calibrate with three nitrate standard solutions including the 1.0 mg/L and 10.0 mg/L. The third calibration standard must be in the midrange of the curve (2.0 mg/L or 5.0 mg/L). The subsequent slope result must fall within the acceptance range (-54 mV to -60 mV). The meter must then be used in millivolt mode to generate a curve with at least three nitrate standard concentrations between 0.2 mg/L and 1.0 mg/L. The curve is generated using standard millivolt response vs. standard concentration, and then plotting sample millivolt response along the generated curve.

Note: The calibration procedure must be performed with each sample analysis. Each calibration requires newly poured buffers, which are discarded after calibration.

1. Allow standards to stabilize to room temperature prior to analysis.
2. Prepare calibration standards and samples by using a graduated cylinder to measure 80 mL calibration standard and 20 mL ISA into a clean sample beaker/container.
3. If needed, adjust pH of each sample to between 3.5 and 4.0 by slowly adding 0.1 N H₂SO₄ or 0.1 N NaOH. pH paper is used for verification.

4. Add magnetic stir bars to each of the beakers.
5. Calibrate the nitrate meter following the manufacturer's instructions for a 2 or 3 point calibration.
6. Record the slope value. (Refer to Section 7.1 in this method for detailed acceptance limits.)
7. 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 7.1 for corrective measures.)

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

Note: Probe(s) must be rinsed with reagent water before and between all analyses of samples/standards. The samples/standards must be stirred during analyses.

7.1 Calibration Acceptance Limits

The slope/linearity value must fall in the acceptance range of -54 to -60 mV (displayed in millivolts).

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

7.2 Nitrate QC Sample Analysis

7.2.1 Annual PT Sample Analysis

All laboratories certified for nitrate analysis are required to successfully analyze and record one PT sample prior to initial certification and once every year thereafter.

A provider of PT samples must be accredited by a Proficiency Testing Provider Accreditor that meets the National Environmental Laboratory Accreditation Conference requirements.

The acceptance limits for the QC sample are $\pm 10\%$ of the true value.

7.2.2 Secondary Source QC Sample

A QC sample prepared from a source of nitrate other than the nitrate used for the preparation of the stock solution and calibration standards must be analyzed with each sample batch. The secondary source QC sample concentration must be in the midrange of the calibration curve and the acceptance limits are $\pm 10\%$ of the true value.

7.3 Required Calibration Documentation

The **Nitrate Slope/Linearity Verification (Second Source) Record** on page 130 of this manual may be used to document each calibration procedure. The minimum requirements for documenting each verification procedure are as follows:

- a. Analyst(s) initials.
- b. Date calibration procedure was performed, required to be recorded at a minimum of once per analysis.
- c. Linearity value percent (%) or millivolts (mV).
- d. Confirmation value of the second source QC sample, required to be recorded at a minimum of once per analysis.
- e. Comments.

Nitrite Analysis by Spectrophotometric Method

Quick Reference	Standard/Reagent	Requirements
Standard/Reagent Storage	Liquid Reagents	Room Temperature
	Standards	Refrigerated
Standard/Reagent Expiration	Standard/Reagent	Maximum Storage Time
	Reagents	1 Year After Opening/Manufacturer's Expiration Date
	Standards	1 Year After Opening/Manufacturer's Expiration Date
Required Quality Control	QC Procedure	Frequency
	Generate Calibration Curve	Once Per 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 (4500– NO₂⁻ B)

On-Site Survey Requirements

- Each certified analyst must be able to generate a calibration curve described in Section 7.0 of 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

A known amount of color reagent is added to a collected water sample, producing an intensely colored blue, azo-dye. The nitrite in the sample is then quantitated by absorbance on a spectrophotometer at wavelength 543 nm.

Interferences

Suspended solids, precipitates and dirty glassware may affect results. Excessive amounts of heavy metals can interfere. This is usually overcome by adding EDTA when metals are in the mg/L range.

2.0 Equipment

- a. A spectrophotometer capable of reading 543 nm with a cell light path width of at least 1 cm.
- b. Spectrophotometer vials.
- c. Computer with software capable of generating linear regressions.
- d. Class A volumetric pipet(s).
- e. Standard laboratory glassware.
- f. Balance.

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

Reference: Standard Methods, 22nd Edition, (Page 4-120, Section 3. Reagents)

- a. 100 mg/L Sodium Nitrite Stock Solution: Commercially available or prepare as follows: Dissolve 0.4929 grams of Sodium Nitrite (NaNO_2) in a 1 liter class A volumetric flask, half filled with reagent water. Bring to volume with reagent water. This solution is stable for 3 months if preserved with 2.0 mL chloroform per liter and kept under refrigeration when not in use.

Note: Potassium Nitrite may be substituted for Sodium Nitrite.

- b. 10 mg/L Nitrite-Nitrogen Calibration Standard Solution: Add 10.0 mL of 100 mg/L Sodium Nitrite-Nitrogen Stock Solution in a 100 mL class A volumetric flask, half filled with reagent water. Bring to volume with reagent water. This solution should be prepared fresh daily.
- c. Color Reagent: In a class A volumetric flask dissolve 1.0 gram Sulfanilamide ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$) and 0.1 gram N (1 naphthyl)-ethylenediamine dihydrochloride in a mixture of 10 mL concentrate phosphoric acid (H_3PO_4 , 85%) and dilute to 100 mL with reagent water. Keep in a dark glass container, refrigerate when not in use and discard after 1 month.

4.0 Sample collection/preservation/Storage/hold time

- a. Sample collection: Collect in a clean plastic or glass screw top container (250 to 1000 mL).
- b. Preservation: 4°C.
- c. Maximum sample holding time: 48 Hours. The Laboratory Certification Section recommends analyzing samples immediately after collection.

