

Laboratory Manual
for
Chemical Analyses
of
Public Drinking Water

2000

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Part I Certification Overview

All persons performing analyses of public drinking water in a approved laboratory must be approved by the Ohio EPA. The Ohio EPA/DES Division of Environmental Services Laboratory Certification Section (DES) evaluates laboratories. The Ohio EPA then either grants or denies certification to the laboratory.

There are two types of approval available for utility laboratories: Full Approval ; and Operational Approval. Full approval is meant for individuals analysts who perform all tests, calibrations, standardizations and other QC activities. Operational approval is offered to utility laboratories for analysts that only perform reportable monitoring tests. Operational approval is only available for: turbidity, pH, Alkalinity, Stability (pH and Alkalinity Stability), Hardness, Chloride, Fluoride, and Chlorine. The only calibrations an operational analyst may perform are pH meter calibrations, fluoride meter calibrations and secondary standard checks on a turbidimeter. Operational analysts may not perform routine calibrations, standardizations and other QC activities. Operational approval is offered only to water treatment facilities.

Analysts are only approved at the laboratory for methods noted on the certificate of approval. If an analyst changes or adds methods those methods are not approved. If an analyst moves to another facility that may or may not be approved, that analyst is no longer approved and will need to reapply for certification at the new facility. If the facility is approved and loses all of its approved analysts, the facility is no longer approved and must reapply for approval, when new analysts are hired. It is the laboratory's responsibilities to notify the Ohio EPA/DES of all personnel changes. All certificates of approval remain the property of the Ohio EPA and must be returned to the Ohio EPA/DES when an approved analyst departs.

Each approved analyst shall participate proportionally in the analyses for which he or she is approved. The minimum acceptable proportion shall be 10%, which is typically three days per month. In order to maintain full approval any non-routine tests, including calibrations or standardizations, must be performed at least once per three months by each approved analyst to maintain approval for that test.

Weekly calibration/standardization tests must be performed quarterly (once/three months). Monthly calibration/standardization tests must be performed at least quarterly. Quarterly (once/three months) calibration/standardization tests must be performed as a team or tests must be duplicated. In this manual, quarterly tests refer to tests that must be run a minimum of once every three months. If four months elapse between quarterly tests, then the required test frequency has not been met.

Required Test/Calibration Standardization	Required Minimum Frequency/Analyst
Drinking water analyses by parameter	10% of parameter each month
Weekly QC	One calibration per three months
Monthly QC	One calibration per three months
Quarterly (1/three months) QC	One calibration per three months/may be performed as a team or tests must be duplicated or run at an increased frequency

Certification covers personnel, equipment, records and facility. A person is approved in his or her laboratory, if that person moves to a new facility, he or she must inform the Ohio EPA/DES Laboratory Certification Section of the intended change. If the individual moves to another certified laboratory, the person is no longer approved. Approval will be granted either as either *Full* (all functions of a test including all quality control tests as well as the analysis itself) or *Operational* (for just the analysis itself). Between full surveys interim authorization to perform operational tests may be granted in advance of an on-site inspection. To do this a laboratory must obtain the necessary application and training documentation forms from the Ohio EPA/DES Laboratory Certification Section .

All fully approved lab personnel must be present for a survey. All new operational personnel must be present for a survey. At least 51% of all operational analysts must be present for the on site survey. Call the Laboratory Certification Section for further details.

The drinking water certification program serves laboratories within Ohio for municipal water supplies serving populations of >1000, performing three or more operational tests or performing tests for any chemicals having a USEPA maximum contaminant level (MCL). Additionally, commercial laboratories within Ohio, that perform drinking water tests, must be certified. Inorganic MCL tests commonly performed by water plant laboratories include: turbidity, fluoride, nitrate & nitrite.

If a certified laboratory moves but retains the same personnel, and if the laboratory plans are approved in writing by the Ohio EPA, certification will remain in effect. If a certified laboratory makes a substantial change in physical facility, such as addition of bench space, without prior plans approval and subsequent on-site survey, the laboratory may be subject to loss of certification. If a laboratory has never been previously certified, the initial survey is followed by surveys one year and three years from the initial survey.

Surveys are normally conducted every three years for certification renewal. These "full" surveys will cover all aspects of analyses for which certification is being sought. The surveys will be scheduled upon acceptance of an application for certification.

The survey fee will only be assessed once every three years. Applications can be obtained by contacting the Ohio EPA/DES Laboratory Certification Section.

In addition to the normally scheduled surveys, surveys may also be conducted on a random unannounced basis. The laboratory facility and records must be available for inspection during normal working hours (8:00 am to 5:00 pm) for unannounced surveys. The approved person(s) need not be present for unannounced surveys as long as the survey officer has access to the laboratory and records.

A responsible person must be designated to provide access to the laboratory (city hall, other operator, police, etc.), and laboratory records must be maintained in the building. The laboratory records must be clearly labeled and easily accessible, in a conspicuous location. Copies of the records must be made for survey personnel when requested. Telephone numbers of the responsible personnel must be posted to allow access for emergencies and certification officers.

Part II Requirements for Certification

Rules pertaining to laboratory certification are contained in chapters 3745-89-01 through 3745-89-10 of the Ohio Administrative Code (OAC). Ohio approved test methods are in OAC chapter 3745-81-27. If copies are needed, please contact the Ohio EPA or access the Ohio EPA website: <http://www.epa.ohio.gov/ddagw/ddagwmain.html>.

An application form for a laboratory survey is to be submitted in writing to the Ohio EPA/DES Laboratory Certification Section. This submittal must be made within 120 days in advance of the expiration of the current laboratory certification.

Applications must be submitted at least 30 days prior to the expiration of the current certificates. If a completed application is not submitted by thirty days prior to the expiration date, the laboratory is not eligible for any extension beyond the expiration date of the certification and a prescheduled date for an on-site survey is subject to cancellation. If the prescheduled date for an on-site survey is canceled, a subsequent survey shall **not** be scheduled until at least fourteen days after the expiration date occurs.

Once an application has been submitted and accepted, the current certificates of approval automatically will have the expiration date extended until an on-site survey has been successfully performed, unless the application was submitted with less than 30 days until the expiration of the current certificates as noted above.

In order for an application to be acceptable, the completed application form must be accompanied by an approval letter for laboratory plans issued by the Ohio EPA. Certification fees will be invoiced after the application has been accepted. Fees sent with applications will be returned.

If the above mentioned letter for lab plans approval is not available, it is advisable to contact the Ohio EPA six months prior to the expiration date of your current certification.

A quality assurance (QA) plan shall be submitted with the application for certification (seePart X, below). QA plans are required for laboratories applying for certification for the following test parameters: primary inorganic chemicals (cyanide, nitrate, nitrate-nitrite, nitrite, and sulfate, etc.), total trihalomethanes, volatile organic chemicals, pesticides and other organic chemicals, primary metals, or radioactivity and radioactive chemicals .

Part III Interim Authorization

Analysts may obtain interim authorization to perform drinking water tests. Interim authorization grants operational approval to an analyst who has demonstrated the ability to closely match an approved analyst's results for 20 days. Interim authorization is granted without the need for an immediate on-site survey. The number of individuals requested for interim authorization by the laboratory may not be more than two per application. To obtain interim authorization, first an application must be obtained from the Ohio EPA/DES. Second a 20 day training schedule must be documented on the supplied form. Third, the completed application and training documentation must be submitted to the Ohio EPA/DES. If all data is acceptable, the analyst will be granted interim authorization to perform operational tests. Within six months of an interim authorization, an on-site survey will be scheduled to verify the acceptable performance of the individual(s) granted the interim authorization. Interim authorization shall remain in effect for a period not to exceed six months or, if an on-site survey is scheduled or has been conducted, until the on-site survey report is issued. The interim authorization process allows laboratories to quickly replace analysts when necessary regardless of the current survey schedule backlog. Analysts with interim authorization are considered operational analysts and as such may not perform calibrations, standardizations and other QA activities. Interim authorization, since it is meant only for operational approval, is offered only to water treatment plant laboratories. The previous approval of an individual to perform plant control tests may be considered for satisfying this requirement.

Part IV Provisional Authorization

Provisional authorization is used only to add new methods and/or tests for new contaminants when new regulatory requirements are being implemented.

Provisional authorization will only be available to laboratories which currently have valid certification for the same type of drinking water analyses (microbiological contaminants, primary inorganic, primary metals, etc.) as the drinking water analyses to be included in the provisional authorization.

In order to be considered for provisional authorization, the laboratory shall submit to the Ohio EPA/DES an application for provisional authorization, on a form provided by the Ohio EPA/DES.

An on-site survey shall be scheduled to verify acceptable performance by the laboratory granted provisional authorization. Provisional authorization shall remain in effect for the length of time specified by the director or until the on-site survey is completed, whichever occurs first.

Part V Laboratory Approval Status

Upon completion of the on-site survey, a conclusion is mailed with the narrative report.

Conclusions are as follows:

Approved - A Certificate of Approval will be issued by the Ohio EPA for the chemical tests listed in the report. Certificates of approval are valid for a time period not to exceed three years from the date of issue.

Extended Approval - The deviations listed in the report must be corrected before the date listed in the report. A statement detailing the remedial actions taken to correct each of the listed deviations must be forwarded to the Laboratory Certification Section prior to the expiration date of the report to avoid revocation in accordance with the OAC.

Not Approved - The laboratory will not be certified for the chemical test(s) noted in the report.

Part VI Proficiency Test (PT) Samples

Laboratories must choose an Ohio EPA approved PT supplier and contact the supplier to arrange for shipment of PT samples. Samples are to be analyzed twice each year based on the suppliers schedule. The cost of the samples are to be borne by the laboratory. The laboratories must be notified, as to the exact date of shipment, by the PT supplier at least 30 days prior to shipment. Labs must report data 30 days after receipt of the samples.

A sample set may be considered invalid if >30% of the analysts are out of range, for sets of ten samples or more.

Any PT failure will result in a requirement for the laboratory to submit a statement of probable cause and corrective action to the Ohio EPA. The criteria used for invalidation of certification will be based upon USEPA/National Environmental Laboratory Accreditation Conference (NELAC) guidelines. Two consecutive failures will result in invalidation for the parameter. Two failures out of three, but not successive will require a written statement from the laboratory describing the problem that may have caused the failures and corrective action. There will be one supplemental PT sample allowed after two successive failures. The laboratory must pay for all supplemental samples. If the laboratory passes, their certification will become valid for the parameter. If the laboratory misses the parameter, they must wait for the next scheduled PT sample.

Chemistry pass/fail criteria are based upon USEPA limits which are the same as the past WS limits. For parameter groups, a laboratory must successfully analyze at least 85% of the analytes in a parameter group (rounding up).

Studies will be conducted on a test method basis. PT samples are to be treated as normal drinking water samples. The laboratory is to analyze the sample by the approved method most commonly used by the laboratory for drinking water tests. PT tests will not be required for each individual method if the laboratory is certified for an analyte by more than one method.

Parameter groups and analytes considered:

Nitrate, Nitrite, Sulfate, Lead & Copper, Cyanide, Metals (12), Organohalides (11), Nitrogen/Phosphorus Pesticides (7), Carbamates (8), Chlorinated Acid Herbicides (7), PCB (decachloro-biphenyl), PAH (Benzo-A-Pyrene), Adipate/Phthalate Esters (2), Diquat, Endothall, Glyphosate, Trihalomethanes, VOC (57), Vinyl Chloride, EDB/DBCP,

and analytes as per disinfection byproducts rule.

Specific Analytes Contained in Each Group Are:

- (a) Metals: Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Selenium, Thallium.
- (b) Carbamates: Aldicarb, Aldicarb Sulfone, Aldicarb Sulfoxide, Carbaryl, Carbofuran, 3-Hydroxycarbofuran, Methomyl, Oxamyl (Vydate)
- (c) Chlorinated Acids: 2,4-D, Dalapon, Dicamba, Dinoseb, Pentachlorophenol, Picloram, 2,4,5-TP (Silvex)
- (d) Nitrogen/Phosphorus Pesticides: Alachlor, Atrazine, Butachlor, Metolachlor, Metribuzin, Simazine
- (e) Organohalides: Aldrin, Chlordane, (Total) Dieldrin, Endrin, Heptachlor, Heptachlor Epoxide, Hexachlorobenzene, Hexachlorocyclopentadiene, Lindane, Methoxychlor, Toxaphene, Propachlor
- (f) Adipate/Phthalate Esters: Di(2-ethylhexyl)adipate, Di(2-ethylhexyl)phthalate
- (g) Trihalomethanes: Chloroform, Bromodichloromethane, Dibromochloromethane, Bromoform, Total THM

The acceptance limits of the analytical results have been set by the USEPA, NERL-CI, (formerly EMSL) Cincinnati, Ohio. The Ohio EPA then uses the "Acceptability" or "Unacceptability" findings to determine whether a laboratory has performed "Acceptable" or "Not Acceptable".

The trihalomethanes are evaluated as a group with one error being the maximum allowed for a designation of "Acceptable". The metals, carbamates, chlorinated acids, nitrogen/phosphorus pesticides, organohalides, and regulated/unregulated volatile organic chemicals (excluding vinyl chloride) are evaluated as groups with no more than fifteen percent unacceptable results being the maximum allowed for a designation of "Acceptable". Vinyl chloride is evaluated separately and all results must be within the acceptance limits for a designation of "Acceptable".

All results must be within acceptable limits for a designation of "Acceptable" for Asbestos, Nitrate, Nitrite, Cyanide, Sulfate, Lead & Copper, EDB/DBCP, Diquat, Endothall, Glyphosate, PAHs (Benzo-A-Pyrene), PCB's and Adipate/Phthalate Esters. The criteria used to interpret the Proficiency tests results is subject to revision at any time at the discretion of the USEPA.

Laboratory Approval Status Additional Information

Laboratories seeking initial certification for Cyanide, Nitrate, Nitrite, Sulfate, Metals, THMs, VOCs, Vinyl Chloride, Pesticides or other Synthetic Organic Chemicals must perform "Acceptable" on the most recent proficiency tests before an on-site survey can be considered. Laboratories holding a valid laboratory certificate of approval for the above mentioned analyses must participate in all the proficiency tests with "Acceptable" results being obtained on at least every other study. Laboratories seeking certification for the 57 regulated/unregulated VOCs, excluding Vinyl Chloride, must successfully analyze for unregulated VOCs and also for the regulated VOCs.

Special Requirements for Fluoride Certification

Fluoride QC Check Requirements

All laboratories are required to successfully analyze one QC check in a range of 0.5 to 1.5 mg/L each month. These QC check samples may be obtained from any of the Ohio EPA approved PE suppliers. The cost of these QC check samples will be borne by your laboratory. If the sample result obtained differs from the PT suppliers actual value by $\pm 15\%$, contact the Ohio EPA/DES Laboratory Certification Section for assistance. A fluoride check sample must be analyzed

with the results in the acceptable range, prior to an initial survey for fluoride. Submit the data for the initial fluoride QC check to the Ohio EPA/DES.

Requests for an on-site survey will not be considered until the laboratory obtains acceptable results as required for the proficiency tests, and meets all criteria and prerequisites as set forth in the Ohio Administrative Code; Chapter 3745 -89.

All analyses performed on drinking water in the state of Ohio except for the water quality parameters analyzed in conjunction with the Lead and Copper rule must be performed in an Ohio EPA approved laboratory.

Part VII General Laboratory Practices

Pipet Use - Carefully wipe the tips of volumetric pipets dry before delivering volume. Do not touch the opening in the delivery tip when drying the tips. Do not blow them out.

Glassware Preparation - All glassware must be washed in a warm laboratory detergent solution and thereafter thoroughly rinsed in hot tap water. A laboratory pure water rinse must follow the tap water rinse. This cleaning procedure is sufficient for most analytical needs, but many Standard Methods procedures call for more elaborate precautions to be taken against contamination of glassware. For example: it has been found advantageous to maintain a separate set of glassware (suitably prepared) for the nitrate and iron procedures due to the potential for contamination from the laboratory environment. Laboratories performing phosphate analyses must maintain a separate set of glassware to avoid any potential contamination. For phosphate tests, glassware should be acid rinsed in dilute HCL, followed by several lab pure water rinses.

Standards, Reagents and Chemicals - Reagents and chemicals must be dated upon receipt and again when they are first opened. Store commercial solutions either a maximum of two years after receipt or one year after opening, except for pH buffers. Store pH buffers no longer than six months after opening. Dry reagents may be used for a maximum of six years from the date received. Single use reagents or standards purchased already prepared by a manufacturer, in individual, sealed containers may be used until the manufacturer's expiration date. This includes DPD powder packets and ampuled standards. All materials must be replaced more frequently if: caking or moisture absorption is evident; a change in color, composition or physical state occurs (solidifies, crystallizes, or liquefies).

Refrigerate all stock standards except: pH buffers, "AMCO" and StablCal turbidity standards and metal standards. Refrigerate the 100 mg/l fluoride stock standard, do not refrigerate the 0.5, 1 and 10 fluoride working standards.

All labs must keep a log that documents date of receipt and/or preparation of all standards and reagents.

All solutions as well as any other chemicals used in analyses must be labeled to indicate the chemical name, type, strength, date of receipt and date of opening. Working bottles of reagents and standards must be identified by name, with the rest of the data recorded on the original bottle.

Standardization and Calibration Frequencies - Each approved analyst must initial his/her own calibration and standardization records. A QC notebook with labeled dividers is required for keeping the standardization/calibration records.

Wet chemistries: The laboratory standardization schedule as found in this manual must be utilized as a minimum by the laboratory for tracking the required standardizations and calibrations.

Metals: A calibration curve must be performed prior to each analytical run and documented. Additional requirements are located in the "Primary metals" chapter of this document.

THMs, SOCs, VOCs: please consult the particular requirement of each individual method.

Part VIII General Equipment Information

Analytical Balance - Laboratories preparing their own analytical standards and reagents from pure chemicals must maintain an analytical balance meeting Class S or ASTM Class 1 weight specifications which is readable and accurate to 0.1 milligram or better. Laboratories must have a service contract for each analytical balance that is used for standard and reagent preparation. Such balances must be checked for accuracy and adjusted when necessary by a qualified person at least once per year and service dates recorded. Stone balance tables or stone balance slabs must be provided for the analytical balances. Minimum specifications: Precision ± 0.1 milligram, minimum scale readability 0.1 milligram. Electronic top loading balances are preferred. A desiccator is required for storage and drying. Laboratories that purchase all of their analytical reagents and standards from a reputable supplier in precalibrated form are not required to maintain an analytical balance.

Refrigerator - Refrigeration at 2-10 °C (however, samples for some particular parameters must not exceed 8 °C) is required for storage and preservation of stock standard solutions. Refrigeration is also required for storage and preservation of samples prior to analysis and for proper storage of many lab prepared and purchased laboratory reagents and standards. Laboratories without adequate refrigeration facilities will not be approved. The refrigerator must be equipped with a thermometer with the bulb immersed in a stoppered liquid filled test tube or vial.

Tabletop or under counter refrigerators are acceptable as long as they can hold temperature and are of sufficient size. For sample and nonflammable reagent storage, a standard domestic model will be sufficient. For storing organics, flammables, or other volatile materials, a refrigerator suitable for flammable materials storage is necessary.