5.0 Sample Analysis Procedure

1. Using pH paper or a meter, verify sample pH is between 7.0 and 9.0. If needed, adjust sample pH with dilute HCl or NaOH to the appropriate pH range.
2. Add 2.0 mL of the color reagent to 50 mL of sample, cap and mix. Allow at least 10 minutes for full color development. After full development, the color will remain stable for up to two hours.
3. Measure and record the absorbance of each sample with a spectrophotometer set at a wavelength of 543 nanometers. Matched cuvettes or a single cuvette which is rinsed with a small amount of sample between measurements may be used.

Note: Samples exceeding 1.0 mg/L must be diluted into the working range of the calibration (0.10 mg/L - 1.0 mg/L). Do this by diluting the sample with reagent water. The final value will then be multiplied by a dilution factor.

6.0 Quality Control Requirements

6.1 Calibration Curve Generation

The calibration curve generation procedure must be performed prior to initial use for analyzing potable water and at least once per three months thereafter. (Refer to Section 7.0.) Each calibration curve generation procedure must be dated and recorded.

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the calibration curve generation procedure at least once per 3 months. (Refer to Section 7.0.) Generations must be dated and initialed by all certified analysts participating in each procedure.

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

Operationally Certified Analyst Requirements

Operational certification is not available for this method.

6.3 QC Requirements with Each Analysis

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

- a. Blank (0.0 mg/L): Acceptance: Results < reporting limit.
- b. Reporting limit verification (0.10 mg/L): Acceptance: $\pm 30\%$ of true value.
- c. Midpoint calibration verification (1.00 mg/L): Acceptance: $\pm 10\%$ of true value.

Note: A blank sample is required with each sample analysis. QC samples b and c are required only if an entire calibration curve is not analyzed and generated with the sample batch.

7.0 Calibration Curve Generation Procedure

A minimum of four 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 nitrite (0.1 mg/L). Alternatively, a reporting limit verification sample must be prepared in addition to the four calibration standard concentrations if the curve generation does not include the reporting limit concentration (0.1 mg/L). The reporting limit verification sample results must be within $\pm 30\%$ of the true value.

1. Prepare four 100 mL volumetric flasks containing a known volume of 10.0 mg/L nitrite calibration standard solution and reagent water according to the table in Section 7.2. Label each flask with the calibration standard it contains.
2. Prepare a blank by adding 100 mL reagent water to a volumetric flask.
3. Add 2.0 mL of the color reagent to 50 mL of sample, cap and mix. Allow at least 10 minutes for full color development. After full development, the color will remain stable for up to two hours.
4. Read absorbance of each calibration standard and blank at 543 nm on spectrophotometer. Follow the spectrophotometer manufacturer's instructions to generate and store a calibration curve using the blank and prepared calibration standards.
5. If the spectrophotometer does not have the capability to store calibration curves, read absorbance for each calibration standard at 543 nm on spectrophotometer. Record absorbance.
6. Using the absorbance and concentration of each calibration standard, generate a calibration curve manually on an Excel spreadsheet.

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). In order 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

10.0 mg/L nitrite 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 (0.0 mg/L), 0.10 mg/L, 0.50 mg/L, 1.00 mg/L and 1.50 mg/L. The table in Section 7.2 demonstrates how these standards are prepared in 100 mL volumetric flasks.

7.2 Calibration Standard Concentration Preparation Table

Standard Concentration	mL of 10.0 mg/L Nitrite Calibration Standard Solution Added to 100 mL Flask	Final Volume
Blank (0.0 mg/L)	0.0 mL	100 mL
0.10 mg/L	1.0 mL	100 mL
0.50 mg/L	5.0 mL	100 mL
1.00 mg/L	10.0 mL	100 mL
1.50 mg/L	15.0 mL	100 mL

7.3 Required Calibration Curve Generation Documentation

The **Nitrite Spectrophotometer QC Sample Record** on page 136 of this manual may be used to document the required information. The minimum requirements for documenting each calibration curve generation procedure are as follows:

- a. Analyst(s) initials.
- b. Analysis date.
- c. Blank concentration (mg/L).
- d. Reporting limit concentration (mg/L).
- e. Midpoint concentration (mg/L).
- f. Date calibration curve generated.
- g. Comments.

pH Analysis by Electrometric Method

Quick Reference	Standard/Reagent/Equipment	Requirements
Standard/Reagent/Equipment Storage	pH Probes	pH 7 Buffer/Manufacturer's Solution
	pH Buffers	Room Temperature
Standard/Reagent Expiration	Standard/Reagent	Maximum Storage Time
	pH Buffers	6 Months After Opening
Required Quality Control	QC Procedure	Frequency
	Calibrate Meter	Once Per Shift
	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)

On-Site Survey Requirements

- Each certified analyst must be able to perform the calibration procedure described in Section 7.0 of this method.
- Each operationally certified analyst must be able to perform the calibration procedure described in Section 7.0 of 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 probes. 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

- a. 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) probes are required for pH meters. Analog meters are not acceptable.
- b. A refillable combination probe or separate pH sensing probe and reference probe are acceptable. Sealed probes are not acceptable.
- c. Magnetic stirring devices/stir magnets.

2.1 General pH Probe Maintenance

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

Note: Storing probes in reagent water is not acceptable.

- c. Store probes as they are received until they are put into use.
- d. Probes taking longer than one minute to stabilize in pH buffer may need service or replacement.

3.0 Reagents

- a. 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 preparation.
- b. Reagent water.

4.0 Sample Collection/Preservation/Holding Time

- a. 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.
- b. Sample preservation: No Preservation Required.
- c. 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. Place the probe(s) in the sample while stirring and allow the display to stabilize.
5. Record the reading as the pH of the sample.

Note: Probe(s) must be rinsed with reagent water before and between all analyses of samples/standards. The samples/standards must be stirred during analysis.

6.0 Quality Control Requirements

6.1 pH Meter Calibration.

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.

6.2 Analyst QC Requirements

All certified and operationally certified analysts are required to 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 are required to perform the calibration procedure at least three times per month. (Refer to Section 7.0.) 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. 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.

Operationally Certified Analyst Requirements

All operationally certified are required to 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 pH Meter Calibration Procedure

Note: Calibration must be performed at the beginning of each shift. Each calibration requires newly poured buffers, which are discarded after calibration.

1. If refrigerated, allow the 4.0, 7.0 and 10.0 buffers to stabilize to 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. (Refer to Section 6.2 for pH 4.0 buffer acceptance limits.) This is required of certified analysts. **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.
4. Record the slope value for the calibration. This value must fall in the acceptable range of 95% to 105%, for pH slope value displayed in %, or -56 to -62 mV, for pH value displayed in millivolts.
5. If slope value is outside of acceptable range, the calibration procedure must be repeated until an acceptable value is acquired. (Refer to Section 6.4 for corrective measures.)
6. Meters capable of a 3-point calibration may be calibrated with pH buffers 4.0, 7.0 and 10.0.

Note: 2-point calibrations must require pH buffers 7.0 and 10.0. 3-point calibrations require pH buffers 4.0, 7.0 and 10.0. All laboratory personnel must consistently use the same calibration procedure, either a 2-point calibration or a 3-point calibration.

Note: Probe(s) must be rinsed with reagent water before and between all analyses of samples/standards. The samples/standards must be stirred during analyses.

7.1 Calibration Acceptance Limits

The efficiency value must fall in the acceptable range of 95% to 105%, for pH slope value displayed in %, or -56 to -62 mV, for pH value displayed in millivolts.

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 probe with reagent water to remove all internal crystalline build-up or follow the manufacturer's recommendations for probe cleaning. Replace the probe if needed.
3. Clean the probe following the manufacturer's recommendations.
4. Service the pH meter if all other attempts have failed to acquire acceptable results.

7.2 Required Calibration Documentation

The **pH Meter Slope/Weekly Linearity Verification (4.0 Buffer) Record** on page 142 of this manual may be used to document each calibration procedure. The minimum requirements for documenting each verification procedure are as follows:

- a. Analyst(s) initials.
- b. Date calibration procedure was performed, required to be recorded at a minimum of once per shift.
- c. Linearity value percent (%) or millivolts (mV).
- d. Confirmation value of pH 4.0 ± 0.10 verification buffer, required to be recorded at a minimum of once per week.

8.0 In-line pH Meters

In-line pH meter results must be verified with the results recorded by the bench top 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 bench top 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 bench top 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 bench top 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 chlorine meter and the calibrated bench top pH meter must be recorded. It is recommended to use the **Daily In-line pH Meter Verification Record** on page 143 of this manual may be used to document the required information.

8.1 In-Line pH Meter Calibration

The Laboratory Certification Section recommends in-line meters be calibrated once every 90 days not to exceed manufacturer's calibration requirements.

Phosphorous (Total) Analysis by Ascorbic Acid/Spectrophotometric Method

Quick Reference	Standard/Reagent	Requirements
Standard/Reagent Storage	Liquid Reagents	Room Temperature
	Standards	Room Temperature
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 Per 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 ₂ SO ₄ , 4°C	28 Days

Method Reference

Standard Methods 22nd Edition (4500-P E)

On-Site Survey Requirements

- Each certified analyst must be able to generate a calibration curve described in Section 7.0 of 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

- a. A spectrophotometer capable of reading 880 nm with a cell light path width of at least 1 cm.
- b. Spectrophotometer vials.
- c. Computer with software capable of generating linear regressions.
- d. Class A volumetric pipet(s).
- e. Standard laboratory glassware.
- f. A hot plate large enough to hold all the standards and samples at the same time for digestion.
- g. Heating blocks may be used as long as reagent proportions are not changed.
- h. A fume hood for use with the hot plate digestion.
- i. Autoclave (acceptable alternative to hot plate for the digestion procedure).
- j. 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

Reference: Standard Methods, 22nd Edition, (Page 4-155, Section 3. Reagents)

- a. 50 mg/L Phosphorous Stock Standard: Commercially available.
- b. 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 H₂SO₄. Bring to volume with reagent water.
- c. Sulfuric Acid Solution H₂SO₄ (5N): Commercially available. It may also be prepared as follows: Dilute 70 mL of concentrated H₂SO₄ to 500 mL with reagent water.

- d. Antimony Potassium Tartrate ($\text{K}(\text{SbO})\text{C}_4\text{H}_6\text{O}_6 \times 0.5\text{H}_2\text{O}$) Solution: Prepare as follows: Dissolve 1.3715 g $\text{K}(\text{SbO})\text{C}_4\text{H}_6\text{O}_6$ to 400 mL with reagent water in a 500 mL volumetric flask and dilute to volume.
- e. Ammonium Molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \times 4\text{H}_2\text{O}$) Solution: Prepare as follows: Dissolve 20 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \times 4\text{H}_2\text{O}$ to 400 mL with reagent water in a 500 mL volumetric flask and dilute to volume.
- f. Ascorbic Acid Solution (1 M): Prepare as follows: Dissolve 1.76 g ascorbic acid in 100 mL reagent water.
- g. Combined Reagent: Mix the above reagents (c, d, e and f) in the following proportions for 100 mL of combined reagent: 50 mL (c) Sulfuric Acid Solution (5 N); 5 mL (d) Antimony Potassium Tartrate Solution; 15 mL (e) Ammonium Molybdate Solution; and, 30 mL (f) Ascorbic Acid Solution (1 M). Mix after each addition. This combined reagent is stable for 4 hours after preparation.
- h. Sodium Hydroxide Solution NaOH (1 N): Commercially available.
- i. Reagent water.

4.0 Sample Collection/Preservation/Holding Time

- a. Sample collection: Collect in a clean plastic or glass screw top container (250 to 1000 mL).
- b. Preservation: Adjust to pH < 2.0 with H_2SO_4 , 4°C. No preservation needed if samples are analyzed/digested immediately after collection.
- c. Maximum sample holding time: 28 days. The Laboratory Certification Section 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: Analyses for other forms of phosphorous may not require digestion (Steps 3 through 6, and 9).

6.0 Quality Control Requirements

6.1 Calibration Curve Generation

The calibration curve generation procedure must be performed prior to initial use for analyzing potable water and at least once per three months thereafter. (Refer to Section 7.0.) Each calibration curve generation procedure must be dated and recorded.