Laboratory Pure Water - this can either be distilled or deionized water either prepared in the laboratory or purchased) Laboratory pure water used for chemical purposes may be prepared in the laboratory or purchased from a reputable supplier. In either case, laboratory water must exhibit a conductivity less than 2.0 micromhos or resistivity greater than 0.5 megohm per centimeter at 25 °C and must not contain measurable amounts of chlorine or other impurities. Use only natural (amber) latex tubing or "tygon" plastic tubing on laboratory pure water and rinse water dispensing systems. Do not use black rubber tubing. Mixed bed deionizing cartridges with hose nipple fitting are an economical means for improving the quality of single distilled water when properly maintained.

Spectrophotometer - Minimum specifications: Usable wavelength range from 400 to 880 nanometers. Maximum setting accurate to 2.5 nanometers or less. Spectral band width of 15 nm or less.

Turbidimeters - Use only those that have been evaluated by the Laboratory Certification Section for acceptability. Ratio only meters are not acceptable. Ratio/Non-ratio selectable meters must be calibrated with ratio on and used for samples and low level checks with ratio off.

pH and Specific Ion (fluoride) Meters - Minimum specifications: Accuracy of 0.1 pH unit, expanded scale millivolt capability readable and accurate to 1 millivolt, or a direct reading concentration scale providing the equivalent or readability to 1 millivolt or better. Meters must be designed for a minimum of a two standard calibration and % slope or efficiency read-out. Digital display meters are required. Analog (needle) meters are not acceptable. Direct readout of concentration (activity), is recommended for fluoride determination by the electrode method. Automatic temperature compensation (ATC) probes are required for pH meters.

Fill holes on all probes must be uncovered when in use and covered when not in use. Store pH electrodes in pH 7.0 buffer or pH storage solution. Never store pH probes in lab pure water. Store fluoride reference probes in lab pure water. Store fluoride sensing probes dry. Fluoride combination probes are unacceptable.

Amperometric Titration Equipment - Amperometric titrators must provide sufficient electrical range to allow the determination of both free and total chlorine.

Magnetic Stirring Apparatus - Units may be strictly for sample stirring or may contain a built-in light source for aiding in the detection of titrimetric endpoints.

Desiccator - Glass or plastic models may be appropriate depending on your application.

Drying oven - Must operate within $\pm 2.0^{\circ}\text{C}$ of the target temperature.

Heating block - Must operate within $\pm 2.0^{\circ}\text{C}$ of the target temperature.

Hot Plate - Hot plates for use in digestion procedures must be large enough to handle all standards and samples simultaneously.

Water Bath - Shall be capable of maintaining temperatures from ambient to $100 \pm 0.2^{\circ}\text{C}$.

Glassware - All glassware purchased for laboratory use shall be of borosilicate type glass. This type of glass is more resistant to damage by heat, chemicals, and abuse than regular flint glass.

Excellent quality volumetric glassware is marked Class A, denoting that it meets national specifications for volumetric glassware and need not be calibrated before use. Class A glassware must be used where volumetric accuracy is required, such as for standard measurement or dilutions.

Microliter Pipette - Adjustable volume microliter pipettes in appropriate ranges may be used for some calibrations. Micropipettors should be of good quality and deliver 20-250 μl or 50-200 μl range. Only one replicate spike can be measured and only above the midrange volume of the pipettor. Example: to measure 400 μl you may use a 200 μl pipettor twice. You may not use it three times to measure 600 μl . Another example: to measure 220 μl you may use a 200 μl pipettor set on 110 μl twice to get to 220 μl . However, you may not use one spike at 150 μl and another at 60 μl , since 60 μl would be <50% of the total capacity of the instrument. Each instrument is accurate within a certain percentage of the actual value. Using it more than once for one total volume multiplies the error factor by the number of deliveries.

Burets - Burets may be Class A, but this is not necessary as long as they are accurate. They must be self-leveling with a total volume that is sufficient to perform a titration without having to refill it during the titration. The tips must not be chipped. For chloride testing, amber burets are required, unless the buret is covered with aluminum foil or other light block.

Part IX Back-up Laboratory Equipment

All back-up or duplicate equipment must be calibrated or standardized at least once every three months as an instrument performance verification if it is kept with power on and stored on the bench. If it is strictly backup and kept with power off in a cabinet it may be tagged as "Backup". In this case regular QC can be eliminated provided that QC is performed prior to initial use. Records of the results of all QC tests must be kept on file. Equipment includes but is not limited to: pH/Ion meter; Turbidimeters; Spectrophotometers; Electronic DPD Chlorine Kits; and Amperometric titrators.

Part X QC Plans/SOPs

As previously noted a QC plan/SOP shall be submitted with the application for certification. QC plans/ SOPs are required for laboratories applying for certification for the following test parameters: primary inorganic chemicals (**cyanide, nitrate, nitrate-nitrite, nitrite, and sulfate**), total trihalomethanes, volatile organic chemicals, pesticides and other organic chemicals, primary metals, or radioactivity and radioactive chemicals .

The QC plan/SOP shall contain the following information:

1. Sampling procedures that include an example of the written sampling instructions accompanying each sampling kit.

2. Sample handling procedures, including:
 - A. Directions for maintaining the integrity of the samples by tracking samples from receipt to testing to disposal.
 - B. Directions for sample preservation, dechlorination, etc. as required by the reference method and the documentation used by the laboratory to verify that proper sample treatment is done.
 - C. Directions to ensure that adequate sample information is obtained to allow the proper analysis and reporting of results; and
 - D. Chain of custody forms;
3. Calibration and standardization procedures for instruments and equipment, including the frequency such procedures will be implemented;
4. Standard operating procedures including identification of the USEPA approved reference methods used to perform the drinking water analyses;
5. Data validation procedures including the conversion of raw data to standard units and the maintenance of accuracy for calculations and transcriptions;
6. Reporting procedures including directions followed to ensure that reporting is completed as specified in rule 3745-89-08 of the administrative code;
7. Standard and reagent procedures including directions followed for preparation and for documentation of the expiration of drinking water standards and reagents;
8. Quality control procedures as specified by the director or required by each method of analysis;
9. Preventative maintenance procedures including directions and scheduling for instrumentation servicing;
10. Routine practices to maintain the precision and accuracy of data as specified by the director or required by each method of analysis;
11. Corrective action procedures taken when unacceptable results are obtained from the analysis of performance evaluation samples or quality control checks.
12. Table of laboratory organization which delineates the responsibilities of all laboratory personnel associated with drinking water analyses and designates the individual(s) responsible for quality assurance of drinking water analyses in the laboratory.

Part I Laboratory Facilities

Laboratory space must be adequate, six linear feet of uncluttered bench space in unbroken sections per analyst, per shift under normal working. Working space requirements must include sufficient bench top area for analytical equipment, processing samples, storage space for chemicals, glassware, etc. The space required for both laboratory work and materials preparation in small water plant laboratories may be consolidated into one room with the various functions allocated to different parts of the room. Work space must be increased proportionally for laboratories engaged in multiple disciplines. Wastewater and microbiology tests may be performed in the same room, however, all bench areas and equipment must be clearly segregated.

Laboratory Construction and Remodeling

It is a requirement that all laboratory areas, as well as adjacent areas utilized by the laboratory, be approved by the Ohio EPA in writing before an on-site survey can be scheduled.

It will be the responsibility of each laboratory to notify the Ohio EPA, in advance of intended structural changes or modification of the laboratory area. Examples of remodeling and structural changes are relocation of walls, doors, and addition of analytical benches, cabinets, plumbing, wiring, etc. If in doubt, submit plans.

In the event that a laboratory is to be relocated within a building or at some other outside location, the Ohio EPA must be notified in writing prior to the intended move.

General Facility Requirements

Facilities must be clean, air conditioned, heated, and with adequate lighting at bench top (100 foot-candles). Humidity levels must not be excessive. Rugs in laboratories are unacceptable. Bench counter tops must be in good condition. Rusted, unfinished, or badly worn cabinets are unacceptable and must be repaired or replaced. Windows must be covered with appropriate sun blocks.

No food or drinks are to be stored or consumed in the laboratory. Food and drinks must not be stored in the chemical storage refrigerator. Smoking is not permitted in the laboratory.

The door entering the laboratory should be kept closed at all times except to enter or exit the laboratory.

Laboratory safety, which must be a conscious effort in laboratory operations, must provide safeguards to avoid electric shock, prevent fire and accidental chemical spills, and minimize dangers, facility deficiencies, and equipment failures. The laboratory certification program is not a safety inspection program. It is recommended that each laboratory participate in a laboratory safety training course, if available locally. The laboratory certification program will only point out obvious safety concerns, but will not be responsible for the comprehensive safety plan within the laboratory.

The following are some minimal recommended safety practices:

- ◆ Planned fire exits should exist from the lab
- ◆ A fire extinguisher should be located in the lab
- ◆ A fire extinguisher should be located outside the lab
- ◆ A first aid kit should be kept in the lab

- ◆ Safety glasses should be available and worn when handling corrosives
- ◆ Laboratory aprons or coats should be worn in the lab
- ◆ Mouth pipetting is not permitted, a pipet bulb must be used
- ◆ Always perform acid digestions in a fume hood. Fume hoods must be approved for the intended use. Fume hoods must be properly vented, not recirculating hoods.
- ◆ Know the proper procedures for chemical handling, chemical disposal and spill procedures for all chemicals used in your laboratory.
- ◆ Use special carriers when moving bottles of concentrated acids and bases.
- ◆ Material safety sheets should be on file
- ◆ No smoking in the lab
- ◆ No food or drinks stored or consumed in the lab

Part II Record Retention

All laboratory records, including: bench sheets; data sheets; sample identification sheets; calibration sheets; standardization sheets; result sheets; copies of Ohio EPA monthly reports; and all other required laboratory records are to be retained for the following minimum period:

Type of Record	Retention Time
Microbiological records	5 Years
General Chemical/Laboratory Records	10 Years
Records Pertaining to the Copper & Lead Rule	12 Years

Records must be kept readily available to the laboratory, either within the laboratory offices, or in the same building for a minimum of three years. For the remainder of the retention period, the records may be kept off-site in an area such as a warehouse.

If quality control and test records are to be entered and stored via computer, the following requirements must be met:

1. Hard copies of all data are to be printed out. The ability to print out forms that are only partially completed is also required.
2. Hard copies must be initialed by the analyst.
3. Hard copies must be in the same format and contain the same information as the forms contained in this manual.
4. Data is to be entered in the computer as soon as practical after the results are obtained. Handwritten data used

to transfer the information to the computer must be in a standard printed form format with all fields clearly identified.

5. All systems adopted for the computerization of records are subject to full review and modification if in the opinion of the survey officer, certain elements are lacking or missing or otherwise unacceptable.

Part III Daily Chemical Analyses Record

Public water supply laboratories are required to record test results on a standardized "bench sheet". Fill out the forms completely and legibly; do not use ditto marks or arrows unless they represent a common block of data that was generated together. Use a complete space for a complete entry, i.e. do not record entries on half lines or above or below the limits of the form. This practice indicates that the records may have been modified in an attempt to avoid deviations on a survey. Accidentally forgetting to record an occasional entry is not a major offense, even though it may be listed as a deviation on the survey report. Please keep in mind that knowingly, falsifying official state documents such as these may be treated as a criminal offense.

Do not recopy from a rough data sheet onto the official log. The official log must be the original entry. Deviations will not be given if the data is not perfectly neat. It is better to have an original record that is a little sloppy (but legible) than a record that has been recopied, possibly with errors. Keep one set of handwritten records only. If you feel better about photocopying the original record for safety's sake each month, it is permissible, but not required.

Information required on bench sheets include the following:

Sample Number: Sample numbers should be consecutive by year (i.e., January 1st is #1; December 31st is last #). Include only potable and pretreated samples in the system. Sample numbers must only be given to water samples. Do not assign a number to any non-potable water. Please note when a sample is a retest.

Date: Month/Day/Year is the standard acceptable format. Date stamps are permissible.

Time: This is required for certain tests (consult each method for further information).

Analyst: The analyst is the person who actually performed the test, not the person who supervised the test or the person who watched the procedure.

Tests: List all tests performed and the results.

Please refer to the form: "Chemical Analysis: Daily Bench Sheet" for an example of an acceptable bench sheet. You may use this form as-is or modify it for your individual needs, as long as all the above information is included. This form is to be used in addition to any other required Ohio EPA report sheets.

Analytical Testing Information

A brief general method summary is included for each test, with the exception of organic chemistry and primary metals, and is meant to be used in conjunction with the cited method reference. A complete procedure summary is included for some select tests. For the convenience of the user, record keeping forms are included for most of the parameters. These forms should be photocopied and used as the official QA forms.

Information pertaining to the requirements for radiological testing are not included in this section. Guidelines for this parameter can be obtained by request from the Laboratory Certification Section.

The mention of trade names in this manual does not constitute endorsement by the Ohio EPA.

TURBIDITY/NEPHELOMETRIC METHOD

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent Storage Conditions	Formazin 4000 NTU	Refrigerated
	AMCO Standards	Room Temperature
	StablCal Standards	Room Temperature
	Secondary Standards	Room Temperature
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Formazin 4000 NTU	1 year after opening
	AMCO Standards	1 year after opening
	StablCal Standards	1 year after opening
	Secondary Standards	Significant change in value
	Diluted formazin	Discard after use
Required Quality Control	Frequency	Required QC
	Daily (2100N)	Check/Record two low range secondary standards
	Quarterly (1/three months)	Recalibrate secondary standards
	Quarterly (1/three months)	Recalibrate meter
Sampling	Preservation	Holding Time
	None	24 Hours

Method Reference

Standard Methods, 18th Edition (2130) MCAWW (3/83), Method 180.1, GLI Method 2

Equipment

Nephelometric Turbidimeter - Must be a non-ratio turbidimeter. Ratio turbidimeters are not acceptable because they do not conform to the USEPA definition of a nephelometer according to the published method. Models with ratio switches must be used for drinking water analysis with the ratio mode off. Calibrations may have to be performed with the ratio mode on. In this case perform a low level check with a low level secondary standard before each test with the ratio mode off. Signal averaging, when available, may be used.

Glassware/volumetric pipets - Class "A" volumetric glassware for formazin dilutions.

Graduated cylinder - To deliver (TD) for sample measurement.

Test Cells - The cells must be indexed. To index the cells, place them in the turbidimeter until a stable reading is seen. Slowly turn them until the lowest turbidity reading is seen. Etch a vertical mark on the very top of the cell and a corresponding "line up" mark on the meter. They may also be calibrated at the required volume.

Materials

Primary Standard - Formazin concentrate 4000 NTU or AMCO/AEPA prediluted turbidity standards or Hach Stabl Cal standards. The 4000 NTU formazin standard must be refrigerated. Do not refrigerate AMCO or Hach Stabl Cal standards. Primary standards are meant to be used once then discarded. Ampuled, multiple use primary standards are actually secondary standards and should not be used as primary standards.

Instrument Secondary Standards (one for each of the instrument ranges) - Replace liquid secondary standards for turbidity after any change in physical appearance. Gelex brand turbidity standards are good until they become discolored or become excessively scratched. Discard secondary standards when they vary by more than 40% for 0-2 NTU standards, by 30% for 0-20 NTU standards and 15% for 0-200 NTU standards, from the original value.

Low Turbidity Water (LTW) - for formazin dilutions, must be less 0.10 NTU. May be the laboratories distilled, deionized or purchased water (for formazin dilutions) or in the case of commercial primary standards, the standard manufacturer's supplied LTW.

Sample Container/Preservative

A clean plastic or glass screw top container (250 mL - 1000 mL). No preservative necessary.

Maximum Holding Time: 24 hours, refrigerate at 2 - 10° C

General Method Summary

Turbidity in water is caused by suspended matter such as clay, silt, organic or inorganic matter or microscopic organisms.

The nephelometric method of measurement is based on the intensity of light scattered at a right angle by the suspended matter contained in the sample. The higher the intensity of scattered light, the higher the turbidity.

Before each use, the turbidimeter's calibration must be set or checked using recently calibrated secondary standards. Samples should be measured using a graduated cylinder or a properly calibrated and indexed cell. Sample cells must be kept scrupulously clean both inside and out. Cold samples should be warmed, by holding them in your hand so that condensation is eliminated.

Some manufacturers recommend the use of silicon oil on the outside of the cell. Consult your turbidimeter's owner's manual for details. Discard the test cells when they become scratched or damaged. Allow instrument read -out to stabilize before recording the value.

On-Site Survey Requirements

1. Each fully approved analyst participating in the survey for turbidity must be able to perform a primary standard calibration check of the instrument and secondary standard(s).
2. Sufficient glassware must be available so that it does not have to be washed and reused during the survey by fully approved analysts.

3. The following techniques will be checked for the formazin calibrations: proper matching and indexing of sample cells; proper preparation of formazin dilutions, proper determination of turbidity in the laboratory pure water used for formazin dilutions; and proper calibration of instrument and/or secondary standards.
4. Instrumentation will be checked for proper functioning.
5. Proper procedural technique will be observed in the use of secondary standards.
6. Calibration records will be checked for the previous three years. All standards, reagents and solutions used for the test will be checked for proper labeling and dating.
7. Analysts may be required to analyze performance samples during the survey.
8. "Operational" analysts will be required to set or check the instrument calibration using the secondary standards, analyze a performance sample and a plant tap sample.

Required Quality Control

Secondary Standard/Instrument Calibration

The secondary standard calibration or internal instrument calibrations must be performed quarterly (1/three months) or more often if the secondary standards fail to remain within the acceptable range.

Secondary standard calibration or internal instrument calibrations must be performed at a minimum frequency of once per three months using freshly diluted formazin standards or prediluted AMCO/AEPA primary standards or Hach StablCal Standards.

Some digital models such as the Hach 2100AN and 2100N will not allow a calibration below a value of 20 NTU or with ratio off. In these cases, calibrate with the standards called for by the manufacturer with ratio on but check a low range standard, such as 1.0 or 0.5 NTU with ratio off. The low reading must be within +10% of the true value or corrective action must be taken.

For Hach 2100 N/AN instruments, the air reading, i.e. the reading of the instrument in air, without a sample cell, must be less than or equal to 0.035 NTU. If it is higher than this, contact the manufacturer.

Hach model 2100P meters are not acceptable since they are designated as portable meters and are ratio only.

Weekend Analysis

Samples collected on Saturdays and Sundays may be retained for analysis a maximum of 24 hours. Such a delay in analysis will be allowable only if all of the following conditions are met:

1. Samples must be refrigerated immediately after collection at 2 - 10C and stored so as not to be exposed to direct or indirect lighting.
2. Free chlorine residual must not be less than 0.2 mg/L at the time of sample collection.

In-line Turbidimeters

- ▲ In-line turbidimeter calibrations must be checked with the results recorded at least once each day by taking a sample as close to the in-line turbidimeter as possible and checking it against a calibrated bench top turbidimeter. Note the in-line turbidimeters reading at the time of collection and record on the form provided.
- ▲ The Great Lakes in-line turbidimeter is a ratio turbidimeter, however, it is acceptable for use since the method for its use is a USEPA approved method.
- ▲ Other brand ratio in-line turbidimeters may be used since they are checked daily with a non-ratio bench top meter. If the reading is not $\pm 10\%$ of the bench top meter, reset the in-line meter.
- ▲ You must be approved for turbidity to check the calibration of an in-line turbidimeter.
- ▲ The in-line turbidimeter's results must agree with the bench top model $\pm 10\%$ if the bench top reading is 0.5 NTU or greater. If the reading is not within $\pm 10\%$ set the in-line turbidimeter to agree with the bench top model. If the bench top meter reads <0.5 NTU and the in-line meter reading varies more than ± 0.1 NTU, adjust the in-line meter to agree with the bench top meter. Most in-line turbidimeters are very easy to reset.
- ▲ The daily check between the in-line turbidimeter and the bench top unit must be recorded. Record the analyst's initials, the date and time, the reading obtained by the bench top model and the reading of the in-line unit at the time of sample collection on the form provided.

Analyst Name _____ Date _____

Step 1

Insert 0.5 NTU prediluted primary standard; Set the meter to 0.50 on the 0-1 range; Insert the 0 to 1.0 secondary standard; Record result as "A"

Step 2

Insert 5.0 NTU prediluted primary standard; Set the meter to 5.0 on the 0 to 10 range; Insert the 0 to 10.0 secondary standard; Record result if the value is ≤10.0 as "B"; If the result is >10.0 reset the meter to 10.0 NTU; Insert 5.0 AMCO standard again; Record result as "B₁"; Calculate result:

$$D\% = \frac{5}{B_1} \times 100$$

If D is between 100 to 105% use a value of 10.0 NTU; If D > 105% set meter to 10.0 and calculate:

$$\text{Correction Factor} = \frac{\text{Actual \%} > 105}{100}$$

Step 3

Insert the cell riser and 40.0 NTU prediluted primary standard; Set the meter to 40.00 on the 0 to 100 range; Insert the 0 to 100.0 secondary standard; Record result if the value is ≤100.0 as "C"; If the result is >100.0 reset the meter to 100.0 NTU; Insert 40.0 AMCO standard again; Record result as "C₁"; Calculate result:

$$D_1\% = \frac{40}{C_1} \times 100$$

If D₁ is between 100 to 105% use a value of 100.0 NTU; If D₁ > 105% set meter to 100.0 and calculate:

$$\text{Correction Factor} = \frac{\text{Actual \%} > 105}{100}$$

Secondary Standard	Assigned Value	Correction Factor
A - 0-1 NTU		
B - 0-10 NTU		
C - 0-100 NTU		

Secondary Standard	Value when first calibrated	Current assigned value
0-1 NTU		
0-10 NTU		
0-100 NTU		

Secondary Standards Must Be Replaced if: ▲ Cells are excessively scratched ▲ Flaking or discoloration of liquid occurs
 ▲ A significant change in the calibrated value occurs from the original initial calibration value

Daily Calibration Data Sheet: Hach 2100 N/AN

Quarterly Secondary Standard Calibration Data Sheet

Ranges(NTU)→	0 - 2.0	0 - 20
Initial Calibration		
Previous Quarter Calibration		

Date _____ Analyst _____

Ranges(NTU)→	0 - 2.0	0 - 20
Today's Calibration		
LTW NTU		
1.0 NTU reading		
Corrected 1.0 NTU (1.0 NTU minus LTW)		
Air Reading (No Cell: Must be <0.035 NTU)		

Date _____ Analyst _____

Ranges(NTU)→	0 - 2.0	0 - 20
Today's Calibration		
LTW NTU		
1.0 NTU reading		
Corrected 1.0 NTU (1.0 NTU minus LTW)		
Air Reading (No Cell: Must be <0.035 NTU)		

2100N/AN Calibration Procedure

The manufacturer's calibration procedures should be followed with the following exceptions: 1) prepare a 1.0 NTU formazin standard for the low level "calibration check" standard; 2) If AMCO/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.

Air Reading

With no sample cell in the cell holder note and record the air reading. If it is >0.035 NTU, contact the manufacturer for repair. If it is ≤ 0.035 NTU proceed to the next step.

Matching of Sample Cells

Cells used for testing are matched, calibrated and indexed? Yes [] No []

If above is "NO" then follow this procedure:

1. Fill all cells used for testing with low turbidity deionized/distilled 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

Calibration of Meter: to be performed quarterly or if Gelex standards are out of range

1. Fill a cell with LTW
2. Place the cell into the cell 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 cell with a well-mixed 20 NTU primary standard
6. Place the sample cell 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 cell with a well-mixed 200 NTU primary standard
9. Place the sample cell into the cell holder and close the cover and Press ENTER
10. The instrument will count down from 60 to 0
11. Fill a clean cell with a well-mixed 1000 NTU primary standard
12. Place the sample cell into the cell holder and close the cover and Press ENTER
13. The instrument will count down from 60 to 0
14. Fill a clean cell with a well-mixed 4000 NTU primary standard
15. Place the sample cell 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. It then returns to the normal measurement mode

LTW/Low Level Check

1. Fill a clean cell with LTW
2. Place the sample cell into the cell holder and close the cover and Press ENTER
3. Record the LTW value
4. Fill a clean cell with a well-mixed 1.0 NTU primary standard
5. Place the sample cell into the cell holder and close the cover and Press ENTER
6. Subtract the LTW value from the 1.0 NTU reading and record the results
7. Ascertain that the reading is $\pm 10\%$, if it is not, start again at step #1 above and recalibrate the instrument.

Secondary Standard Calibration

1. Place the 0-2 NTU secondary standard into the cell holder and close the cover and Press ENTER
2. Assign this reading as the 0-2 NTU secondary standard reading and record the results.
3. Place the 0-20 NTU secondary standard into the cell holder and close the cover and Press ENTER
4. Assign this reading as the 0-20 NTU secondary standard reading and record the results.

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	pH Probes	Storage solution or pH 7/4 buffer
	pH Buffers	Room Temperature
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	pH Buffers	6 months after opening
Required Quality Control	Frequency	Required QC
	Each shift	Calibrate meter
	Monthly	Linearity/Slope/pH 4 buffer
Sampling	Preservation	Holding Time
	None	15 Minutes

Method Reference

Standard Methods, 18th Edition (4500-H+) MCAWW (3/83) Method 150.1 & 150.2

Equipment

A pH or selective ion meter capable of at least a two buffer calibration, accurate and reproducible to 0.1 pH units or better. A % slope read-out or efficiency is required for the linearity check. Digital displays and ATC probes are required.

A "Fill-type" combination probe or separate pH sensing and reference probes. Do not use sealed or gel filled probes.

"Tri-combination" probes, i.e. combination probes with a temperature sensor built in are not recommended.

Automatic temperature compensating (ATC) probes are required for pH meters .

pH buffers at 4, 7 and 10. **pH buffers are to be discarded six months after opening.**

Magnetic stirring devices should be used for calibration and sample analysis.

Sample Container/Preservative

A clean plastic or glass screw top container (250 - 1000 mL). Sample containers should be completely filled and kept sealed prior to analysis. No preservative can be used.

Maximum Sample Holding Time

Samples must be kept sealed from the air and analyzed within 15 minutes from the collection time. Allow the sample temperature to warm within this time.

General Method Summary

pH measurement is one of the most important and frequently performed tests in water chemistry. The probe method is relatively simple to perform but certain precautions must be taken to ensure accurate results.

The use of an automatic temperature compensating probe is required because samples and buffers may be at different temperatures when analyzed within the holding time. A two buffer calibration using fresh portions of pH 7 and 10 buffers is required at the beginning of each shift. Thorough rinsing of the probe with laboratory pure water and blotting dry between each buffer and sample analysis is imperative to prevent cross contamination.

Calibration slope or efficiency should be checked once each shift, each time the meter is calibrated, to insure acceptable probe sensitivity. However it is only required to record this data once each month.

Requirements for pH Probes

Probes should be kept clean and free from crystalline build-up. Both sensing and reference probes must be stored in either pH 7/4 buffer or in the solution recommended by the manufacturer. Do not store probes in laboratory pure water.

Store probes as they are received until they are put into use.

Probes should be drained and refilled once each month.

After a probe is refilled, hang it vertically in dry air for 15-30 minutes to wet the junction. Then place in storage solution or pH 7 buffer for at least 2 hours before use.

If the probe takes longer than one minute to stabilize in pH buffer, it is in need of service or replacement.

On-Site Survey Requirements

1. Each fully approved analyst must be able to demonstrate the three buffer probe linearity response test and 4.0 buffer check.
2. Proper procedural technique will be observed during the linearity test and sample analysis. Instrumentation will be checked for proper functioning.
3. pH linearity records will be checked for the previous three years.
4. All buffers and reagents used for the test will be checked for proper labeling and dating.
5. Each analyst may be required to analyze a performance sample during the survey.
6. "Operational" analysts will be required to calibrate the pH meter using two buffers, analyze a performance sample and a plant tap sample.

Required Quality Control: pH Probe Response Check

Frequency

At least once per month, record of the results must be kept on file.

pH Probe Response Check Procedure

1. Allow the 4, 7, and 10 buffers to stabilize at room temperature.

2. Immerse the rinsed and dried probe in a fresh portion of pH 7 buffer, while stirring with a magnetic stirring device, allow the meter readout to stabilize and calibrate to read 7.00.
3. Rinse the probe with laboratory pure water and blot dry.
4. Immerse the probe in a fresh portion of pH 10 buffer; while stirring with a magnetic stirring device, allow the meter readout to stabilize; adjust the second calibration setting and set the meter to 10.0. Some older model meters use the slope control for the second point.
5. Record the % slope, efficiency or the mV reading for this two buffer calibration. This value must be between 95-105% or 56-62 mV.
6. Rinse the probe with laboratory pure water and blot dry.
7. Immerse the probe in a fresh portion of pH 4 buffer; while stirring with a magnetic stirring device, allow the meter to stabilize and record the noted value for the 4 buffer. This value must be 4.0 ±0.1 pH unit.
8. Meters capable of a multi-buffer calibration may be calibrated with three buffers: 4, 7, and 10. Record the % slope, acceptable calibration slope must be greater than 95% and <105%.

Conclusion

Whenever the calibration slope is <95% or >105% or the value for the 4.0 buffer varies >0.1 pH units, a linearity problem is indicated and corrective action must be taken.

Corrective Action

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 laboratory pure 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. Have the meter serviced if all other attempts have failed to obtain acceptable results.

Test Procedures

1. Standardize the meter, using at least two buffers bracketing the expected test range, once each shift.
2. Rinse suitable container with 7.0 buffer and discard.
3. Fill the container with 7.0 buffer.
4. Rinse the probe(s) with laboratory pure water and blot dry with a tissue.
5. Place the probe(s) in the solution in the 7.0 buffer, while stirring with a magnetic stirring device, and allow the display to stabilize.
6. Adjust the display to 7.00.
7. Rinse suitable container with 4.0 or 10.0 buffer and discard.

8. Fill the container with 4.0 or 10.0 buffer.
9. Rinse the probe(s) with laboratory pure water and blot dry with a tissue.
10. Place the probe(s) in the solution in the 4.0 or 10.0 buffer, while stirring with a magnetic stirring device, and allow the display to stabilize.
11. Adjust the display to 4.00 or 10.00.
12. Between shift calibrations check the slope to be sure it is in acceptable range.
13. Collect a suitable size sample.
14. Rinse suitable container with sample and discard.
15. Fill the container with sample.
16. Rinse the probe(s) with laboratory pure water and blot dry with a tissue.
17. Place the probe(s) in the sample while stirring with a magnetic stirring device, and allow the display to stabilize.
18. Record the reading as the pH of the sample.

In-line pH Meters

In-line pH meters must be checked, with the results recorded at least once each day, by taking a sample as close to the in-line pH meter as possible and checking it against a calibrated bench top pH meter. Note the in-line pH meters reading at the time of collection and record it.

You must be operationally or fully approved for pH to check or calibrate an in-line pH meter. The in-line pH meter's results must agree with the bench top model ± 0.2 pH unit. If the reading is not within ± 0.2 set the in-line pH meter to agree with the bench top model. Most in-line pH meters are very easy to reset. The daily check between the in-line pH meter and the bench top unit must have the results recorded. Record the analyst's initials, the date and time, the reading obtained by the bench top model and the reading of the in-line unit at the time of sample collection.

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Reference Probe	Laboratory pure 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 Storage Times	Standard/Reagent	Maximum Storage Time
	TISAB	1 year after opening
	0.5/5.0/1.0 mg/L Standards	1 year after opening
	100 mg/L Standard	1 year after opening
Required Quality Control	Frequency	Required QC
	Each shift	Calibrate meter
	Monthly	QC Check sample
	Weekly	Linearity/Slope/Check 1.0 mg/L
Sampling	Preservation	Storage
	None	7 days at 4°C

Method Reference

Standard Methods 18th Edition (4500-F, C); Technicon 308-75WF

Sample Container/Preservative

A clean plastic screw top container (250 - 1000 mL)
 No preservative is necessary

Maximum Sample Holding Time

7 days, Cool to 4°C

General Method Summary

1. Use only dilute, liquid TISAB II, not TISAB III (concentrated) or dry TISAB.
2. Do not use standards that are premixed with TISAB.
3. Keep the fluoride sensing probe dry and the reference probe in laboratory pure water when not in use.
4. Measure fluoride test reagents and samples with any instrument that will give reproducible results. A graduated cylinder or better measuring instrument is required.
5. Do not use fluoride combination probes. You must have a separate sensing probe and a separate reference probe.
6. Do not use automatic temperature (ATC) probes for fluoride analysis.
7. Standards and samples should be at room temperature before analysis.
8. A two standard calibration using fresh portions of 0.5 and 5.0 mg/L standards is required once each shift before the test is performed. In between these calibrations the meter may be used by checking it with a 1.0 standard. The reading must be $\pm 10\%$ or the meter must be recalibrated.
9. Standards and samples must be analyzed while stirring with a magnetic stirring device. Meter readings should stabilize in less than three minutes when all factors are performing properly.
10. Thorough rinsing of the probes with laboratory pure water and blotting dry between each standard and sample analysis is imperative to prevent cross contamination.
11. Calibration slope or mV reading must be performed at least once each shift to insure acceptable (-54 to -60 mV) electrode sensitivity before analyzing samples.
12. The sensing electrode should be cleaned periodically (on the bottom only) using fluoride toothpaste to improve response time. The sensing probe can be stored dry in the air when not in use.
13. The reference probe should be kept free from crystalline build-up and kept filled with solution. The reference probe can be stored in laboratory pure water when not in use.
14. Standards must be stored in suitable plastic containers. Do not store fluoride standards in glass containers.

On-Site Survey Requirements

1. Each analyst must be able to calibrate the ion meter using two standards and determine the calibration slope or mV reading.
2. Instrument and electrodes will be checked for proper functioning.
3. Proper procedural technique will be observed during instrument calibration and sample analysis.
4. Calibration slope records will be checked for the previous three years.
5. All reagents, standards and solutions will be checked for proper labeling and dating.

6. Each analyst will be required to analyze a performance sample during the survey.
7. "Operational" analysts will be required to set the meter using two standards (0.5 and 5.0) and analyze a performance sample and plant tap sample.
8. Fully approved analysts will be required to set the meter using two standards (0.5 and 5.0) and check a 1.0 mg/L standard and analyze a performance sample and plant tap sample.

Fluoride: Calibration Procedures

Equipment

1. A specific ion meter capable of being calibrated with a minimum of two standards and equipped with a slope indicator or readout. Analog ion meters are not recommended.
2. A fluoride selective ion electrode
3. A sieve type reference electrode (combination electrodes are not acceptable)
4. A magnetic stirring device and a least three TFE-coated (Teflon) stirring bars.

Reagents

1. Stock fluoride solution (100 mg/L). This is available commercially.
2. Calibration standard solutions (0.5, 5.0 and 1.0 mg/L). This is commercially available at specified concentrations. They may also be laboratory prepared by volumetric dilutions using class "A" volumetric glassware. They may also be prepared by following the procedures outlined in Standard Methods, 18th Edition, page 4 - 61. Working standard solutions may **not** be pre-diluted with TISAB and stored, prior to use. The 1.0 mg/L standard is used for the weekly slope quality control test.
3. Buffer Solution (TISAB) - Commercially available in dilute or concentrated form. It may also be prepared by following the procedures outlined in Standard Methods, 18th Edition, page 4 - 61. Do not use TISAB III or any other concentrated TISAB.

Glassware

1. Class "A" volumetric pipets and flasks of appropriate size to dilute stock standard to 0.5, 5.0 and 1.0 mg/L concentrations.
2. (2) 25 mL graduated cylinders (TD)
3. Disposable or reusable plastic beakers (50 - 100 mL)

Procedure (Beginning of Each Shift)

1. Place a TFE-coated stirring bar into each of three plastic beakers
2. Using a graduated cylinder, measure 25 mL of 0.5 mg/L standard and pour into beaker #1. Rinse the cylinder with laboratory pure water.
3. Using the other graduated cylinder, measure 25 mL of the dilute buffer and pour into beaker #1.
4. Turn the magnetic stirring device on, adjust the speed to properly mix the sample without creating a vortex.

5. While continuously mixing, lower the probes into the 0.5 mg/L calibration standard mixture.
6. Allow the meter read-out to stabilize, (this should take less than three minutes) then calibrate the meter to the standard value.
7. Remove probes from sample. Using a wash bottle thoroughly rinse the probes with laboratory pure water.
8. Repeat steps 2 through 7 using the 5.0 mg/L standard and the second plastic beaker.
9. Check the calibration slope. Acceptable slope is -54 to -60mV or greater than 95%.
10. The meter is now properly calibrated and ready to analyze the sample(s), repeat steps 2 through 7 substituting the sample(s) for the standards. The meter will read-out in concentration (mg/L) in step 6.

Procedure (Once each week to be performed by fully approved analysts)

1. Place a TFE-coated stirring bar into each of three plastic beakers
2. Using a graduated cylinder, measure 25 mL of 0.5 mg/L standard and pour into beaker #1. Rinse the cylinder with laboratory pure water.
3. Using the other graduated cylinder, measure 25 mL of the dilute buffer and pour into beaker #1.
4. Turn the magnetic stirring device on, adjust the speed to properly mix the sample without creating a vortex.
5. While continuously mixing, lower the probes into the 0.5 mg/L calibration standard mixture.
6. Allow the meter read-out to stabilize, (this should take less than three minutes) then calibrate the meter to the standard value.
7. Remove probes from sample. Using a wash bottle thoroughly rinse the probes with laboratory pure water.
8. Repeat steps 2 through 7 using the 5.0 mg/L standard and the second plastic beaker.
9. Check the calibration slope. Acceptable slope is -54 to -60mV or greater than 95%.
10. Using a graduated cylinder, measure 25 mL of 1.0 mg/L standard and pour into beaker #3. Rinse the cylinder with laboratory pure water.
11. Using the other graduated cylinder, measure 25 mL of the dilute buffer and pour into beaker #3.
12. Turn the magnetic stirring device on, adjust the speed to properly mix the sample without creating a vortex.
13. While continuously mixing, lower the probes into the 1.0 mg/L calibration standard mixture.
14. Allow the meter read-out to stabilize, (this should take less than three minutes) note the reading.
15. If the reading is not 1.0 ± 10%, take corrective action, such as cleaning/replacing electrodes.