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

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the calibration curve generation procedure at least once per 3 months. (Refer to Section 7.0.) 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.

6.3 QC Requirements with Each Analysis

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

- a. Blank (0.0 mg/L): Acceptance: Results < reporting limit.
- b. Reporting limit verification (0.03 mg/L): Acceptance: $\pm 30\%$ of true value.
- c. Midpoint calibration verification (0.10 mg/L): Acceptance: $\pm 10\%$ of true value.

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

7.0 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 $\pm 30\%$ 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 the table in Section 7.2. 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: Analyses for other forms of phosphorous may not require digestion (Steps 5 through 8, and 11).

Correlation Coefficient (R)/Coefficient of Determination (R²)

Once the calibration curve has been generated, acceptance of the curve is determined by the correlation coefficient (R) or the coefficient of determination (R²). In order for the curve to be acceptable for sample analysis, the correlation coefficient (R) must be greater than 0.995 or the coefficient of determination (R²) 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 (R²).

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. The table in Section 7.2 demonstrates how these standards are prepared in 50 mL volumetric flasks.

7.2 Calibration Standard Concentration Preparation Table

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

7.3 Required Calibration Curve Generation Documentation

The **Phosphorous (Total) Ascorbic Acid/Spectrophotometer QC Sample Record** on page 150 of this manual may be used to document the required information. The minimum requirements for documenting each calibration curve generation procedure are as follows:

- Analyst(s) initials.
- Analysis date.
- Blank concentration (mg/L).
- Reporting limit concentration (mg/L).
- Midpoint concentration (mg/L).
- Date calibration curve generated.
- Comments.

Stability Analysis by Alkalinity/pH Method

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
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)

On-Site 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 certified analysts will be required to participate in the analysis of a stability sample.
- Each certified analyst 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 CaCO₃ is measured using approved methods for both pH and alkalinity. All certification requirements for the alkalinity and pH methods must be met in order 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 un-dissolved CaCO_3 passing into the alkalinity/pH analysis beaker will render those results invalid. The analysis will require repeating.

2.0 Equipment

- a. Two 300 mL glass BOD bottles with glass stoppers.
- b. Magnetic stirring device and TFE-coated stir bar.
- c. Filter funnel and flask.
- d. Whatman Grade 934AH filter or equivalent.
- e. All equipment required for Alkalinity method analysis.
- f. All equipment required for pH method analysis.

3.0 Reagents

- a. Calcium Carbonate (CaCO_3): Reagent grade.
- b. All reagents required for alkalinity method analysis.
- c. All reagents required for pH method analysis.
- d. Reagent water.

4.0 Sample Collection/Preservation/Holding Time

- a. 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.
- b. Preservation: No Preservative Required.
- c. Maximum sample hold time: Sample preparation must begin immediately after collection.

5.0 Stability Analysis Procedure

A. Rapid Saturation

1. **CaCO₃ Saturated Sample:** Carefully add approximately 1.0 to 2.0 grams of CaCO₃ powder to one of the water samples collected in the 300 mL BOD bottles. Add a magnetic stirring bar and stopper it with no headspace. If all of the CaCO₃ dissolves, begin the analysis from sample collection (collect both samples again). On the subsequent analysis add 4.0 grams CaCO₃ to the saturated sample.
2. **Unsaturated Sample:** The unsaturated bottle sample will remain as collected while the CaCO₃ saturated sample undergoes Steps 3 - 4.
3. Stir the saturated bottle for a minimum of 30 minutes at moderate speed on a magnetic stirring device. The unsaturated sample will not be stirred.
4. After stirring for 30 minutes, allow the un-dissolved CaCO₃ in the CaCO₃ saturated sample to settle for an additional 30 minutes.
5. **From this point on both samples will be treated identically.**
6. Filter both samples separately; do not use the same filter paper to filter both samples and do not collect the filtrate in the same container. Use Whatman Grade 934AH or equivalent filter paper. **Note:** Care should be taken when filtering the saturated sample to ensure no un-dissolved CaCO₃ is transferred into the collection container.
7. 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.
8. Analyze the CaCO₃ saturated sample filtrate for pH and alkalinity. Record the results.
9. Analyze the unsaturated sample filtrate for pH and alkalinity. Record the results.
10. Refer to Section 5.1 for the instructions on interpreting the results.

B. Slow Saturation

1. **CaCO₃ Saturated Sample:** Carefully add approximately 1.0 to 2.0 g of CaCO₃ powder to one of the water samples collected in the 300 mL BOD bottles. Agitate this sample by shaking for 1 minute. If all of the CaCO₃ dissolves, begin the analysis from sample collection (collect both samples again). On the subsequent analysis add 4.0 g CaCO₃ to the CaCO₃ saturated sample.
2. **Unsaturated Sample:** The unsaturated bottle sample will remain as collected.
3. **From this point on both samples will be treated identically.**
4. Allow both CaCO₃ saturated and unsaturated samples to stand for 8 hours with periodic agitation of both samples every hour. Allow samples to settle overnight prior to proceeding to Step 5.
5. Filter both samples separately; do not use the same filter paper to filter both samples and do not collect the filtrate in the same container. Use Whatman Grade 934AH or equivalent filter paper. **Note:** Care should be taken when filtering the saturated sample to ensure no un-dissolved CaCO₃ 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 CaCO₃ 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 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 pH and alkalinity results between the CaCO₃ saturated sample and the unsaturated sample.

The interpretation is as follows:

Stable: There is no significant change of pH and alkalinity results between the CaCO₃ saturated sample and the unsaturated sample.

Example:

CaCO₃ saturated sample results: pH – 7.55, alkalinity – 84 mg/L
Unsaturated sample results: pH – 7.60, alkalinity – 86 mg/L

Note: Significant change may be defined as an increase/decrease in pH greater than 0.1 pH units and alkalinity increase/decrease in mg/L greater than 3% of the CaCO₃ saturated sample result.

Corrosive: The pH and alkalinity results are higher for the CaCO₃ saturated sample than the pH and alkalinity results for the unsaturated sample.

Example:

CaCO₃ saturated sample results: pH – 7.45, alkalinity – 84 mg/L
Unsaturated sample results: pH – 7.25, alkalinity – 78 mg/L

Scale Forming: The pH and alkalinity results are lower for the CaCO₃ saturated sample than the pH and alkalinity results for the unsaturated sample.

Example:

CaCO₃ saturated sample results: pH – 7.55, alkalinity – 84 mg/L
Unsaturated sample results: pH – 7.75, alkalinity – 90 mg/L

Invalid: If the pH and alkalinity results are not both either higher or lower in the CaCO₃ saturated sample than they are in the unsaturated sample, the stability analysis is invalid and must be prepared and analyzed again.

Example:

CaCO₃ saturated sample results: pH – 7.55, alkalinity – 84 mg/L
Unsaturated sample results: pH – 7.25, alkalinity – 90 mg/L

5.2 Langelier Index

The Langelier Index is an acceptable method for reporting corrosivity of potable water.

The required parameters are as follows: measured total dissolved solids (mg/L), measured temperature (°C), measured pH, measured alkalinity as CaCO₃ (mg/L) and measured calcium as CaCO₃ (mg/L). Sulfate and chlorine are not required for most potable water.

Each facility will need to determine acceptable Langelier limits by completing parallel water analysis between the marble test and the Langelier Index to define these limits.

6.0 Quality Control Requirements

6.1 Analyst Requirements

All requirements for pH and alkalinity method analysis (Section 6.0) of this manual apply.

6.2 Required Standardization Documentation

All requirements for pH method analysis (Section 7.2) and alkalinity method analysis (Section 7.5) of this manual apply.

The **Stability Method Interpretation Record** on page 156 of this manual may be used to document each analytical procedure. The minimum requirements for documenting each verification procedure are as follows:

- a. Analyst(s) initials.
- b. Analysis date.
- c. pH and alkalinity results for CaCO₃ saturated sample and unsaturated sample.

Total Dissolved Solids Analysis

Quick Reference	Standard/Reagent	Requirements
Standard Storage	1000 mg/L KCl Standard	Room Temperature
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
Sample Collection	Preservation	Maximum Hold Time
	4°C	7 Days

Method Reference

Standard Methods 22nd Edition (2540 C)

On-Site 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 0.45 µm glass fiber filter and placed into a weighed 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 weigh dishes are prone to mineral deposits after prolonged use. Care should be taken to assure they are properly cleaned after analysis.

2.0 Equipment

- a. Balance.
- b. Drying oven or steam bath capable of maintaining a temperature of 98 to 105°C.
- c. A drying oven capable of maintaining a temperature of $180 \pm 2^\circ\text{C}$.
- d. Desiccator with a humidity indicator.
- e. Evaporating dishes with a capacity of 50-100 mL.
- f. 50 mL volumetric flask or pipet.
- g. Filtering flask, holder, funnel and vacuum pump.
- h. Glass fiber filters, Whatman 934AH or equivalent.
- i. Laboratory tongs.

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

3.0 Reagents

- a. 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 1000 mL class A volumetric flask, half filled with reagent water. Bring to volume with reagent water.
- b. Reagent water.

4.0 Sample Collection/Preservation/Holding Time

- a. Sample collection: Collect in a clean glass screw top container (250 to 1000 mL).
- b. Preservation: 4°C.
- c. Maximum sample holding time: 7 Days. The Laboratory Certification Section recommends analyzing samples immediately after collection.

5.0 TDS Analysis Procedure

1. Oven dry the evaporation dishes at 180°C for one hour and allow them to cool in desiccator for one hour.
2. 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.
5. Assemble filter apparatus. **Note:** Use laboratory forceps when handling filters.
6. Filter enough of each sample to rinse the filter flask with two 75 mL aliquots of sample water.
7. Filter enough sample to supply approximately 100 mL of water.
8. Volumetrically deliver 50 mL of each sample to an assigned dish.
9. Place evaporation dishes containing the samples in an oven and allow the samples to evaporate to dryness at 98 to 105°C.
10. Dry the evaporating dishes at 180°C in an oven for at least one hour after they have evaporated to dryness.
11. Allow the dishes to cool in desiccator for 1 hour or until room temperature is reached.
12. Weigh the dishes and record weight.
13. Return the evaporating dishes to the 180°C oven for an additional hour.
14. Weigh the dishes and record weight.
15. The consecutive weights must agree to less than 0.5 mg.
16. Repeat cycle of drying, cooling, desiccating and weighing until consecutive weights agree to less than 0.5 mg.
17. Subtract weight of dish from weight of dish and sample. Record result as mg/L TDS.

6.0 Quality Control Requirements

6.1 Analyst Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the analysis once every three months.

Operationally Certified Analyst Requirements

Operational certification is not available for this method.

6.2 QC Requirements with Each Analysis

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

- a. Blank (0.0 mg/L): One per analysis and following every 10 samples. Acceptance: Results < 10 mg/L
- b. Duplicate sample: One per analysis and following every 10 samples. Acceptance: < 5% difference from average of two duplicate samples.
- c. Potassium chloride QC sample at (10 to 200 mg/L): One per analysis and following every 10 samples. Acceptance: $\pm 10\%$ of true value.

7.0 Required TDS Documentation

The **Total Dissolved Solids QC Analysis Record** on page 161 of this manual may be used to document the required information. The minimum requirements for documenting each analysis procedure are as follows:

- a. Analyst(s) initials.
- b. Analysis date.
- c. Blank concentration (mg/L).
- d. Duplicate sample analysis results.
- e. Potassium chloride (KCl) quality control sample true value.
- f. Potassium chloride (KCl) quality control sample actual result.