Documentation

1. Date and analyst initials.
2. Expiration date of the stock standard/calibration standard.

3. Calibration slope and 1.0 mg/L standard (required once a week).
4. Any maintenance or replacement of apparatus.

Test Procedures (Direct Reading Meters, beginning of each shift)

1. Rinse a 25 mL cylinder with sample.
2. Measure 25 mL of sample and transfer it to a clean 50 mL beaker.
3. Rinse a 25 mL cylinder with TISAB.
4. Measure 25 mL of TISAB and add it to the sample.
5. Use the meter's temperature probe or a thermometer, ascertain that the temperature of the sample/TISAB mixture is room temperature. Do Not use an ATC probe for this.
6. Stir the sample while testing. Read the results and record the reading as fluoride mg/L.

Special Requirements for Fluoride Certification

Fluoride QC Check Requirements

All laboratories are required to successfully analyze one QC check in a range of 0.5 to 1.5 mg/L each month. These QC check samples may be obtained at this time from any of the Ohio EPA approved PE suppliers. The cost of these QC check samples will be borne by your laboratory. If the sample result obtained differs from the PT suppliers actual value by $\pm 10\%$, contact the Ohio EPA/DES Laboratory Certification Section for assistance.

Record the results of the QC check on the official form.

If you have any questions concerning this program, please contact the Ohio EPA/DES Laboratory Certification Section.

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Fluoride Monthly QC Check

Laboratory Name _____

Date	Analyst	Results (mg/L)	Actual Value (mg/L)	Within $\pm 10\%$?	PE Supplier's Name	Sample Lot #

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	0.020 N Sulfuric Acid (H_2SO_4)	Room temperature
	Indicator (Bromcreosol Green/Methyl Red)	Room temperature
	Sodium Thiosulfate	Room temperature
	0.02 N Sodium Carbonate (NaCO_3) Standard	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	0.020 N Sulfuric Acid (H_2SO_4)	1 year after opening
	Indicator (Bromcreosol Green/Methyl Red)	1 year after opening
	Sodium Thiosulfate	1 year after opening
	0.02 N Sodium Carbonate (NaCO_3) Standard	1 year after opening
Required Quality Control	Frequency	Required QC
	Monthly	Standardize Titrant
Sampling	Preservation	Holding Time
	None	7 Days

Method Reference

Standard Methods 18th Edition (2320)

Equipment

1. 25-50 mL self leveling automatic buret.
2. 20 mL Class "A" volumetric pipet(s)
3. 50 mL graduated cylinder
4. Titration vessels of appropriate volume.
5. Graduated cylinder (TD - 50 to 100 mL).
6. Magnetic string device & stirring bars (optional)
7. Adequate fluorescent lighting, you may use a lit stirring device.

Reagents

1. Sulfuric Acid Titrant (0.020 N) - commercially available as 0.10 N or 0.020 N H₂SO₄ or prepared as per Standard Methods 18th Edition pages 2-26, 27.
2. Color Change Indicators - commercially available or prepared as per Standard Methods 18th Edition pages 2-26, 27
3. Laboratory pure water- Run a blank consisting of 30 mL of the distilled/laboratory pure water and subtract any value obtained from the titrated values.
4. 0.1 N or 10% sodium thiosulfate solution, commercially available or prepare as in Standard Methods, to be used for dechlorination when free chlorine levels are 1 mg/L.

Standard

0.0200 N Na₂CO₃ - Dry 2 to 3 g primary standard grade Na₂CO₃ at 250° C for 4 hours and cool in a desiccator. Weigh 1.0599 g and transfer to a 1-liter volumetric flask and dilute to the mark with laboratory pure water. This reagent is stable for 1 year when kept tightly sealed and under refrigeration when not in use.

Commercially Prepared Standards

0.0200 N Na₂CO₃ - Commercially Available as 0.0200 N Sodium Carbonate Standard Solution. this is also available as (1 mL = 1 mg Na₂CO₃) Sodium Carbonate Standard solution. This reagent is stable for 1 year when kept tightly sealed and under refrigeration when not in use. Do not use ampuled standards for this test.

Sample Container/Preservative

A clean plastic or glass screw top container (250-1000 mL)
No preservative necessary

Maximum Sample Holding Time

7 days, in the refrigerator at 2-10 °C.

General Method Summary

Titration may be performed potentiometrically or manually in the presence of a suitable endpoint indicator solution. Phenolphthalein indicator or metacresol purple can be used to indicate an endpoint at a pH of 8.3. Methyl orange, bromocresol green or a mixed indicator- bromocresol green/methyl red can be used to indicate an endpoint at a pH of 4.5. Samples must not be filtered, diluted or chemically preserved.

On-Site Survey Requirements

1. Each fully approved analyst must be able to perform the alkalinity titrant standardization. Proper procedural technique will be observed during the titrant standardization and sample analysis.
2. Alkalinity titrant standardization records will be checked for the previous three years.
3. All reagents, standards and solutions used for the test will be checked for proper labeling and dating. Each analyst

will be required to analyze a performance sample during the survey.

4. "Operational" analysts will be required to analyze a performance sample and a plant tap sample.

Required Quality Control: Acid Titrant Standardization

Frequency

The 0.020 N H₂SO₄ alkalinity titrant must be standardized initially upon preparation or first use and thereafter on a monthly basis. Records of the results must be kept on file.

Reagents

1. Sulfuric Acid Titrant (0.020 N) - commercially available as 0.10 N or 0.020 N H₂SO₄ or prepared as per Standard Methods.
2. Color Change Indicators - commercially available or prepared as per Standard Methods.
3. Laboratory pure water - Run a blank consisting of 30 mL of the laboratory pure water and subtract any value obtained from the titrated values.
4. 10% sodium thiosulfate solution, commercially available or prepare as in Standard Methods, to be used for dechlorination when freechlorine levels are 1 mg/L.

Standard

0.0200 N Na₂CO₃ - Dry 2 to 3 g primary standard grade Na₂CO₃ at 250° C for 4 hours and cool in a desiccator. Weigh 1.0599 g and transfer to a 1-liter volumetric flask and dilute to the mark with laboratory pure water. This reagent is stable for 1 year when kept tightly sealed and under refrigeration when not in use.

Commercially Prepared Standards

0.0200 N Na₂CO₃ - Commercially Available as 0.0200 N Sodium Carbonate Standard Solution. This is also available as (1 mL = 1 mg Na₂CO₃) Sodium Carbonate Standard solution. This reagent is stable for one year when kept tightly sealed and under refrigeration when not in use. Do not use ampuled standards for this test.

Equipment for Standardization

Balance - An analytical balance readable to 0.0001g must be used to measure primary standard grade reagents. The balance must be covered by an annual service contract and must be located on a stone balance table or stone slab.

Glassware for Testing and Standardizations

1. 25-50 mL automatic, self leveling burette
2. 20 mL Class "A" volumetric pipet(s)
3. Titrating vessels of appropriate volume
4. 50mL graduated cylinder

Procedure for Standardizations

1. Add 30 mL of laboratory pure water using a graduated cylinder and the color indicator to the vessel.
2. If the color indicates that the endpoint has already been reached, i.e., there is no alkalinity in the laboratory pure water, record your Blank value as 0". and proceed to step 3 and skip step 7. If there is alkalinity, proceed to step 3 and do not skip step 7.
3. Deliver 20 mL of 0.020 N standard solution using a class "A" volumetric pipet into the titrating vessel.
4. Titrate with the acid titrant to the appropriate endpoint.
5. Record the volume of titrant used.
6. Repeat steps 1 through 4 using a fresh portion of standard solution.
7. Run a blank on 30 mL of laboratory pure water and subtract the volume used from each of the two standard titration results.

Conclusion

The acceptable range for the adjusted amount of titrant used is $\pm 5\%$ of theoretical value (20.0 mL). 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.

Correction Factor

Repeat steps 1 through 4 listed above using a fresh portion of standard solution, subtract the blank value and calculate as follows:

$$20 \text{ mL} = \text{Correction Factor}$$

Average of two titrations (mL)

Multiply all subsequent titration answers by the correction factor, this equals the adjusted alkalinity concentration. Do not use correction factors on purchased titrants. They must be within range or discarded.

Required Documentation

Records must contain:

1. Date standardization performed
2. Analysts initials
3. Expiration date of alkalinity standard
4. Amount of acid titrant used for the two titrations
5. Blank value
6. Correction factor and the third titration value, if necessary

Test Procedure (Colorimetric Titration)

1. Ascertain that the buret is filled to the meniscus with 0.02 N H₂SO₄ titrant
2. Note the total volume of titrant
3. Rinse out the titrating vessel with sample and discard
4. Measure the sample with an appropriately sized graduated cylinder
5. If a free chlorine residual of >1 mg/L, is present add one or more drops of a 10% sodium thiosulfate solution to the sample. To determine the correct amount, using DP,D check tap water by using a series of sodium thiosulfate drops (measure sample, add 1 drop, check chlorine; new sample, add two drops, check chlorine, etc.) until no chlorine is detected.
6. Add 2 - 4 drops of indicator to the sample
7. Slowly add titrant to the sample, mixing with a magnetic stir bar or glass rod
8. If you are not sure what the color change should look like, you should use a pH meter to check the endpoint, which should be 4.5 ± 0.2 pH units.
9. Multiply the volume of titrant used by the multiplier factor
10. Record this value as total alkalinity as CaCO₃

Test Procedure (Potentiometric Titration)

1. Ascertain that the buret is filled to the meniscus with 0.02 N H₂SO₄ titrant
2. Note the total volume of titrant
3. Rinse out the titrating vessel with sample and discard
4. Measure sample with an appropriately sized graduated cylinder
5. Standardize the pH meter (see pH section)
6. Place the pH probe in the sample container
7. Slowly add titrant to the sample, mixing with a magnetic stir bar or glass rod
8. Stop adding titrant when a stable pH of 4.5 is reached
9. Note on the buret the amount of titrant used, subtract the reading from the total volume
10. Multiply the volume of titrant used by the multiplier factor
11. Record this value as total alkalinity as CaCO₃

General Notes on Titrations for Alkalinity

You must mix laboratory pure water with the standard. Using the standard alone will not allow enough volume to properly show the color change. Use a volume of laboratory pure water to make a total volume of 50 or 100 mL.

- ▲ Do not use correction factors on purchased titrants. They must be within range or discarded.
- ▲ Do not use ampuled standards for alkalinity.
- ▲ Your buret must be of sufficient capacity so that all tests and standardizations can be performed without refilling the buret. In other words, if it takes 35 mL of titrant to test for alkalinity in your water and you have a 25 mL buret, you must get a 50 mL buret.

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	EDTA	Room temperature
	Indicator	Room temperature
	Buffer	Room temperature
	1000 mg/L Calcium Chloride (CaCl ₂) Standard	Refrigerated
	Commercial Dry Reagents	Room Temperature
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	EDTA	1 year after opening
	Indicator	1 year after opening
	Buffer	1 year after opening
	1000 mg/L Calcium Chloride (CaCl ₂) Standard	1 year after opening
	Commercial Dry Reagents	Manufacturer's expiration date or six years after opening
Required Quality Control	Frequency	Required QC
	Monthly	Standardize Titrant
Sampling	Preservation	Holding Time
	HNO ₃ to adjust the pH to less than 2.0	7 days

Method Reference

Standard Methods 18th Edition (2340)

Equipment

1. 25-50 mL self leveling automatic buret.
2. 20 mL Class "A" volumetric pipet(s)
3. 50mL graduated cylinder
4. Titration vessels of appropriate volume.

5. Graduated cylinder (TD - 50 to 100 mL).
6. Magnetic stirring device & stirring bars (optional)
7. Adequate lighting, you may use a lit stirring device.

Reagents

1. Standard EDTA titrant (0.01M) - commercially available or prepared as per Standard Methods 18th Edition page 2-37.
2. Buffer Solution - commercially available or prepared as per Standard Methods, 18th Edition page 2-37.
3. Eriochrome Black T Indicator - commercially available or prepared as per Standard Methods 18th Edition page 2-37.

Standard

Calcium Standard - Commercially available Calcium Chloride, 1000 mg/L as CaCO₃, or prepared as per Standard Methods 18th Edition page 2-37.

Sample Container/Preservative

A clean plastic or glass screw top container (250 - 1000 mL). Run sample as soon as possible or cool to 4 ° C and add enough HNO₃ to adjust the pH to less than 2.0

Maximum Sample Holding Time

7 days, cool to 4 ± 2.0 ° C, store at 2-10 ° C

General Method Summary

Calcium and magnesium ions are sequestered by the addition of EDTA. The endpoint of the reaction is detected by means of eriochrome black-T indicator at a pH of 10.0. The indicator has a red color in the presence of calcium and magnesium ions and a distinct blue color when the cations are sequestered. Excessive amounts of heavy metals can interfere. This is usually overcome by complexing the metals with an inhibitor.

For best results, 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.

On-site Survey Requirements

1. Each analyst must be able to perform the hardness titrant standardization
2. Proper procedural technique will be observed during the titrant standardization and sample analysis (the titration is completed when the sample turns a distinct blue color)
3. Hardness titrant standardization records will be checked for the previous three years.
4. All reagents, standards and solutions used for the test will be checked for proper labeling and dating.

5. Each analyst will be required to analyze a performance sample during the survey.
6. "Operational" analysts will be required to analyze a performance sample and a plant tap sample.

Required Quality Control: Titrant Standardization

Frequency

Initially upon opening or preparation of titrant and thereafter at least once per month. Records of the results must be kept on file.

Reagents

1. Standard EDTA titrant (0.01M) - commercially available or prepared as per Standard Methods 18th Edition page 2-37.
2. Buffer Solution - commercially available or prepared as per Standard Methods, 18th Edition page 2-37.
3. Eriochrome Black T, Indicator - commercially available or prepared as per Standard Methods 18th Edition page 2-37.

Standard

Calcium Standard - Commercially available Calcium Chloride, 1000 mg/L as CaCO₃, or prepared as per Standard Methods 18th Edition page 2-37.

Glassware

1. 25-50 mL automatic, self-leveling buret
2. 20 mL class "A" volumetric pipet(s)
3. Titrating vessels of appropriate volume
4. 50 mL graduated cylinder.

Standardization Procedure

1. Add 30 mL of laboratory pure water, add appropriate amounts of buffer and indicator.
2. If the color indicates that the endpoint has already been reached, i.e., there is no hardness in the laboratory pure water, record your Blank value as 0". and proceed to step 3 and skip step 7. If there is alkalinity, proceed to step 3 and do not skip step 7.
3. Deliver 20 mL of standard CaCO₃, using the class A volumetric pipet, into the titrating vessel.
4. Titrate with EDTA to a distinct blue endpoint.
5. Record the volume of titrant used.
6. Repeat this procedure using a second fresh 20 mL portion of standard CaCO₃.

7. Run a blank sample using 30 mL of laboratory pure water. Record the milliliters of EDTA used for the blank sample.
8. Subtract the blank value (mL) from the two standard titration values (mLs).

Conclusion

The acceptable range for the adjusted amount of titrant used is $\pm 5\%$ of theoretical (20 mL) for laboratory prepared titrants. The acceptable range is 19.0 - 21.0 mL. If the EDTA titrant is not within the acceptable range, replace the titrant or calculate a correction factor.

Correction Factor

Repeat steps 1 through 4 using a third fresh portion of standard CaCO_3 and calculate a correction factor as follows:

$$\frac{20 \text{ mL}}{\text{Average of three titrations (mL)}} = \text{Correction Factor}$$

Average of three titrations (mL)

Correction factor times all subsequent titration results equals the true hardness value.

Required Documentation

1. Date standardization performed
2. Analysts initials
3. Expiration date of CaCO_3 standard
4. Amount of EDTA titrant used for the two titrations
5. Blank value in mL
6. Correction factor and third titration value if necessary.

Test Procedure (Colorimetric Titration)

1. Ascertain that the buret is filled to the meniscus with EDTA titrant
2. Note the total volume of titrant
3. Rinse out the titrating vessel with sample and discard
4. Measure the sample with an appropriately sized graduated cylinder
5. Add 1 - 2 mL of buffer to the sample (buffer the sample to a pH of 10.0 and mix (or use combination buffer indicator)
6. Add indicator to the sample (or use combination buffer indicator)
7. Slowly add titrant to the sample, mixing with a magnetic stir bar or glass rod

8. Stop adding titrant when the color change occurs. If you are not sure what the color change should look like, prepare a positive control by adding indicator to a sample and titrating well past the point when the color does not change with the addition of any more titrant. Use this test sample as a color standard for the "real" sample. Never add additional titrant past the color change endpoint. If you are not sure that you have reached the endpoint, record the volume of titrant used then continue adding titrant. If the color does not change, use the recorded value. If it changes to a "new" endpoint, use the new volume.
9. Multiply the volume of titrant used by the multiplier factor as listed above
10. Record this value as hardness in mg/L as CaCO_3

General Notes on Titrations for Hardness

You must mix laboratory pure water with the standard. Using the standard alone will not allow enough volume to properly show the color change. Use a volume of laboratory pure water to make a total volume of 50 or 100 mL.

- ▲ Use 20 mL of standard for the test.
- ▲ Do not use correction factors on purchased titrants. They must be within range or discarded.
- ▲ Do not use ampuled standards for hardness.
- ▲ Your buret must be of sufficient capacity so that all tests and standardizations can be performed without refilling the buret. In other words, if it takes 35 mL of titrant to test for hardness in your water and you have a 25 mL buret, you must get a 50 mL buret.

Chloride

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/ Equipment Storage Conditions	0.0141 N silver nitratetitrant	Room temperature, no light
	Potassium chromate Indicator	Room temperature
	0.0141 N sodium chloride standard	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	0.0141 N silver nitratetitrant	1 year after opening
	Potassium chromate Indicator	1 year after opening
	0.0141 N sodium chloride standard	1 year after opening
Required Quality Control	Frequency	Required QC
	Monthly	Standardize Titrant

Method Reference

Standard Methods 18th Edition (4500-Cl-B)

Equipment/reagents/standard

1. Amber, or aluminum foil covered, self-leveling, automatic buret of adequate size to perform titration without refilling
2. Titration vessels of appropriate volume
3. Class A volumetric glassware for standardization
4. Graduated cylinder (TD, 50 or 100 mL)
5. Magnetic stirring device and stirring bars (optional)
6. 0.0141 N silver nitrate titrant
7. 0.0141 N sodium chloride standard
8. Potassium chromate color change endpoint indicator

Sample Container/Preservative

A clean plastic or glass screw top container (250 - 100 mL)

No preservative necessary

Maximum Sample Holding Time

7 days

General Method Summary

The silver nitrate titration procedure is the most widely used for water analysis because there is no sample pH adjustment required provided the sample pH is between 7 and 10. However, the pink to red -yellow endpoint is rather difficult to determine accurately due to a white silver chloride precipitate which is produced during the titration. To assist in determining the proper endpoint, use a deionized water blank with 0.20 - 0.40 mL of titrant added to compare the target shade of color. The titrant is light sensitive and should be stored away from light. Amber or aluminum foil covered titrating burettes and reservoirs are required to prevent light deterioration.