Turbidity Analysis by Nephelometric Method

<i>Quick Reference</i>	Standard/Reagent	Requirements
Standard/Reagent Storage	Formazin 4000 NTU	Refrigerated
	AMCO Standards	Room Temperature
	StablCal Standards	Room Temperature
	Secondary Standards	Room Temperature
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
	Turbidimeter Calibration	Once Per Three Months
	Secondary Standard Value Assignment	Once Per Three Months, Following Calibration Procedure
Sample Collection	Preservation	Maximum Hold Time
	4°C	48 Hours

Method Reference

Standard Methods 22nd Edition (2130)

On-Site Survey Requirements

- Each certified analyst must be able to perform the calibration procedure described in Section 7.0 of this method.
- Each operationally certified analyst must be able to perform the calibration procedure described in Section 7.0 of 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

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

- 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 .050 NTU.
- Class A volumetric pipet(s).
- Sample Vial. Follow procedure detailed in Section 7.2 to index the sample vials.

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 2-13 & 14, Section 3. Reagents)

- Primary Standard: Commercially available in required concentrations. Acceptable calibration standards are as follows:

Formazin: concentrate 4000 NTU.

Hach StablCal: standard set for laboratories meter and a 1.0 NTU standard.

AMCO Clear: standard set for laboratories meter and a 1.0 NTU standard.

Note: Primary standards are to be poured and/or diluted prior to each calibration, used once and then discarded. Purchasing the required concentrations is recommended although preparing Formazin primary standards is acceptable.

- Secondary Standards: Commercially available as Gelex standards. Two concentrations are required: 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.
- Low Turbidity Water (LTW) - Laboratory reagent water with less than 0.10 NTU or commercially available LTW.

4.0 Sample Collection/Preservation/Holding Time

- a. 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.
- b. Preservation: 4°C.
- c. Maximum sample holding time: 48 hours. The Laboratory Certification Section recommends analyzing samples immediately after collection.

5.0 Turbidity Sample Analysis

1. Fill test vial with sample and cover.
2. 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 Quality Control Requirements

6.1 Standard/Instrument Calibration

The turbidimeter calibration procedure must be performed prior to initial use for analyzing potable water and at least once per three months thereafter. (Refer to Section 7.0.) Each calibration procedure must be dated and recorded. The **Quarterly Turbidimeter Calibration Record** on page 169 of this manual may be used to document each calibration procedure.

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

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

Secondary standards must be analyzed, verified to be within acceptance 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 acceptance range and recorded at least once per 8 hour shift. Operationally certified analysts must participate in this procedure at least three times a month. The **Daily Secondary Standard Record** on page 168 of this manual may be used to document the required information.

7.0 Calibration Procedure

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 2100N calibration kit; and, (3) use only Class A volumetric glassware for formazin dilutions.

7.1 Air Reading

The turbidimeter must display an NTU ≤ 0.035 while empty and closed. If the NTU display is greater than 0.035, 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

Note: This procedure details the calibration for Hach 2100. Refer to manufacturer's calibration instructions for each instrument.

1. Fill a sample vial with LTW.
2. Place the sample vial into the holder and close the cover.
3. Press CAL, the S_0 annunciator will light.
4. Press ENTER, the display will count down from 60 to 0.
5. Fill a clean sample vial with a well-mixed 20 NTU primary standard.
6. Place the sample vial into the cell holder and close the cover and Press ENTER.
7. The instrument will count down from 60 to 0.
8. Fill a clean sample vial with well-mixed 200 NTU primary standard.
9. Place the sample vial into the holder, close the cover and Press ENTER.
10. The instrument will count down from 60 to 0.

11. Fill a clean sample vial with a well-mixed 1000 NTU primary standard.
12. Place the sample vial into the holder and close the cover and Press ENTER.
13. The instrument will count down from 60 to 0.
14. Fill a clean sample vial with a well-mixed 4000 NTU primary standard.
15. Place the sample vial into the cell holder and close the cover and Press ENTER.
16. The instrument will count down from 60 to 0.
17. Press **CAL**, the meter will store the calibration data internally. The turbidimeter will return to measurement mode.

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 $\pm 10\%$ of the 1.0 NTU. If it is not, begin the calibration procedure again (Section 7.3).

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 $\pm 10\%$ 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 $\pm 10\%$ acceptance range, the meter may need to be calibrated.
7. The **Daily Secondary Standard Record** on page 168 of this manual may be used to document the required information.

8.0 In-Line Turbidimeter Requirements

Filtered Water

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 bench top 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 bench top 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 bench top turbidimeter must be recorded. The **Daily In-line Turbidity Meter Verification Record** on page 170 of this manual may be used to document the required information.

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 bench top 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 bench top turbidimeter immediately and compared to the in-line turbidimeter result at the time of sample collection.

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 bench top turbidimeter within $\pm 10\%$. If the result is not within $\pm 10\%$, follow manufacturer's instructions to adjust the in-line meter to coincide with the turbidity result from the calibrated bench top 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 bench top 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 bench top 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.

8.1 In-Line Turbidity Meter Calibration

The Laboratory Certification Section recommends in-line meters be calibrated once every 90 days not to exceed manufacturer's calibration requirements.

Quarterly Turbidimeter Calibration Record

Date _____ Analyst(s) _____

	Result (NTU)
LTW Result (NTU)	
1.0 Result (NTU)	
1.0 NTU Acceptance Range (0.9 to 1.1)	Circle One: Yes or No
Corrected 1.0 NTU (1.0 NTU minus LTW NTU) ¹	
Air Display (Required <0.035 NTU)	

¹Not applicable for AMCO Clear or Hach StablCal

Secondary Standard Assigned Values

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

Quarterly Turbidimeter Calibration Record

Date _____ Analyst(s) _____

	Result (NTU)
LTW Result (NTU)	
1.0 Result (NTU)	
1.0 NTU Acceptance Range (0.9 to 1.1)	Circle One: Yes or No
Corrected 1.0 NTU (1.0 NTU minus LTW NTU) ¹	
Air Display (Required <0.035 NTU)	

¹Not applicable for AMCO Clear or Hach StablCal

Secondary Standard Assigned Values

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

UV₂₅₄ - Organic Constituent Analysis by UV Absorption/Spectrophotometric Method

Quick Reference	Standard/Reagent	Requirements
Standard/Reagent Storage	Liquid Reagents	Room Temperature
	Standards	Room Temperature
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 Per 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)

On-Site Survey Requirements

- Each certified analyst must be able to generate a calibration curve described in Section 7.0 of 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

- a. A spectrophotometer capable of reading 254 nm with a cell light path width of at least 1 cm.
- b. Spectrophotometer vials.
- c. Computer with software capable of generating linear regressions.
- d. Glass-filters (Whatman 934AH or equivalent).
- e. Gravity filter apparatus, including glass funnel and glass collection flask.
- f. Class A volumetric pipet(s).
- g. Standard laboratory glassware.

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

3.0 Reagents

Reference: Standard Methods, 22nd Edition, (Page 5-75 & 76, Section 3. Reagents)

- a. 1000 mg/L Organic Carbon Stock Solution, Potassium Biphthalate (KHP): Commercially available.
- b. 100 mg/L Organic Carbon Calibration Standard (KHP): Prepare as follows: 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.
- c. Hydrochloric Acid (HCl) Solution (0.1 N): Commercially available.
- d. Sodium Hydroxide (NaOH) Solution (0.1 N): Commercially available.
- e. Reagent water.

4.0 Sample Collection/Preservation/Holding Time

- a. Sample collection: Collect in a clean glass screw top container (250 to 1000 mL).
- b. Preservation: 4°C.
- c. Maximum sample holding time: 48 hours. The Laboratory Certification Section recommends analyzing samples immediately after collection.

5.0 UV₂₅₄ Analysis Procedure

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

1. Prepare a filter assembly for each sample.
2. Wash each filter assembly with at least 50 mL reagent water. Do not collect this wash in the sample collection flasks.
3. If the pH of the sample(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.
4. After pH adjustment, filter and collect at least 50 mL of the sample(s).
5. Read the absorbance at wavelength 254 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 or graph paper.

Note: Calculate using the following correlation equation: $UV_{254} = 0.0144 * X + 0.0018$ to determine the approximate UV₂₅₄ 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 UV₂₅₄ absorbance of approximately 0.0738.

6.0 Quality Control Requirements

6.1 Calibration Curve Generation

The calibration curve generation procedure must be performed prior to initial use for analyzing potable water and at least once per three months thereafter. (Refer to Section 7.0.) Each calibration curve generation procedure must be dated and recorded.

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

6.2 Analyst QC Requirements

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

Certified Analyst Requirements

All certified analysts are required to perform the calibration curve generation procedure at least once per 3 months. (Refer to Section 7.0.) 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.

6.3 QC Requirements with Each Analysis

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

- a. Blank (0.0 mg/L): Acceptance: Results < reporting limit.
- b. Reporting limit verification (1.0 mg/L): Acceptance: $\pm 30\%$ of true value.
- c. Midpoint calibration verification (5.0 mg/L): Acceptance: $\pm 10\%$ of true value.

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

7.0 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 UV 254 (1.0 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 (1.0 mg/L). The reporting limit verification sample results must be within $\pm 30\%$ of the true value.

1. Prepare three 100 mL volumetric flasks containing a known volume of 100.0 mg/L KHP calibration standard and reagent water according to the table in Section 7.2. Label each flask with the calibration concentration it contains.
2. Prepare a blank by adding 100 mL reagent water to a fourth volumetric flask.
3. Prepare a 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 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 manually on an Excel spreadsheet.

Correlation Coefficient (R)/Coefficient of Determination (R²)

Once the calibration curve has been generated, acceptance of the curve is determined by the correlation coefficient (R) or the coefficient of determination (R²). In order for the curve to be acceptable for sample analysis, the correlation coefficient (R) must be greater than 0.995 or the coefficient of determination (R²) 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 (R²).

Note: Calculate using the following correlation equation: $UV_{254} = 0.0144 * X + 0.0018$ 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.

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 (0.0 mg/L), 1.0 mg/L, 5.0 mg/L and 10.0 mg/L. The table in Section 7.2 demonstrates how these standards are prepared in 100 mL volumetric flasks.

7.2 Calibration Standard Concentration Preparation Table

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

7.3 Required Calibration Curve Generation Documentation

The **UV₂₅₄-Organic Constituent/Spectrophotometer QC Sample Record** on page 177 of this manual may be used to record the required information. The minimum requirements for documenting each calibration curve generation procedure are as follows:

- a. Analyst(s) initials.
- b. Analysis date.
- c. Blank concentration (mg/L).
- d. Reporting limit concentration (mg/L).
- e. Midpoint concentration (mg/L).
- f. Date calibration curve generated.
- g. Comments.

Inorganic Analytical Methods

Analysis of inorganic constituents in drinking water must be performed following Ohio EPA accepted analytical methods referenced in rule 3745-81-27(A) of the OAC.

In addition to individual method quality control (QC) requirements, the Laboratory Certification Section requires that, at minimum, the following program specific inorganic analysis QC be met.

- Laboratory analyte reporting limits must meet reporting limit concentrations referenced in rule 3745-89-03, Appendix B, of the OAC.
- An Initial Demonstration of Capability (IDC) study must be completed and documented for each instrument used for certified drinking water method analysis.
- An annual Method Detection Limit (MDL) study must be completed and documented for each instrument used for certified drinking water method analysis. Analysts seeking initial certification must complete an MDL for each method prior to survey.
- Calibration curves for certified analytical methods must be generated at a minimum of once per three months.
- Certified analysts must generate a curve at least once annually for all analytical methods for 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 (R²) greater than 0.990 to be acceptable for drinking water analysis.
- Individual method Linear Dynamic Range requirements are exempted if all sample results are diluted to within the calibration standard range.
- 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. The acceptance limits are $\pm 30\%$ of true value.
- A secondary source QC sample must be extracted and/or analyzed with each sample batch. The acceptance limits are $\pm 10\%$ 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 $\frac{1}{2}$ of the reporting limit concentration for individual analytes.
- Heating equipment used for digestion/preparation of samples must be verified to within $\pm 2^\circ\text{C}$ of method required temperature
- At least once every 3 months, a drinking water sample must be analyzed using the inorganic analytical methods for which the laboratory is certified.