On-Site Survey Requirements

1. Each fully approved analyst must be able to perform the chloride titrant standardization.
2. Proper procedural technique will be observed during the titrant standardization and sample analysis.
3. Chloride titrant standardization records will be checked for the previous three years.
4. All reagents, standards and solutions used for the test will be checked for proper labeling and dating.
5. Each analyst will be required to analyze a performance sample during the survey.
6. Operational analysts will be required to analyze a performance sample and a plant tap sample.

Required Quality Control - Titrant Standardization

Silver Nitrate Titrant Standardization

Frequency

Initially upon opening or preparation of titrant and thereafter at least once per month.

Records of the results must be kept on file.

Reagents/Equipment

1. Silver Nitrate Titrant (0.0141 N): Commercially available or prepared as per Standard Methods, 18th Edition pages 4 - 49.
2. Potassium Chromate Indicator: Commercially available or prepared as per Standard Methods, 18th Edition pages 4 - 49.
3. Sodium Chloride (0.0141N) Standard: Commercially available (500 mg/Cl) or prepared as per Standard Methods, 18th Edition pages 4 - 49.

4. An analytical balance readable to 0.0001g must be used to measure primary standard grade reagents. The balance must be covered by an annual service contract and must be located on a stone balance table or stone slab.
5. 10-25 mL Automatic, self-leveling Burette
6. 5 mL Class "A" Volumetric Pipets
7. Titrating Vessels of Suitable Volume
8. 50 mL Graduated Cylinders (TD)

Procedure

1. Run a blank using 45 mL of laboratory pure water and the appropriate indicator. Record the mL of titrant used (less than 0.5 mL of titrant is normal). Retain this sample to compare the end point color with the standard titrations.
2. Deliver 5 mL of the sodium chloride standard solution, using a class "A" volumetric pipet, into another titrating vessel.
3. Add 45 mL of laboratory pure water using a graduated cylinder and the appropriate indicator.
4. Titrate with 0.0141 N silver chloride titrant to the color end point which closely resembles the blank sample.
5. Record the volume of titrant used.
6. Repeat 2 through 5 using a second fresh portion of standard solution.
7. Subtract the blank value (mL) from each of the standard titration values (mL).

Conclusion

The acceptable range for the adjusted amount of laboratory prepared titrant used is $\pm 5\%$ of the value (5.0 mL). The acceptable range is 4.75 mL to 5.25 mL.

If the amount of titrant used is outside of the acceptable range, replace the titrant.

Correction Factor

Repeat steps 2 through 5 using a third fresh portion of standard and calculate a correction factor as follows:

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

Multiply all subsequent titration answers by the correction factor, this equals the adjusted chloride concentration.

Documentation

1. Date standardization performed
2. Analysts initials
3. Expiration date of the sodium chloride standard

4. Amount of chloride titrant used for the two titrations
5. Blank value (mL)
6. Correction factor and third titration value if necessary

Test Procedure (Colorimetric Titration)

1. Ascertain that the buret is filled to the meniscus with silver nitrate titrant
2. Note the total volume of titrant
3. Rinse out the titrating vessel with sample
4. Measure the sample with an appropriately sized graduated cylinder
5. Add about 0.5 mL of indicator to the sample
6. Slowly add titrant to the sample, mixing with a magnetic stir bar or glass rod
7. Stop adding titrant when the reddish-yellow color is observed.
8. Multiply the volume of titrant used by the multiplier factor as listed above
9. Record this value as chloride in mg/L

General Notes on Titrations for Chloride

- ▲ You must mix laboratory pure water with the standard. Using the standard alone will not allow enough volume to properly show the color change. Use a volume of laboratory pure water to make a total volume of 50 mL.
- ▲ Test limits for standardizations are $\pm 5.0\%$.
- ▲ Do not use correction factors on purchased titrants. They must be within range or discarded.
- ▲ Do not use ampuled standards for chloride.
- ▲ Your buret must be of sufficient capacity so that all tests and standardizations can be performed without refilling the buret.
- ▲ **Mercuric nitrate must not be used as chloride titrant.**

pH/Alkalinity Stability

<i>Quick Reference</i>		
	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Calcium Carbonate (dry)	Room temperature
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Calcium Carbonate (dry)	6 years after opening
Required Quality Control	Frequency	Required QC
	None (see pH & Alkalinity)	(See pH & Alkalinity)

Method Reference

Standard Methods 18th Edition (2330)

Sample Container/Preservative

Two clean, 300-500 mL, glass stoppered BOD bottles. Sample containers must be completely filled and kept sealed prior to analysis.

No preservative can be used.

Maximum Sample Holding Time

Sample must be kept sealed from the air and prepared as soon as possible after collection.

General Method Summary

The analytical results of this test are indicative of the corrosive properties of the water analyzed. The change in sample alkalinity and pH after saturation with calcium carbonate is measured using approved methods for both alkalinity and pH. All requirements for the alkalinity and pH test must be fulfilled in order to acquire approval for the stability test.

Excess calcium carbonate must be removed from the saturated sample by filtration, (filtration is not necessary for the slow saturation technique) before titrating to prevent an inaccurate alkalinity result. Exposure to the air must be kept to a minimum to prevent a pH change due to contact with carbon dioxide.

On-Site Survey Requirements

At least one stability test for every three analysts must be prepared prior to the survey so that it may be completed at the time of the survey. The actual analysis will be performed during the survey.

Each analyst must be familiar with the procedure and interpretation of results if asked questions during the survey.

Reagents used for the test will be checked for proper labeling and dating.

"Operational" analysts will be required to participate in the analysis of a stability sample on the plant tap.

Equipment

1. Two 300 mL glass BOD bottles with glass stoppers
2. Magnetic stirring device and TFE-coated stir bar (for rapid saturation)
3. Filter funnel and flask
4. Whatman #4 filter or equivalent
5. Alkalinity testing equipment
6. pH testing equipment

Reagents

1. Calcium Carbonate, reagent grade or laboratory grade
2. Alkalinity test reagents
3. pH test reagents
4. *Test Procedure*

Rapid Saturation Technique

1. Add a scoop (approximately 0.5 to 2.0 grams) of calcium carbonate powder to a clean 300 mL BOD bottle. Add a magnetic stirring bar and fill the bottle to overflowing with sample water and stopper it. If all of the calcium carbonate dissolves, begin again. On the subsequent test add an additional quantity of calcium carbonate.
2. Fill a second clean 300 mL BOD bottle to overflowing with sample water add and stopper it. There should be no calcium carbonate added to this sample.
3. Stir the saturated bottle for 30 minutes at moderate speed on a magnetic stirring device.
4. Allow the excess carbonate to settle for an additional 30 minutes. Filter **both samples**. This is done to remove the excess calcium carbonate from one bottle. The other bottle is filtered so that the treatment of both bottles are identical. A Whatman #4 or similar fast paper filter should be satisfactory. Rinse the filter, funnel and flask with the solution then discard the first 25 to 50 mL of filtrate.
5. Determine the "initial" pH + alkalinity of the aliquot of the sample to which no calcium carbonate was added; record the results.
6. Determine the "final" pH + alkalinity of the aliquot of the sample to which the calcium carbonate was added; record the results.

7. Determine the difference in pH and alkalinity by subtracting the saturated sample results from the unsaturated sample results.

Slow Saturation Technique

8. Add a scoop (approximately 0.5 to 2.0 grams) of calcium carbonate to a clean 300 mL BOD bottle. Fill the bottle to overflowing with sample water and stopper it. Agitate the sample by shaking. If all of the calcium carbonate dissolves, begin again. On the subsequent test add an additional quantity of calcium carbonate.
9. Fill a second clean 300 mL BOD bottle to overflowing with sample water and stopper it. There should be no calcium carbonate added to this sample.
10. Agitate both sample bottles about once an hour over the 8 hour working day.
11. Allow the calcium carbonate to settle to the bottom of the container by standing overnight.
12. Remove a suitable aliquot of both samples by filtration as in step #4 under the "Rapid Saturation Technique", or by carefully pipetting the required amount of supernatant liquid out of the container with calcium carbonate without disturbing the settled calcium carbonate. If any of the excess carbonate gets picked up by accident, both samples will have to be filtered before determining "final" alkalinity. The determination of "final" pH should not be affected by small amounts of turbidity.
13. Determine the pH + alkalinity of the aliquot of the sample to which no calcium carbonate was added; record the results.
14. Determine the pH + alkalinity of the aliquot of the sample to which calcium carbonate was added; record the results.

Conclusion

Interpretation of the results is done by comparing initial and final test results.

1. If no significant difference between the initial & final alkalinity and initial & final pH results occurs, the water is considered to be stable.
2. If the alkalinity and the pH increase in the saturated sample, the water is considered to be corrosive and has a tendency to dissolve calcium carbonate.
3. If the alkalinity and pH decrease in the saturated sample, the water is considered to be scale forming and has a tendency to deposit calcium carbonate.
4. If the alkalinity and pH shift in opposite directions in the saturated sample, the saturated sample may have been contaminated with undissolved calcium carbonate or over exposure to the air may have caused a bias in pH. The problem should be corrected and the test rerun.

Required Documentation

1. Date and analysts initials
2. Results for the initial and final pH and alkalinity
3. Expiration date of calcium carbonate

Chlorine DPD/Colorimetric

<i>Quick Reference</i>		
	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Liquid DPD reagents	Room temperature
	Single use, sealed DPD powder pillows	Room temperature
	DPD single dose dispensers	Room temperature
	Potassium Permanganate 1000 mg/L std	Refrigerated
	Potassium Permanganate 100 mg/L diluted std	Discard after preparation
	Commercial sealed ampouled stds	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Liquid DPD reagents	6 months after opening
	Single use, sealed DPD powder pillows	Manufacturer's expiration date
	DPD single dose dispensers	6 months after first use
	Potassium Permanganate 1000 mg/L std	1 year after opening or preparation
	Potassium Permanganate 100 mg/L diluted std	Prepare, use and discard in the same day
Required Quality Control	Frequency	Required QC
	Quarterly (1/three months)	Standardize Titrant
	Quarterly (1/three months)	Check total chlorine of lab pure water

Method Reference

Standard Methods 18th Edition (4500 Cl-G)

1. *Equipment*
2. Electronic filter photometer kit or Spectrophotometer
3. 3 minute timer

4. Class A volumetric glassware for standardization and standard dilutions
5. An adjustable microliter pipettor for the DPD kit calibration
6. Chlorine standard solution
7. DPD indicator reagent
8. Laboratory pure water that is free of chlorine and has no chlorine demand

Sample Container

A clean plastic or glass screw top container (250 - 1000 mL).

Maximum Sample Holding Time/Preservative

Free chlorine - Must be analyzed immediately after collection. Alternately, the sample may be collected directly into the test cell.

No preservative is necessary agent to the sample. Test the sample immediately.

Total chlorine - No preservative is necessary agent to the sample. Must be analyzed immediately after collection.

General Method Summary

The DPD colorimetric method is the simplest and most frequently used method for the determination of free and total chlorine in potable water.

Sample color and turbidity may interfere with the colorimetric method, however, these are not factors when analyzing most potable water. The calibration of the DPD kits must be checked against a series of standards on a regular frequency of once per three months. Kits are considered in calibration provided the observed readings agree within $\pm 10\%$ of the theoretical values.

Use a range of five standards when performing chlorine calibrations for colorimetric tests. Be sure the ranges that you select will bracket the complete range of chlorine levels seen in your system.

On-Site Survey Requirements

1. Each fully approved analyst must be able to perform the DPD kit calibration or construct a calibration curve (spectrophotometer).
2. All reagents, standards and solutions used for the calibration and the analysis will be checked for proper labeling and dating.
3. Calibration records will be checked for the previous three years.
4. Each analyst will be required to analyze a performance sample during the survey.
5. "Operational" applicants will be required to analyze a performance sample and a tap sample for free and total chlorine.
6. Proper kit use and procedural technique will be observed

Required Quality Control

DPD Kit Calibration

Frequency

Initially when kit is purchased and thereafter at least once per three months. This must be done for each kit used for official testing.

Equipment/Reagents/Standards

1. Reagents
 2. N,N-Diethyl-p-phenylenediamine Indicator (DPD), commercially available.
 3. Laboratory pure water - Chlorine free/chlorine demand free.
 4. Potassium permanganate Stock Standard: Commercially available as 0.891 g/L KMnO_4 or laboratory prepared as follows: Weigh 0.891g of desiccated reagent grade potassium permanganate using an analytical balance. Add this to a 1000 mL class A volumetric flask and bring to volume with laboratory pure water. This solution will be equivalent to 1000 mg/L of Chlorine. Discard one year after preparation. **Important Note: When using potassium permanganate as a standard, TOTAL CHLORINE DPD reagent must be used with the required 3 minute reaction time.**
 5. Working Standard: Using class "A" volumetric glassware dilute 10 mL of the 1000 mg/L stock with laboratory pure water to a final volume of 100 mL. (This solution must be made fresh for each calibration).
 6. Optional Ampuled Chlorine Standard Solution: Commercially available from Hach Chemical Co. as voluette ampules. The concentration will vary within each lot. The laboratory must be sure their micropipettor will deliver enough ampuled chlorine standard to bracket the entire range of chlorine seen in the water system. Discard two years after receipt.
 7. Balance: An analytical balance readable to 0.0001g must be used to measure primary standard grade reagents if the laboratory will prepare their own stock standard. The balance must be covered by an annual service contract and located on a stone balance table or stone slab.
 8. Glassware
 9. Class "A" volumetric pipets - (2) 10 mL
 10. Class "A" volumetric flasks - 100 mL, 1000 mL
1. *DPD Kit Calibration Procedure*
 2. Pipet 10 mL of laboratory pure water into a clean test cell.
 3. Zero the instrument with the laboratory pure water.
 4. Add one DPD total chlorine pack pack to the laboratory pure water.
 5. Wait three minutes.

6. Read the laboratory pure water test results in the chlorine test instrument.
7. 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 new source of laboratory pure water and begin again with step 1.
8. Pipet 10 mL of chlorine free/chlorine demand free laboratory pure water into a clean sample cell and add free chlorine DPD indicator (for ampules) or total chlorine pack (for potassium permanganate) pack to the laboratory pure water.
9. Zero the instrument using this blank.
10. Using an adjustable microliter pipettor spike the prepared sample (blank) with a known volume of standard.
11. Mix thoroughly. If using total chlorine DPD (using potassium permanganate), wait 3 minutes, test at once for free chlorine DPD (for ampules). Place into the kit, record the observed concentration.
12. Adjust the microliter pipettor to a larger volume.
13. Repeat steps 1 through 5 using five different standard concentrations which will span the functional range of the kit. **Double the DPD dose when the spike levels will be <2.0 mg/L.** The functional range of the kit is the highest level of chlorine leaving the plant to the lowest level in the distribution system. If a multiple spike is necessary to achieve a volume, it is limited to a double spike above 50% of the total capacity of the micropipettor; i.e. to deliver 120uL with a 100uL micropipettor, use two 60uL portions, not one 100uL + 20uL. Avoid using multiple spikes whenever possible.

Calculations

Using the 100 mg/L Potassium Permanganate KMnO₄ Standard and the following chart, determine the theoretical concentration by cross referencing the volume of each standard spike (ul) with the corresponding value under the kit sample volume used.

KMnO ₄ 100mg/L as Chlorine							
μl	Kit Sample Volume			μl	Kit Sample Volume		
	5 mL	10 mL	25 mL		5 mL	10 mL	25 mL
20	0.40	0.20	NA	110	2.20	1.10	NA
25	0.50	0.25	0.10	125	2.50	1.25	0.50
30	0.60	0.30	NA	140	2.80	1.40	NA
40	0.80	0.40	NA	150	3.00	1.50	0.60
50	1.00	0.50	0.20	160	3.20	1.60	NA
60	1.20	0.60	NA	170	3.40	1.70	NA
70	1.40	0.70	NA	175	3.50	1.75	0.70
75	1.50	0.75	0.30	180	3.60	1.80	NA
80	1.60	0.80	NA	190	3.80	1.90	NA
90	1.80	0.90	NA	200	4.00	2.00	0.80
100	2.00	1.00	0.40				

Using the Chlorine Ampule Standard

Chlorine ampules are at various concentrations depending on the individual production batch. A calculation is necessary to determine each theoretical concentration of the individual spike volumes. Use the following formula:

$$\frac{(\text{Standard concentration mg/L})}{(\text{Volume of Kit Sample in milliliters})} \times \frac{(\text{Theoretical Microliters Added})}{1000 \text{ (mg/L)}} = \text{Theoretical concentration}$$

Example:

$$\frac{(85.7 \text{ mg/L}) \times (50 \text{ } \mu\text{L})}{10 \text{ mL} \times 1000} = 0.4285 \text{ mg/L}$$

Conclusion

Compare the observed value to the theoretical value of each spike. The acceptable range is $\pm 10\%$ of the theoretical concentration. If concentrations are outside the acceptable range, the kit can be serviced or replaced (this is recommended).

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

Example:

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

Required Documentation

1. Date calibration was performed
2. Results of calibration
3. Analyst initials
4. Stock standard concentration
5. Stock standard expiration date
6. Correction factor/correction curve
7. Microliter pipettors

Chlorine Sample Test Procedure ("Hach" Pocket Colorimeter)

This procedure is written for the "Hach" Pocket colorimeter. Other chlorine testers have different procedures. Please consult the manufacturer's instructions for use. Instructions marked with a "*" are universal instructions, however.

Free Chlorine

1. *Run the sample tap for 2-5 minutes or longer, to ascertain that chlorine from the main water supply is flowing from the sample tap.
2. *Reduce the flow from the tap.
3. Fill a clean 10 mL test cell to the line with water from the sample tap.
4. Remove the colorimeter's protective cap.
5. Wipe the sample cell so that it is dry and clean.
6. Place the cell into the well on the colorimeter, making sure that the index mark faces to the front of the colorimeter.
7. Cover the cell with the instrument's cap.
8. Press "ZERO".
9. Wait for the colorimeter to register "0.00" on the LCD display.

10. Remove the cell from the colorimeter.
11. Fill another sample cell with fresh sample to the 10 mL line.
12. Immediately add one free chlorine DPD powder packet to the sample.
13. Cap the cell and shake it for 10 seconds.
14. Immediately place the cell in the colorimeter's well.
15. Cover the cell with the instrument's cap.
16. Press "READ".
17. Wait for the colorimeter to show the free chlorine results in mg/L.
18. Record the results as Free Chlorine in mg/L.

Total Chlorine

1. *Run the sample tap for 2-5 minutes or longer, to ascertain that chlorine from the main water supply is flowing from the sample tap.
2. *Reduce the flow from the tap.
3. Fill a clean 10 mL test cell to the line with water from the sample tap.
4. Remove the colorimeter's protective cap.
5. Wipe the sample cell so that it is dry and clean.
6. Place the cell into the well on the colorimeter, making sure that the index mark faces to the front of the colorimeter.
7. Cover the cell with the instrument's cap.
8. Press "ZERO".
9. Wait for the colorimeter to register "0.00" on the LCD display.
10. Remove the cell from the colorimeter.
11. Fill another sample cell with fresh sample to the 10 mL line.
12. Immediately add one total chlorine DPD powder packet to the sample.
13. Cap the cell and shake it for 10 seconds.
14. On an accurate timer, time for 3-5 minutes
15. After 3-5 minutes place the cell in the colorimeter's well.

16. Cover the cell with the instrument's cap.
17. Press "READ".
18. Wait for the colorimeter to show the total chlorine results in mg/L.
19. Record the results as Total Chlorine in mg/L.
20. Calculate the combined chlorine by subtracting the free chlorine from the total chlorine.
21. Record the calculated value as Combined Chlorine mg/L.

High Levels of Chlorine

When chlorine levels are 2.0 mg/L or greater, when using dry DPD reagents, it is necessary to use a double dose of DPD reagent. This applies to both free and total chlorine. Use either two powder packets (meant for a 10mL sample) or one powder packet (meant for a 25mL sample) or two doses of an automatic dispenser for each 10ml of sample. For test instruments that use 25mL or larger samples, double the dose of dry reagent when chlorine levels are 2.0 mg/L or greater. It is also necessary to follow manufacturer's recommendations for high levels of chlorine. Most test kits have switchable ranges and use a well insert with smaller tubes for levels above 2.2 mg/L. With some brands of DPD reagent it may be necessary to double the dose for chlorine levels as low as 1.5 mg/L. You can check this in your laboratory by adding one packet of free chlorine reagent to a sample, test it and immediately add an additional packet. If the chlorine reading rises by ≥ 0.2 mg/L then you should use two packets.

Liquid DPD Reagents

Some instrument manufacturer's use liquid DPD reagents. These reagents are reported to be much more unstable than the dry reagents. Replace liquid DPD reagents six months after opening or if you notice that your calibration is questionable.

In-line Chlorine Meters

In-line chlorine meters must be checked with the results recorded at least once each day by taking a sample as close to the in-line chlorine meter as possible and checking it against a calibrated bench top chlorine meter. Note the in-line chlorine meters reading at the time of collection and record it.

You must be operationally or fully approved for colorimetric chlorine to check or calibrate an in-line chlorine meter. The in-line chlorine meter's results must agree with the bench top model within ± 0.1 mg/L. If the reading is not within ± 0.1 mg/L set the in-line chlorine meter to agree with the bench top model. Most in-line chlorine meters are very easy to reset.

The daily check between the in-line chlorine meter and the bench top unit must be recorded. Record the analyst's initials, the date and time, the reading obtained by the bench top model and the reading of the in-line unit at the time of sample collection. Most brands of in-line chlorine meters are acceptable. If you are not sure, contact the Ohio EPA/DES Laboratory Certification Section.

Approval of Field Personnel for Chlorine Testing

Persons who analyze for chlorine via DPD colorimetric tests in the distribution system only need not be approved for chlorine tests. Municipalities that normally check and record chlorine readings when microbiological samples in the distribution system are collected or for any other reason, in the distribution system, must document additional information in lieu of actual approval for those individuals for chlorine testing. Each collector who collects samples in the distribution system and tests for chlorine at each distribution system site must have at least five days of documented training in sample collection/chlorine testing. The training can be conducted by any qualified (approved) individual within your certified laboratory. Forms are provided in this manual that must be used to list the samplers and their training dates. These forms should be located in the front the QC record book. Additionally, the sampling protocol used by your laboratory must be documented and located in the front of the QC book. This only applies to analysts who are analyzing chlorine samples from a distribution system and are using a DPD chlorine kit. Analysts who test plant taps or who use another procedure such as amperometric titration must be chemically approved to do this.

Three Month DPD Kit Calibration

LaboratoryName _____

Date			Date		
Analyst			Analyst		
Std Conc			Std Conc		
Std Exp Date			Std Exp Date		
Standard Volume	Calculated Concentration	Observed Concentration	Standard Volume	Calculated Concentration	Observed Concentration
#1			#1		
#2			#2		
#3			#3		
#4			#4		
#5			#5		
Comments			Comments		
Date			Date		
Analyst			Analyst		
Std Conc			Std Conc		
Std Exp Date			Std Exp Date		
Standard Volume	Calculated Concentration	Observed Concentration	Standard Volume	Calculated Concentration	Observed Concentration
#1			#1		
#2			#2		
#3			#3		
#4			#4		
#5			#5		
Comments			Comments		

Chlorine: Amperometric Titration

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Liquid reagents	Room temperature
	Standards	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Liquid reagents	1 year after opening
	Standards	1 year after receipt
Required Quality Control	Frequency	Required QC
	Monthly	Standardize Titrant
	Monthly	Check total chlorine of lab pure water

Method Reference

Standard Methods 18th Edition (4500-Cl D)

Equipment/Reagent

Amperometric titrator with the following:

Platinum electrode - must be free of deposits and foreign materials. Clean it periodically with abrasive cleaners or follow manufacturer's recommendations.

Salt bridge - must be in good operating condition, must not be plugged. Keep the salt bridge solution supplied with salt. Follow manufacturer's recommendations for this.

Silver-silver chloride reference electrode

Agitator - clean this regularly as outlined in Standard Methods (18th Edition, page 4-42)

Glassware - all glassware used for this test must be clean.

Class "A" volumetric glassware for standardization

pH 7 phosphate buffer solution

Potassium Iodide solution

pH 4 acetate buffer solution

Sample Container/Preservative

A clean plastic or glass screw top container or use the titrating vessel

No preservative is necessary

Maximum Sample Holding Time

If you are using amperometric titration in the laboratory, distribution system samples can be tested in the laboratory as long as the following conditions will be met:

- ▶ The sample must completely fill the sample container with no air space.
- ▶ The sample must be collected in a sample container with a tightly capped screw cap.
- ▶ The sample must be immediately iced and kept iced until it has been tested.
- ▶ The sample must be analyzed within three hours of collection.

General Method Summary

The amperometric titration method is most accurate when analyzing samples with chlorine residuals that are less than 2 mg/L.

This method requires a greater amount of operator skill than the DPD method, however it is considered the most accurate and reliable method provided the electrodes are kept clean and in good condition to obtain sharp end points. Interferences such as turbidity, color, temperature or presence of common oxidizing agents have little affect on the results. Some loss of chlorine may occur due to the rapid stirring of some instruments.

As with all other titrametric methods, laboratories are required to standardize the PAO titrant at least once per month using at least two aliquots of standard.

On-site Survey Requirements

1. Instrument will be checked for cleanliness and proper functioning.
2. Each analyst must be able to perform the PAO titrant standardization procedure. All reagents, standards and solutions used for the test will be checked for proper labeling and dating.
3. Calibration records will be checked for the past three years.
4. Each analyst will be required to analyze a performance sample during the survey.
5. "Operational" analysts will be required to analyze a tap sample and/or a performance sample for free and total residual chlorine. Proper instrument use and analytical technique will be observed.

Required Quality Control: Phenylarsine Oxide (PAO) Titrant Standardization

Frequency

Initially upon opening or preparation of titrant and thereafter at least once per month. Records of the results must be kept on file.

Reagents

PAO Titrant (0.00564N) - Commercially available or prepared per Standard Methods 18th Edition page 4-39.

Potassium Iodide Crystals (Reagent Grade) - May substitute the Potassium Iodide Solution used with the instrument provided there is no yellow color observed.

Sulfuric Acid Solution (20%) - Using class "A" volumetric glassware, dilute 20 mL of concentrated sulfuric acid to 100 mL, cool before adjusting to volume.

Stock Standard

Potassium Biiodate: (Laboratory prepared 0.0025N) Dry 2 - 4g of reagent grade potassium biiodate for two hours at 105 C. Desiccate to room temperature, dissolve 1.6245g of potassium Biiodate in laboratory pure water and using class "A" volumetric flask, dilute to a final volume of 500 mL. This is a 0.100N solution. Using class "A" volumetric glassware, dilute 25 mL of the 0.100 N solution with laboratory pure water to a final volume of 1000 mL. This is a 0.0025N solution and must be prepared fresh for each standardization.

Working Standard

Potassium Biiodate (commercially prepared). Available from major distributors at 0.025N. This must be diluted using a Class "A" volumetric glassware to 0.0025N. (10 mL of 0.025N potassium biiodate diluted with laboratory pure water to a final volume of 100 mL. This solution must be made fresh for each standardization.)

Glassware

Class "A" volumetric pipets - 1.0 mL, 5.0 mL, 10.0 mL, 20.0 mL, 25.0 mL

Class "A" volumetric flasks - (2) 100 mL, 500 mL, 1000 mL

Titration vessel with 200 mL graduations

Titration Standardization Procedure

6. Place 200 mL of laboratory pure water in the titration vessel and turn on the stirrer.
7. Add 1.0 mL of 20% sulfuric acid solution.
8. Add approximately 1 gram of Iodide crystals or 1 mL of Potassium Iodide solution.
9. Carefully add 5.0 mL of the 0.0025 N Potassium Biiodate solution. A pale yellow color should develop.
10. Titrate until the meter's needle does not move any farther. It is necessary to titrate in small increments, while keeping track of the buret's volume. If additional titrant is added and the needle does not move any more, record the previous titrant volume as the correct value.
11. Repeat 1 - 5, duplicate titrations should agree within 0.5 mL.

Calculations

The normality of the PAO Titrant can be determined by the following formula:

$$N \text{ PAO} \times \text{mL PAO} = N \text{ Potassium Biiodate} \times \text{mL Potassium Biiodate}$$

$$N \text{ PAO} = \frac{0.0025 \times 5 \text{ mL}}{\text{mL PAO used}}$$

Conclusion

The acceptable range of the PAO Titrant is 5% of theoretical normality (0.00564 N or within 0.005358 - 0.005922). If the normality of titrant used is outside the acceptable range, replace the titrant.

Amperometric Titration Sample Test Procedures

1. Run the sample tap for 2-5 minutes or longer, to ascertain that chlorine from the main water supply is flowing from the sample tap.
2. Reduce the flow from the tap.
3. Fill a clean sample bottle or test cell to the line with water from the sample tap.
4. Collect a 200mL sample.
5. Add 1 mL of pH 7.0 phosphate buffer to adjust the pH.
6. Titrate until the meter's needle does not move any farther. It is necessary to titrate in small (0.05mL) increments, while keeping track of the buret's volume. If additional titrant is added and the needle does not move any more, record the previous titrant volume as the correct value.
7. Record the final titrant volume as Free Chlorine.
8. Add 1.00 mL of KI solution plus 1.00 mL acetate buffer to the same sample in the cell.
9. Titrate again until the meter's needle does not move any farther. It is necessary to titrate in small (0.05mL) increments, while keeping track of the buret's volume. If additional titrant is added and the needle does not move any more, record the previous titrant volume as the correct value.
10. Record the final titrant volume as Total Chlorine.
11. Subtract the Free Chlorine from the Total Chlorine volume and record the result as Combined Chlorine.

Calculations/Conversions

Apply the following formula to the titration volumes and calculate free, total and combined chlorine results:

$$\text{mg CL as Cl}_2 = \frac{(\text{mL of titrant} \times 200)}{\text{mL of sample}}$$

Documentation

1. Date standardization performed
2. Analyst initials
3. Expiration date of 0.100 N or 0.025 N potassium biiodate standard
4. Amount of PAO titrant used for each of the titrations
5. Calculated normality of the PAO titrant
6. Corrective actions taken if outside acceptable range

PAO Standardization Monthly Record

Laboratory Name _____

Date	Name	Standard Volume	Standard Conc/Exp Date	Titration #1	Titration #2	Correction Factor	Calculated N of PAO

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Liquid reagents	Room temperature
	Standards	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Reagents	1 year after opening
	Standards	1 year after receipt
Required Quality Control	Frequency	Required QC
	Quarterly (1/three months)	Construct Graph
	Monthly	FAS Titrant Standardization

Method Reference

Standard Methods 18th Edition

General Method Summary

The DPD/FAS Titrimetric Method is the least frequently used method for determining free and total residual chlorine. It is used more often for the determination of chlorine dioxide, mono and dichloramines and chlorite.

On-site Survey Requirements

1. Each analyst must be able to properly perform the FAS titrant standardization.
2. All reagents, standards and solutions used for the test will be checked for proper labeling and dating.
3. Titrant standardization records will be checked for completeness for the past three years.
4. Each analyst will be required to perform the FAS titrant standardization and analyze a plant tap sample for free and total chlorine.
5. "Operational" analysts will be required to analyze a plant tap sample for free and total chlorine.

Chlorine Dioxide by DPD/FAS Titration

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Liquid reagents	Room temperature
	Standards	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Reagents	1 year after opening
	Standards	1 year after receipt
Required Quality Control	Frequency	Required QC
	Quarterly (1/three months)	Construct Graph
	Monthly	Titration Standardization

Method Reference

Standard Methods 19th Edition (4500 ClO₂-D)

Sample Container

A Clean plastic or glass container (250 - 1000 mL.), avoid excessive light and agitation

Maximum Sample Holding Time

Chlorine species are extremely unstable and cannot be stored. Chlorine dioxide must be analyzed immediately after collection.

General Method Summary

This method is an extension of the DPD method for determining free chlorine and chloramines 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 with this method if needed.

On-Site Survey Requirements

- Each fully approved analyst must be able to demonstrate the standardization of the FAS titrant.

2. All reagents, standards and solutions used for standardization and analysis will be checked for proper labeling, dates and records.
3. Standardization records will be checked for the previous three years.
4. Each analyst will be required to analyze a sample during the survey.
5. Proper procedural technique and interpretation of data will be observed.

Interferences

1. Turbidity and color may interfere with the determination of the endpoint.
2. Oxidized manganese is the most significant source of interference (this typically is not a problem in finished drinking water). To reduce interference, if excess manganese is present, place 5 mL buffer solution and 0.5 mL sodium arsenite solution in flask. Add 100 mL sample and reagents, read absorbance and subtract from readings obtained in method. A 0.25% solution of thioacetamide can be substituted for the sodium arsenite.
3. Interference of copper levels up to approximately 10 mg/L are overcome by the EDTA in the DPD solution. The EDTA also helps the stability the DPD solution.

Equipment

1. Standard laboratory glassware.
2. Class A volumetric pipets for standardizations
3. A microburet 0-2 mL or 0-10mL depending on required range .

Reagents

1. Phosphate buffer solution:

Dissolve 24 g anhydrous Na_2HPO_4 and 46 g anhydrous KH_2PO_4 in approximately 700 mL laboratory pure water. Dissolve 0.8 g disodium EDTA in 100 mL laboratory pure water. Combine these two solutions and dilute to 1 L with laboratory pure water. Add .0020 g HgCl_2 as a preservative. Store in amber glass.

2. DPD Indicator:

Dissolve 1.0 g DPD oxalate, or 1.5 g DPD sulfate pentahydrate, or 1.1 g anhydrous DPD sulfate in Chlorine free laboratory pure water containing 8 mL 1+3 H_2SO_4 (6 mL water + 2 mL H_2SO_4) and 0.2 g disodium EDTA. Dilute to 1L and store in amber glass.

3. Ferrous Ammonium Sulfate (0.00282 N):

Dissolve 1.106g of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in laboratory pure water containing 1 mL 1+3 H_2SO_4 (6 mL water + 2 mL H_2SO_4) and dilute to 1 liter.

4. Potassium Iodide, KI crystals

5. Glycine Solution

Dissolve 10 g glycine (amino acetic acid) in 100 mL laboratory pure water.

6. 5% sulfuric acid solution

Dilute 5 mL Concentrated H_2SO_4 to 100 mL laboratory pure water.

7. Sodium Bicarbonate Solution

Dissolve 27.5 g Na_2HCO_3 in 500 mL laboratory pure water.

8. Potassium dichromate (0.100 N):

Dissolve 4.904 g potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in laboratory pure water and dilute to 1 liter.

9. Potassium dichromate (0.0025 N):

Using a 25 mL volumetric pipet dilute 25 mL of 0.100 N potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in laboratory pure water and dilute to 1 liter. This standardization solution must be made fresh each month.

10. Sodium Arsenite Solution (Recommended for Interference suppression if needed)

Dissolve 0.5 g NaAsO_2 in laboratory pure water and dilute to 100 mL.
(CAUTION TOXIC- take care to avoid ingestion)

11. Thioacetamide Solution

Dissolve 0.250 g CH_3CSNH_2 in 100 mL Laboratory pure water. (CAUTION: Cancer suspect agent. Take care to avoid skin contact or ingestion)

12. Ferroin indicator:

Dissolve 1.485g 1,10-phenanthroline monohydrate and 0.695g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in laboratory pure water and dilute to 100 mL.

Monthly Standardization

1. Add 100 mL of chlorine free laboratory pure water into the titrating vessel .
2. Add 15 mL of concentrated sulfuric acid slowly while mixing and add one to three drops of ferroin indicator.
CAUTION: Concentrated sulfuric acid will cause burns if it comes into contact with skin.
3. Titrate to an orange endpoint. Record the volume of titrant used and retain this sample to compare color endpoint with standard titrations.
4. Add 100 mL of chlorine free laboratory pure water into another titrating vessel .
5. Add 15 mL of concentrated sulfuric acid slowly while mixing and add one to three drops of ferroin indicator.

CAUTION: Concentrated sulfuric acid will cause burns if it comes into contact with skin.

6. Using a volumetric pipet add 2 mL of 0.0025N Potassium dichromate to titration vessel if using a 2 mL buret or 10 mL of 0.0025N Potassium dichromate if using a 10 mL buret.
7. Titrate using FAS titrant to the same orange color intensity as the blank sample. Record the amount of titrant used.
8. Repeat steps 4 thru 7.
9. Subtract the blank value from each of the standard titration values.

Standardization Conclusion:

The acceptance criteria is 5% of theoretical value

2 mL of 0.0025N $K_2Cr_2O_7$ = 1.77 mL of FAS titrant (1.68 to 1.86 mL)

10 mL of 0.0025N $K_2Cr_2O_7$ = 8.86 mL of FAS titrant (8.42 to 9.30 mL)

Procedure

Chlorine dioxide:

1. Place 100 mL sample in beaker.
2. Add 2 mL glycine solution
3. Place 5 mL phosphate buffer in a flask
4. Add 5 mL DPD reagent.
5. Add the sample with glycine to flask and mix.
6. Titrate rapidly with FAS titrant until red color is discharged .
7. Record the volume of FAS used as **G**
8. Discard solution

Free Available Chlorine and Chloramine:

1. Place 5 mL phosphate buffer in a flask
2. Add 5 mL DPD reagent.
3. Add the 100 mL fresh sample to flask and mix.
4. Titrate rapidly with FAS titrant until red color is discharged .
5. Record the volume of FAS used as **A**
6. Add one very small crystals KI (about 0.5 mg) or 0.1 mL (2 drops) KI solution. Mix to dissolve.

7. Titrate rapidly with FAS titrant until red color is discharged .
8. Record the volume of FAS used as **B**
9. Add several crystals KI (about 1 g). Mix to dissolve.
10. Wait 2 minutes.
11. Titrate with FAS titrant until red color is discharged .
12. Record the volume of FAS used as **C**

Total available chlorine including chlorite:

13. Add 1 mL H₂SO₄ Solution. Mix
14. Wait 2 minutes.
15. Add 5 mL NaHCO₃ solution. Mix
16. Titrate rapidly with FAS titrant until red color is discharged .
17. Record the volume of FAS used as **D**
18. Discard solution.