Metals Analytical Methods

Analysis of metal constituents in drinking water must be performed following Ohio EPA accepted analytical methods referenced in rule 3745-81-27 of the OAC.

In addition to individual method quality control (QC) requirements, the Laboratory Certification Section requires that at minimum the following program specific metals analysis QC be met.

- Laboratory analyte reporting limits must meet reporting limit concentrations referenced in rule 3745-89-03, Appendix B, of the OAC.
- An Initial Demonstration of Capability (IDC) study must be completed and documented for each instrument used for certified drinking water method analysis.
- An annual Method Detection Limit (MDL) study must be completed and documented for each instrument used for certified drinking water method analysis. Analysts seeking initial certification must complete an MDL for each method prior to survey.
- Calibration curves for certified analytical methods must be generated at a minimum of once per three months.
- Certified analysts must generate a curve at least once annually for all analytical methods for which they are certified.
- Calibration curves are limited to 1st order. The calibration curve must result in a Correlation Coefficient (R) greater than 0.995 or a Coefficient of Determination (R²) greater than 0.990 to be acceptable for drinking water analysis.
- Individual method Linear Dynamic Range requirements are exempted if all sample results are diluted to within the calibration standard range.
- 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. The acceptance limits are $\pm 30\%$ of true value.
- A secondary source QC sample must be extracted and/or analyzed with each sample batch. The acceptance limits are $\pm 10\%$ 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 $\frac{1}{2}$ of the reporting limit concentration for individual analytes.
- Heating equipment used for digestion/preparation of samples must be verified to within $\pm 2^\circ\text{C}$ of method required temperature.
- At least once every 3 months, a drinking water sample must be analyzed using the metals analytical methods for which the laboratory is certified.

Organic Analytical Methods

Analysis of organic constituents in drinking water must be performed following Ohio EPA accepted analytical methods referenced in rule 3745-81-27(B) of the OAC.

In addition to individual method quality control (QC) requirements, the Laboratory Certification Section requires that at minimum the following program specific organic analysis QC be met.

- Laboratory analyte reporting limits must meet reporting limit concentrations referenced in rule 3745-89-03, Appendix B, of the OAC.
- An Initial Demonstration of Capability (IDC) study must be completed and documented for each instrument used for certified drinking water method analysis.
- An annual Method Detection Limit (MDL) study must be completed and documented for each instrument used for certified drinking water method analysis. Analysts seeking initial certification must complete an MDL for each method prior to survey.
- Calibration curves for certified analytical methods must be generated at a minimum of once per three months.
- 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 (R²) greater than 0.990 to be acceptable for drinking water analysis. Response Factor may be used if cited in method.
- 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. The acceptance limits are $\pm 50\%$.
- A mid-range secondary source QC sample must be extracted and/or analyzed with each sample batch. The acceptance limits are $\pm 30\%$ of true value unless stated otherwise for the laboratory fortified blanks referenced in each approved method.
- 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 $\frac{1}{2}$ of the reporting limit concentration for individual analytes.
- Heating equipment used for extraction of samples must be verified to within $\pm 2^\circ\text{C}$ of method required temperature.
- At least once every 3 months, a drinking water sample must be analyzed using the organic analytical methods for which the laboratory is certified.

Appendices

A. Glossary and Acronyms

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 the analyte(s) 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: 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.

Laboratory Certification Section: The section at Ohio EPA, administering the Ohio 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.

On-site Survey: An on-site inspection of laboratory capabilities. On-site surveys can be scheduled or unannounced.

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.

2. Acronyms

Ohio EPA: Ohio Environmental Protection Agency

USEPA: United States Environmental Protection Agency

NELAP: National Environmental Laboratory Accreditation Program

NPDWR: National Primary Drinking Water Regulations

QA: Quality Assurance

QAP: Quality Assurance Plan

QC: Quality Control

ORC: Ohio Revised Code

SOP: Standard Operating Procedure

OAC: Ohio Administrative Code

SDWA: Safe Drinking Water Act

DES: Division of Environmental Services

PT: Proficiency Test

B. General Laboratory Benchsheets

1. The **Reagent/Standard Preparation Record** on page 184 of this manual may be used to record the required information. The minimum requirements for documenting each verification procedure are as follows:
 - a. Supplier/Analyst(s) initials.
 - b. Type of reagent/standard.
 - c. Reagent/standard lot number.

- d. Date received or prepared.
 - e. Reagent/standard expiration date.
2. The **Calibration/Standardization Schedule** on page 185 of this manual may be used to record the required information. The minimum requirements for documenting each verification procedure are as follows:
- a. Weekly
 - Fluoride 1.0 Standard Verification*
 - pH 4.0 Buffer Verification*
 - b. Monthly (standardization)
 - Alkalinity
 - Chloride
 - Chlorine Dioxide FAS
 - Chlorine FAS
 - Chlorine PAO
 - Hardness
 - c. Quarterly: Once Every Three Months (per analysis)
 - Chlorine Dioxide DPD Curve
 - Chlorine DPD Verification
 - Copper Curve
 - Iron Curve
 - Manganese Curve
 - Nitrate Cd Reduction Curve
 - Nitrate Probe Curve
 - Phosphate Curve
 - Turbidity Calibration
 - UV254 Curve

Reagent/Standard Preparation Record

Laboratory _____

Supplier/Analyst(s) Initials	Type of Reagent/Standard	Reagent/Standard Lot Number	Date Received/Prepared	Reagent/Standard 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												
Hardness												
Quarterly	Once Every Three Months (per analysis)											
Chlorine Dioxide DPD Curve												
Chlorine DPD Verification												
Copper Curve												
Iron Curve												
Manganese Curve												
Nitrate Cd Reduction Curve												
Nitrate Probe Curve												
Phosphate Curve												
Turbidity Calibration												
UV ₂₅₄ Curve												

*Unless a three-point calibration curve is performed.