Calculations

For a 100 mL sample and 0.00282 N FAS

1 mL of FAS solution = 1 mg/L chlorine.

1. Chlorine dioxide = **5G** (or **1.9G** expressed as ClO₂)
2. Chlorite = **D - (C+4G)**
3. Free available Chlorine = **A-G**
4. Total Chlorine = **C+(4.0G)** (in absence of Chlorite)
5. Total Chlorine = **D** (in presence of Chlorite)
6. Monochloramine = **B-A**
7. Dichloramine = **C-B**

Method Reference

Standard Methods 19 th Edition (4500 ClO₂-D)

Sample Container

A Clean plastic or glass container (250 - 1000 mL.) avoid excessive light and agitation

Maximum Sample Holding Time

Chlorine species are extremely unstable and cannot be stored
Chlorine dioxide must be analyzed immediately after collection

General Method Summary

This method is an extension of the DPD method for determining free chlorine and chloramine in water.

1. 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.
2. 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.

On-Site Survey Requirements

1. Each fully approved analyst must be able to demonstrate the construction of the DPD calibration curve.
2. All reagents, standards and solutions used for calibration and analysis will be checked for proper labeling, dates and records.
3. Calibration records and standardization curves will be checked for the previous three years.
4. Each analyst will be required to analyze a sample during the survey.
5. Proper procedural technique and interpretation of data will be observed.

Interferences

1. Turbidity and color may interfere with the determination of the absorbance contribution from DPD.
2. Oxidized manganese is the most significant source of interference (this typically is not a problem in finished

drinking water). To reduce interference, if excess manganese is present , place 5 mL buffer solution and 0.5 mL sodium arsenite solution in flask. Add 100 mL sample and reagents, read absorbance and subtract from readings obtained in method. A 0.25% solution of thioacetamide can be substituted for the sodium arsenite.

3. Interference of copper levels up to approximately 10 mg/L are overcome by the EDTA in the DPD solution. The EDTA also helps the stability the DPD solution.

Equipment

1. Standard Laboratory glassware.
2. Class A volumetric pipets or an acceptable microliter pipettor for standardizations
3. A spectrophotometer capable of reading 515 nm with a cell light path width of at least 1 cm.
4. Graph paper or a computer with software capable of performing linear regressions.

Reagents

1. Phosphate buffer solution:
2. Dissolve 24 g anhydrous Na_2HPO_4 and 46 g anhydrous KH_2PO_4 in approximately 700 mL laboratory pure water. Dissolve 0.8 g disodium EDTA in 100 mL laboratory pure water. Combine these two solutions and dilute to 1 L with laboratory pure water. Add 0.0020 g HgCl_2 as a preservative. Store in amber glass.
3. DPD Indicator:
4. Dissolve 1.0 g DPD oxalate, or 1.5 g DPD sulfate pentahydrate, or 1.1 g anhydrous DPD sulfate in Chlorine free laboratory pure water containing 8 mL 1+3 H_2SO_4 (6 mL water + 2 mL H_2SO_4) and 0.2 g disodium EDTA. Dilute to 1 L and store in amber glass.
5. Potassium Permanganate Solutions
6. (See DPD Chlorine Method)
7. Potassium Iodide, KI crystals
8. Glycine Solution: Dissolve 10 g glycine (amino acetic acid) in 100 mL laboratory pure water.
9. 5% sulfuric acid solution: Dilute 5 mL Concentrated H_2SO_4 to 100 mL laboratory pure water.
10. Sodium Bicarbonate Solution: Dissolve 27.5 g Na_2HCO_3 in 500 mL laboratory pure water.
11. Sodium Arsenite Solution (Recommended for Interference suppression if needed): Dissolve 0.5 g NaAsO_2 in laboratory pure water and dilute to 100 mL. (**CAUTION TOXIC- take care to avoid ingestion**)
12. Thioacetamide Solution: Dissolve 0.250 g CH_3CSNH_2 in 100 mL Laboratory pure water. (**CAUTION: Suspected carcinogen. Take care to avoid skin contact or ingestion**)

Monthly Calibration curve

1. Prepare a series of permanganate standards in 100 mL volumetric flasks which bracket the range of chlorine

concentrations seen in laboratory samples. This should be similar to the curve used for the free and total chlorine calibration procedure. A minimum of a blank and 5 standard concentrations must be run.

2. Place 5 mL phosphate buffer in a flask.
3. Add 5 mL DPD reagent.
4. Add 100 mL of standard
5. Read absorbance at 515 nm on spectrophotometer.
6. Repeat with each standard concentration and record the absorbance readings.
7. Plot the absorbance of the standard solutions on the vertical axis and the concentration of the solutions on the horizontal axis. Draw a line of best fit through the points.

Procedure

Chlorine dioxide:

1. Place 100 mL sample in beaker.
2. Add 2 mL glycine solution
3. Place 5 mL phosphate buffer in a flask
4. Add 5 mL DPD reagent.
5. Add the sample with glycine to flask and mix.
6. Read absorbance at 515 nm on spectrophotometer .Record as **G**
7. Discard solution

Free Available Chlorine and Chloramine:

1. Place 5 mL phosphate buffer in a flask
2. Add 5 mL DPD reagent.
3. Add the 100 mL fresh sample to flask and mix.
4. Read absorbance at 515 nm on spectrophotometer. Record as **A**
5. POUR BACK INTO FLASK
6. Add one very small crystal KI (about 0.5 mg) or .1 mL (2 drops) KI solution. Mix to dissolve.
7. Read absorbance at 515 nm on spectrophotometer. Record as **B**
8. POUR BACK INTO FLASK
9. Add several crystals KI (about 1 g). Mix to dissolve.

10. Wait 2 minutes.
11. Read absorbance at 515 nm on spectrophotometer. Record as **C**
12. POUR BACK INTO FLASK.

Total available chlorine including chlorite:

1. Add 1 mL H₂SO₄ Solution. Mix
2. Wait 2 minutes.
3. Add 5 mL NaHCO₃ solution. Mix
4. Read absorbance at 515 nm on spectrophotometer. Record as **D**
5. Discard solution.

Calculations

Locate the absorbances of the sample on the vertical axis of the calibration curve and read the concentration on the horizontal axis. convert all the absorbances to concentration values.

1. Chlorine dioxide = **5G** (or **1.9G** expressed as ClO₂)
2. Chlorite = **D - (C+4G)**
3. Free available Chlorine = **A-G**
4. Total Chlorine = **C+(4.0G)** (in absence of Chlorite)
5. Total Chlorine = **D** (in presence of Chlorite)
6. Monochloramine = **B-A**
7. Dichloramine = **C-B**

Iron: Phenanthroline Method

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Liquid reagents	Room temperature
	Standards	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Reagents	1 year after opening
	Standards	1 year after receipt
Required Quality Control	Frequency	Required QC
	Quarterly (1/three months)	Construct Graph
	Each test	Spec QC

Method Reference

Standard Methods 18th Edition (3500-Fe, D)

Sample Container/Preservative

A clean plastic or glass screw top container (500 - 1000 mL)

No preservative is necessary if run immediately after collection

Lower the pH to less than 2.0 with concentrated Nitric Acid

Maximum Sample Holding Time

Six months if pH is less than 2.0

General Method Summary

Note: This method is intended only for use by those water plants where iron removal treatment is used.

Iron in water samples and standards must first be reduced to the ferrous state by boiling with hydrochloric acid and hydroxylamine hydrochloride before treatment with 1 - 10 phenanthroline at a pH of 3.2 or 3.3. Zinc and polyphosphate interferences are eliminated by the acid digestion. If a hot plate is to be used for the digestion, extreme caution must be taken to prevent any bumping of the sample. If sample loss occurs due to bumping that sample or standard cannot be used for the analysis. **A fume hood must be used for this type of digestion to exhaust caustic fumes and to contain samples in case of an accident.**

New standard curves must be constructed at least once per three months, in the interim, routine standard curve verification may be used with a minimum of a reagent blank and a midrange standard. A 10% acceptance range is the minimum allowed for calibration curve verification if the standard is outside the acceptance range, then a new standard curve must be run.

It may be advantageous to maintain a special set of glassware to be used for this procedure to reduce the possibilities of iron contamination.

Spectrophotometers with microprocessors may be used to eliminate drawing an absorbance vs concentration graph provided the standard absorbance readings are entered into the meter and are kept on file. Manufacturers' programmed curves may not be used.

On-Site Survey Requirements

1. Each analyst must be able to demonstrate the procedure during the survey. Just prior to the survey a standard curve and a sample should be digested for analysis during the survey. A joint effort may be employed to conserve time.
2. The spectrophotometer will be checked for proper operation. Records of the calibration curves, absorbance readings, standard curve verifications instrument log and related information will be checked.
3. All reagents, standards and solutions used for the test will be checked for proper labeling and dating.
4. Analysts may be required to analyze a performance sample during the survey.

Phenanthroline Procedure

Equipment

1. A spectrophotometer which meets chemical certification minimum specifications, (contact the Ohio EPA/DES Laboratory Certification Section for details).
2. A hot plate large enough to hold all the standards and samples at the same time for digestion.
3. Heating blocks may be used as long as reagent proportions are not changed.
4. A fume hood for use with the hot plate digestion.
5. Autoclaves may not be used for digestion.
6. An analytical balance readable to 0.0001g must be used to measure primary standard grade reagents. The balance must be covered by an annual service contract and placed on a stone balance table or stone slab.

Glassware

1. Adequate quantity of glassware preferably used exclusively for the iron test to prevent contamination.
2. Class A glassware used for standard preparation and reagent additions.
3. All glassware must be acid rinsed using dilute hydrochloric acid and rinsed well with laboratory pure water to remove any iron oxide deposits.

Reagents

1. Stock Standard - Use a commercial 100 mg/L iron standard. Store in the refrigerator for up to one year after

opening.

- Intermediate Standard - Dilute 10.0 mL of stock standard to 1000 mL in a liter volumetric - this will produce a 1.0 mg/L standard.

Working Standards			
Standard Concentration mg/L	Amount of 1.0 mg/L Standard	Amount of Laboratory pure water	Final Volume
Blank	0.0 mL	100 mL	100 mL
0.2	20.0 mL	80 mL	100 mL
0.3	30.0 mL	70 mL	100 mL
0.4	40.0 mL	60 mL	100 mL
0.5	50.0 mL	50 mL	100 mL

Carefully add the specified amounts of 1.0 mg/L standard to labeled erlenmeyer flasks or beakers. Use a graduated cylinder to add the proper amounts of laboratory pure water to each flask.

- Concentrated Hydrochloric Acid
- Hydroxylamine Hydrochloride - Prepared as in Standard Methods or use a commercially prepared solution.
Ammonium Acetate Buffer Solution - Prepared as in Standard Methods.
- Phenanthroline Color Reagent - Prepared as in Standard Methods or use a commercially prepared reagent.

Required Quality Control

Frequency

Quality control tests must be run with the results recorded at least once every three months.

Procedure

- Measure 100 mL of sample into an erlenmeyer flask or beaker. Use a class "A" volumetric pipet to add each of the following reagents).
- Add 2.0 mL of concentrated HCL to this flask and to each of the standard flasks.
- Add 2.0 mL of hydroxylamine hydrochloride to each of the samples and standards.
- Evaporate the samples and standards to a volume of 15 - 20 mL on a hot plate. The hot plate must be large enough to evaporate all samples and standards simultaneously. A fume hood is required for this procedure.
- Remove the flask from the hot plate and cool. Quantitatively transfer the samples and standards to 100 mL Class A volumetric flasks.

6. Add 10.0 mL of Ammonium Acetate buffer to each flask. Place them in a pan of cold tap water.
7. Add 2.0 mL of phenanthroline color reagent to each flask and dilute to a final volume of 100 mL with laboratory pure water. Allow 15 minutes for color development.
8. Read the absorbance of each standard and sample at 510 nanometers using the largest spectrophotometer cell possible.
9. Construct a standard curve plotting absorbance vs. concentration. Determine sample concentration from the standard curve.

Required Documentation

1. Records must be properly identified and labeled with date and analyst's initials and kept on file.
2. Calibration curves displaying concentration and absorbance readings must be generated at least once per three months.
3. Concentrations and absorbance reading of the blanks and standards for all curve verifications.
4. Expiration dates of the stock standards.
5. Reagent preparation log with reagent, name, date prepared and analyst's initials.
6. Standard concentrations, absorbance readings and correlation coefficients. Graph or print-outs associated with the use of a microprocessor spectrophotometer or computer for calculation purposes.
7. Instrument and maintenance log book for spectrophotometer.
8. Quality control results if QA samples are used for accuracy and precision.

Manganese: Persulfate Method

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Liquid reagents	Room temperature
	Standards	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Reagents	1 year after opening
	Standards	1 year after receipt
Required Quality Control	Frequency	Required QC
	Quarterly	Construct Graph
	Each test	Spec QC

Method Reference

Standard Methods 18th Edition (3500 - Mn, D)

Sample Container/Preservative

A clean plastic or glass screw top container (500 - 1000 mL)
No preservative is necessary if run immediately after collection.
Lower pH to less than 2.0 with concentrated nitric acid.

Maximum Sample Holding Time

Six months if pH is less than 2.0

General Method Summary

Note: This method is intended only for use by those water plants where manganese removal treatment is used.

The persulfate method is the only colorimetric method which is acceptable for total manganese determination. If a hot plate is to be used for the digestion, extreme caution must be taken to prevent any bumping of the sample. If sample loss occurs due to bumping that sample or standard cannot be used for the analysis. A fume hood must be used for this type of digestion to exhaust caustic fumes and to contain samples in case of an accident. A larger initial sample may also be used to concentrate the sample and increase absorbance readings. Spectrophotometers with microprocessors may be used to eliminate drawing and absorbance vs concentration graph provided the standard absorbance readings are entered into the meter and are kept on file. Manufacturers programmed curves may not be used.

On-Site Survey Requirements

1. Each analyst must be able to demonstrate the procedure during the survey. A standard curve and a sample should be

digested just prior to the survey for analysis during the survey. A joint effort may be employed to conserve time. The spectrophotometer will be checked for proper operation.

2. Records of the calibration curves, absorbance readings, standard curve verifications, instrument log and related information will be checked.
3. All reagents, standards and solutions used for the test will be checked for proper labeling and dating.
4. Analyst may be required to analyze a performance sample during the survey.

Persulfate Method: Procedure

Equipment

1. A spectrophotometer which meets chemical certification minimum specifications.
2. A hot plate large enough to hold all the standards and samples at the same time for digestion.
3. A fume hood for use with the hot plate digestion.
4. Autoclaves must not be used for digestion.
5. An analytical balance readable to 0.0001g must be used to measure primary standard grade reagents. The balance must be covered by an annual service contract and placed on a stone balance table or stone slab.

Glassware

1. Adequate quantity of glassware preferably used exclusively for the manganese test to prevent contamination.
2. Heating blocks may be used as long as reagent proportions are not changed.
3. Class A glassware used for standard preparation and reagent additions.
4. All glassware must be acid rinsed using dilute hydrochloric acid and rinsed well with laboratory pure water.

Reagents

1. Stock Standard - Use a commercially prepared 1000 mg/L standard or dissolve 0.3076 grams manganous sulfate, monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) in a mixture of 5.0 mL of H_2SO_4 and 100 mL of laboratory pure water and dilute to 1 liter - this is a 100 mg/L stock.
2. Intermediate Standard - Using 1000 mg/Mn standard dilute 10 mL of stock to 100 mL Class A volumetric flask - this is a 100 mg/L standard. Using the lab prepared 100 mg/L stock - dilute 10 mL of stock to 1000 mL in a liter volumetric to produce a 1.0 mg/L intermediate standard.

Working Standards

Standard Concentration mg/L	Amount of 1.0 mg/L Intermediate Standard	Amount of Laboratory pure water	Final Volume
Blank	00.0 mL	150.0 mL	150.0 mL
0.05 mL	07.5 mL	142.5 mL	150.0 mL
0.10 mL	15.0 mL	135.0 mL	150.0 mL
0.15 mL	22.5 mL	127.5 mL	150.0 mL
0.20 mL	30.0 mL	120.0 mL	150.0 mL
0.30 mL	45.0 mL	105.0 mL	150.0 mL

Using a buret, carefully add the specified amounts of 1.0 mg/L intermediate to labeled erlenmeyer flasks or beakers. Use a graduated cylinder to add the proper amounts of laboratory pure water to the erlemeyers.

Special Preventive Reagent - Prepare as in Standard Methods or use a commercially prepared reagent for manganese.

Reagent grade Ammonium Persulfate - Commercially available.

Required Quality Control

Quality Control Frequency

New standard curves must be constructed at least once per three months. In the interim, routine standard curve verifications may be used with a minimum of a reagent blank and a midrange standard. A 10% acceptance range is the maximum allowed for calibration curve verification. If the verification standard is outside the acceptance range, then a new standard curve must be run. It may conserve time to construct a new standard curve each time the test is run since the absorbance readings are generally very low and the verification standard acceptance criteria may be difficult to maintain. To increase absorbance readings, use the largest spectrophotometer sample cell available. Some spectrophotometers are designed to accept 5.0 cm and 10.0 cm sample cells.

Quality Control Procedure

1. Using a class "A" volumetric pipet measure 150 mL sample into an erlenmeyer flask.
2. Add 5.0 mL of Special Reagent to this flask and to each of the standard flasks.
3. Evaporate the samples and standards to a volume of about 75 mL on a hot plate. The hot plate must be large enough to evaporate all samples and standards simultaneously. A fume hood is required for this procedure.
4. Remove the samples and standards from the hot plate and add 1 gram of ammonium persulfate to each. Bring the flasks to a boil for one minute, remove from heat and cool on the bench top for one minute.
5. Cool the flasks to room temperature rapidly by setting them in a pan of cold tap water.
6. Quantitatively transfer the samples and standards to Class A 100 mL volumetric flasks and dilute to volume.
7. Read the absorbance of each standard and sample at 525 nanometers using the largest cell possible.
8. Construct a standard curve plotting absorbance vs. concentration. Determine sample concentration from the standard curve.

Required Documentation

1. Records must be properly identified and labeled with date and analysts initials, and kept on file.
2. Calibration curves must be generated at least once per three months, displaying concentration and absorbance readings.
3. Concentrations and absorbance reading of the blanks and standards for all curve verifications.
4. Expiration dates of the stock standards.
5. Reagent preparation log with reagent, name, date prepared and analyst's initials.
6. Standard concentrations, absorbance readings, correlation coefficients. Graph or printouts associated with the use of a microprocessor spectrophotometer or computer for calculation purposes.
7. Instrument and maintenance log book for spectrophotometer.
8. Quality control results if QC samples are used for accuracy and precision.

Copper: Bathocuprine Method

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Liquid reagents	Room temperature
	Standards	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Reagents	1 year after opening
	Standards	1 year after receipt
Required Quality Control	Frequency	Required QC
	Quarterly	Construct Graph
	Each test	Spec QC

Method Reference

Standard Methods 18th Edition (3500 - Cu, E)

Sample Container/Preservative

A clean plastic or glass screw top container (500 - 1000 mL)

No preservative is necessary if run immediately after collection. Lower pH to less than 2.0 with hydrochloric acid.

Maximum Sample Holding Time

Six months if pH is less than 2.0

General Method Summary

Note: 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 bathocuprine reagent in the pH buffered reaction solution. Optimum color differences in potable water should not be present in sufficient concentrations to be a problem. Total residual chlorine levels of 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. Reagents must be added using class "A" volumetric pipets to insure reproducibility and accurate sample volume. It may be advantageous to maintain a special set of glassware to be used for this procedure to reduce the possibilities of contamination. Spectrophotometers with microprocessors may be used to eliminate drawing an absorbance vs concentration graph provided the standard absorbance readings are entered into the meter and are kept on file. Manufacturers' programmed curves may not be used.

On-Site Survey Requirements

1. Each analyst must be able to demonstrate the procedure during the survey. A joint effort may be employed to conserve time.
2. The spectrophotometer will be checked for proper operation.
3. Records of the calibration curves, absorbance readings, standard curve verifications instrument log and related information will be checked.
4. All reagents, standards and solutions used for the test will be checked for proper labeling and dating.
5. Analysts may be required to analyze a performance sample during the survey.

Equipment

1. A spectrophotometer which meets chemical certification minimum specifications.
2. Adequate class A volumetric glassware to add reagents and prepare standards.
3. Glassware should be rinsed with dilute hydrochloric acid and thoroughly rinsed with laboratory pure water before use.

Reagents

Stock standards and reagents are commercially available or can be prepared as per Standard Methods.

Required Quality Control/Frequency

New standard curves must be constructed at least once per three months, in the interim, routine standard curve verifications may be used with a minimum of one reagent blank and a midrange standard. A 10% acceptance range is the maximum allowed for calibration curve verification. If the verification standard is outside the acceptable limits, then a new standard curve must be run.

Required Documentation

1. Records must be properly identified and labeled with date and analysts initials, and kept on file for 12 years.
2. Calibration curves must be generated at least once per three months displaying concentrations and absorbance readings.
3. Concentrations and absorbance readings of the blanks and standards for all curve verifications.
4. Expiration dates of the stock standards and reagent preparation log with reagent name, date prepared and analyst's initials.
5. Standard concentrations, absorbance readings and correlation coefficients, graph or print-outs associated with the use of a microprocessor spectrophotometer or computer for calculation purposes.
6. Instrument and maintenance log book for spectrophotometer.
7. Quality control results if QC samples are used for accuracy and precision

Total Phosphorus: Ascorbic Acid/ Colorimetric Method

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Liquid reagents	Room temperature
	Standards	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Reagents	1 year after opening
	Standards	1 year after receipt
Required Quality Control	Frequency	Required QC
	Quarterly	Construct Graph
	Each test	Spec QC

Method Reference

Standard Methods 18th Edition ((4500 - P), B, D, E, F)

Equipment

1. A spectrophotometer which meets chemical certification minimum specifications.
2. A hot plate large enough to hold all the standards and samples at the same time for digestion.
3. A fume hood for use with the hot plate digestion.
4. An autoclave for digestion (optional, would replace the hot plate and fume hood). Please refer to Standard Methods for autoclaving methodology.
5. An analytical balance readable to 0.0001 g. and must be situated on a stone balance table or slab. Balance service contract necessary if used for preparation of standard solutions.

Glassware

1. Adequate quantity of glassware used exclusively for phosphate analysis.
2. Class A glassware for standard preparations.
3. Heating blocks may be used as long as reagent proportions are not changed.
4. You must not use commercial detergents containing phosphate for cleaning. Acid rinse all glassware using dilute hydrochloric acid and rinse well with laboratory pure water.

5. All glassware for this test must be used exclusively for phosphate determination in order to prevent contamination.

Sample Container/Preservative

1. A clean, acid rinsed, plastic or glass screw top container (250 - 1000 mL)
2. No preservative is necessary if analyzed within 24 hours
3. Lower pH to less than 2.0 using concentrated sulfuric acid

Maximum Sample Holding Time

24 hours if unpreserved

28 days, acidified with sulfuric acid to pH less than 2.0, cool to 2-10 ° C and stored in a glass container.

General Method Summary

For the determination of phosphate, total phosphorous, a preliminary digestion step is necessary. Both standards and samples must be carried through the entire digestion procedure. The use of the persulfate digestion procedure has generally been found to be adequate for most samples encountered by water treatment facilities. If a hot plate is to be 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. A fume hood must be used for this type of digestion to exhaust caustic fumes and to contain samples in case of an accident. The ascorbic acid method and the stannous chloride method of colorimetry work equally well for phosphate levels found in potable water.

A separate set of glassware, including pipets, must be maintained specifically for phosphate analysis due to the potential for contamination from the laboratory environment.

Spectrophotometers with microprocessors may be used to eliminate drawing an absorbance vs concentration graph provided the standard absorbance readings are entered into the meter and are kept on file. Manufacturer's preprogrammed curves may not be used.

On-Site Survey Requirements

1. Each analyst must be able to demonstrate the procedure during the survey. Just prior to the survey a standard curve and a sample should be digested for analysis during the survey. A joint effort may be employed to conserve time.
2. The spectrophotometer will be checked for proper operation.
3. Records of the calibration curves, absorbance readings, standard curve verifications, instrument log and related information will be checked.
4. All reagents, standards and solutions used for the test will be checked for proper labeling and dating.
5. Analysts may be required to analyze a performance sample during the survey.

Procedure

Reagents

Prepare as per Standard Methods 18th Edition.

Standard

Stock Standard, Commercially available or prepared as per Standard Methods page 4-113, Weigh 0.2195g of Anhydrous KH_2PO_4 , dilute to 1.0 liter with laboratory pure water. This is a 50.0 mg/L stock.

Intermediate Standard - 10 mL of stock diluted to 1 liter will give a 0.5 mg/L intermediate. Use only Class "A" volumetric glassware.

Working Standards

Standard mg/L	Intermediate mL	Laboratory pure water mL
Blank	0.0	50.0
0.03	3.0	47.0
0.05	5.0	45.0
0.10	10.0	40.0
0.20	20.0	30.0
0.30	30.0	20.0
0.40	40.0	10.0
0.50	50.0	0.0

Digestion

1. Add phenolphthalein solution to the sample. If it is red, add H_2SO_4 solution dropwise until it becomes clear.
2. Samples and standards - add 1 mL H_2SO_4 solution and 0.4 g ammonium persulfate for each 50 mL of sample.
3. Boil gently on a hot plate for 30 - 40 minutes or until a 10 mL volume is reached.
4. Dilute to about 30 mL.
5. Add 1 drop phenolphthalein solution - add NaOH solution dropwise until a faint pink color develops.

Colorimetry - Ascorbic Acid Method

1. Quantitatively transfer samples and standards to 100 mL volumetric flasks.
2. Add 8 mL of combined reagent to each and mix.
3. Bring each to 100 mL with laboratory pure water and mix.

- After 10 minutes, read absorbance values on spectrophotometer at 880 nm.

EXAMPLE: 1 inch cell used on Spectronic 100

Standard (mg/L)	Absorbance	Absorbance Blank
Blank	0.34	
0.03	0.54	0.020
0.05	0.067	0.033
0.10	0.102	0.068
0.20	0.177	0.143
0.30	0.247	0.213
0.40	0.322	0.288
0.50	0.398	0.364
QC Sample 0.31mg/L	0.248	0.214

Required Quality Control/Frequency

New standard curves must be constructed at least once per three months. In the interim, routine standard curve verifications may be used with a minimum of one reagent blank and a midrange standard. A $\pm 10\%$ acceptance range is the maximum allowed for calibration curve verification. If the verification standard is outside the acceptable limits then a new standard curve must be run.

Required Documentation

- Records must be properly identified and labeled with date and analysts initials, and kept on file for 10 years.
- Calibration curves displaying concentration and absorbance readings must be generated at least once per three months.
- Concentrations and absorbance reading of the blanks and standards for all curve verifications.
- Expiration dates of the stock standards
- Reagent preparation log with reagent, name, date prepared and analyst's initials.
- Standard concentrations, absorbance readings and correlation coefficients. Graph or print-outs associated with the use of a microprocessor spectrophotometer or computer for calculation purposes.
- Instrument and maintenance log book for spectrophotometer.
- Quality control results for QC samples that are used for accuracy and precision.

Nitrate: Cadmium Reduction Method

<i>Quick Reference</i>		
	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Liquid reagents	Room temperature
	Standards	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Reagents	1 year after opening
	Standards	1 year after receipt
Required Quality Control	Frequency	Required QC
	Quarterly	Construct Graph
	Each test	Spec QC

Method Reference

Standard Methods 18th Edition (4500 - NO₃, E, F)

Cadmium Reduction General Method Summary

The cadmium reduction method is most accurate in the less than 1.0 mg/L concentration range. Sample concentrations greater than 1.0 mg/L must be diluted to less than 1.0 mg/L for this procedure. Sample must be within the pH 5 to 9 range in order for the buffer solution to be effective. Samples, preserved or unpreserved, should be neutralized to within this range with 1N Ammonium Hydroxide or Hydrochloric Acid. Excessive amounts of turbidity can clog the reduction column and reduce column efficiency. If the sample is visibly turbid, filter through a 0.45 micrometer membrane filter. Since nitrate-nitrogen is found in a soluble state, prefiltering the sample will not effect the results. Any nitrite present in the sample will cause a positive bias. Compensate for this by analyzing a portion of the sample without passing it through the reduction column and subtracting the result from the nitrate result of the reduced sample.

For measuring concentrations less than 0.10 mg/L, it is recommended to use sample cell with a path length of 2.5 cm or greater to increase absorbance readings. Spectrophotometers with microprocessors may be used to eliminate drawing an absorbance vs concentration graph provided the standard absorbance readings are entered into the meter and kept on file. Manufacturers' preprogrammed curves may not be used.

On-Site Survey Requirements

1. Each analyst must be able to demonstrate the procedure during the survey. Standards may be run through the column on the day of the survey prior to the survey officers arrival. A joint effort may be employed to conserve time.
2. The spectrophotometer will be checked for proper operation.
3. Records of the calibration curves, absorbance readings, nitrate vs nitrite efficiencies, curve verifications, instrument log and related information will be checked.

4. All reagents, standards and solutions used for the test will be checked for proper labeling and dating.
5. Analysts will be required to analyze performance samples during the survey.

Equipment

1. A spectrophotometer which meets minimum specifications.
2. A pH meter and related pH test equipment.
3. A cadmium reduction column, either commercially available or prepared from a 100 mL volumetric pipet according to specifications in figure 1 of this procedure.
4. An analytical balance readable to 0.0001g must be used to measure primary standard grade reagents. The balance must be covered by an annual service contract and placed on a stone balance table or stone slab.

Glassware

1. Adequate quantity of class A volumetric glassware to prepare standards and reagents.
2. Glassware should be cleaned with laboratory detergent, tap rinsed, acid rinsed with 20% HCl and then laboratory pure water rinsed before use. This glassware should be reserved for Nitrate use only.

Sample Container/Preservation

Collect in a glass or plastic container (250 - 1000 mL)

Concentrated H₂SO₄ to obtain a pH of less than 2 and refrigerate at 2-10 °C. (2.0 mL of concentrated H₂SO₄ per liter should produce the proper pH conditions). If the sample is preserved, the sample must be checked for proper preservation prior to 48 hours after collection. The pH MUST be <2.0 if preserved.

Maximum Sample Holding Time

28 days - Refrigerated at 2-10 °C, preserved with 2.0 mL H₂SO₄ per liter.

Reagents

1. Potassium Nitrate Stock solution (100 milligrams per liter) - Commercially available or prepared as follows: Dissolve 0.7218 grams of anhydrous potassium nitrate (KNO₃) in laboratory pure water and dilute to 1.0 liter in a volumetric flask. This solution is stable for 6 months if preserved with 2.0 mL of chloroform per liter and kept under refrigeration when not in use.
2. Nitrate-Nitrogen, Intermediate solution - (10.0 mg/L as N): Dilute 10.0 mL of Stock 100 mg/L solution to 100 mL in a volumetric flask. Standard and intermediate solutions should be prepared fresh daily and discarded after their initial use.
3. Nitrate-Nitrogen, Standard solution - (1.0 mg/L as N): Dilute 10.0 mL of the 10.0 mg/L intermediate solution to 100 mL in a volumetric flask.
4. Nitrate-Nitrogen, Standard solution - (0.5 mg/L as N): Dilute 5.0 mL of the 10.0 mg/L intermediate solution to 100 mL in a volumetric flask.

5. Nitrate-Nitrogen, Standard solution - (0.2 mg/L as N): Dilute 2.0 mL of the 10.0 mg/L intermediate solution to 100 mL in a volumetric flask.
6. Cadmium, granulated 40-0 mesh Commercially available
7. Copper Sulfate - (2% W/v): Dissolve 2 grams of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in laboratory pure water, dilute to 100 mL in a volumetric flask.
8. Full Strength Ammonium Chloride/EDTA: Dissolve 13 grams of Ammonium Chloride (NH_4Cl) and 1.7 grams disodium ethylene- diamine-tetracetate ($\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2\text{Na}_2\text{H}_2\text{O}$) in 900 mL of laboratory pure water. Adjust the pH to 8.5-8.6 with concentrated Ammonium Hydroxide (NH_4OH) using a pH meter. Back adjust with HCl if 8.6 is overshot. Dilute the pH adjusted reagent to 1.0 liter in a volumetric flask.
9. Dilute Ammonium Chloride/EDTA: Combine 300 mL of the "full strength" Ammonium Chloride/EDTA reagent with 200 mL laboratory pure water. Mix to obtain 500 mL of "dilute NH_4Cl - EDTA" solution.
10. Color Reagent: 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) - ethylene-diamine dihydrochloride ($1\text{-C}_{10}\text{H}_7\text{NHCH}_2\text{CH}_2\text{NH}_2\text{HCl}$) in a mixture of 10 mL concentrate Phosphoric acid (H_3PO_4 , 85%) and 80 mL laboratory pure water. Dilute to 100 mL in a volumetric flask. Keep in a glass container, refrigerate when not in use and discard after 1 month old.
11. Potassium Nitrite Stock solution - (100 mg/L as N): Commercially available or prepared as follows: Dissolve 0.607 grams potassium nitrite (KNO_2) in laboratory pure water and dilute to 1.0 liter in a volumetric flask. Stable for 3 months if preserved with 2.0 mL chloroform per liter and kept under refrigeration when not in use.
12. Sodium Nitrite Stock Solution - (100 mg/L as N): Commercially available or prepared as follows : Dissolve 0.4929 grams of Sodium Nitrite (NaNO_2) in laboratory pure water. Dilute to 1.0 liter in a volumetric flask. Stable for 3 months if preserved with 2.0 mL chloroform per liter and kept under refrigeration when not in use.
13. Nitrate-Nitrogen Standard Solution - (1.00 mg/L): Dilute 5.0 mL of stock 100 mg/L solution to 500 mL in a volumetric flask. This solution should be prepared fresh daily.
14. Activation Standard: Combine 25 mL of the mg/L NO_3 and 75 mL of the full strength Ammonium Chloride - EDTA and mix well.

Procedure: Reduction Column Preparation/Regeneration

1. Clean about 25 grams of Cadmium granules with some dilute (10-20%) HCl by swirling in an erlenmeyer flask or large beaker. Rinse the acid cleaned cadmium with laboratory pure water to remove all trace of the acid, again by swirling in the flask and pouring off the liquid portion. Add some fresh laboratory pure water to the erlenmeyer and add sufficient 2% Copper Sulfate to produce a pale sky blue color in the liquid portion covering the cadmium. Swirl until a fine brown precipitate is formed. If blue color fades and no precipitate is formed, carefully decant the liquid portion and repeat with another portion of laboratory pure water and copper sulfate.
2. Rinse the excess copper (the fine, brown precipitate) from the copperized cadmium with at least 10 portions of laboratory pure water. The metallic appearance of the cadmium should be gone, replaced by a dark gray to black appearance. The dark color may be more difficult to achieve with used cadmium.
3. Fill the empty column with laboratory pure water and clamp off the rubber hose. While doing so water should fill the entire stem of the column. Pour sufficient cadmium granules into the column with laboratory pure water.

Remove clamp and drain off most of the laboratory pure water. If the cadmium flows out, use a glass wool plug and repack the column. The Cadmium must remain wet at all times. If an air bubble is introduced into the stem, the column must be repacked.

4. When the column is packed, check the flow rate with laboratory pure water and a graduated cylinder. Adjust the rate to between 7 and 10 mL per minute by partially pinching the hose with an adjustable clamp.
5. Remove any excess laboratory pure water from the column and rinse it by passing 200 mL dilute $\text{NH}_4\text{Cl-EDTA}$ through it. Cut off the flow with a hose pinch, always leaving a small amount of liquid in the column so that the cadmium remains wet.
6. Activate the column by passing 100 mL of the Activation Standard through the column. Discard the eluate.
7. Wash the column with 50 mL of "dilute" $\text{NH}_4\text{Cl-EDTA}$, leaving the column "wet", as before, Stop the flow. The column is now ready for use in the analysis.

NOTE: The Cadmium reduction column should be regenerated periodically. How often will depend on the nature and amount of nitrate in your sample. A freshly regenerated column is less affected by sample carry-over than a 'used' column. If in doubt, regenerate. Store a used column under laboratory pure water when not in use. This avoids the formation of a white precipitate which results from prolonged storage under $\text{NH}_4\text{Cl-EDTA}$ solution. Wash the column with "Dilute" $\text{NH}_4\text{Cl-EDTA}$ after storage under laboratory pure water, as in "8" above.

Each time the test is run the column should be subjected to a Nitrite-versus-Nitrate efficiency test; the reduction column should be functioning at or near 100% efficiency. Reduced-Nitrate results should agree with Nitrite results to within plus-or-minus 10% for the column to be considered acceptable for use. The nitrite standard should be run through the column.

Procedure: Initial Preparation of Standard Curve

A standard curve constructed by analyzing standards spanning the entire range of expected concentration must be prepared. A standard curve for the range of 0.2 to 1.0 mg/L is the usual starting point. If sample concentrations turn out to be lower, a larger path length cell may be used; if sample concentrations turn out to be higher, they can be volumetrically diluted into the working range of the curve.

Prepare the Nitrate-Nitrogen, Intermediate solution - 10.0 mg/L as N.

Prepare the working standards as follows:

- 1) mg/L Nitrate: Dilute 10 mL of the 10.0 mg/L intermediate solution to 100 mL with laboratory pure water in a volumetric flask.
- 2) 0.5 mg/L Nitrate: Dilute 5 mL of the 10.0 mg/L intermediate solution to 100 mL with laboratory pure water in a volumetric flask.
- 3) 0.2 mg/L Nitrate: Dilute 2 mL of the 10.0 mg/L intermediate solution to 100 mL with laboratory pure water in a volumetric flask.
- 4) All samples and standards must be buffered before passing them through the column as in the following manner:
- 5) Blank: measure 25 mL laboratory pure water into a 100 mL volumetric flask.

- 6) 0.2 mg/L Nitrate: measure 25 mL of 0.2 mg/L Nitrate into a 100 mL volumetric.
- 7) 0.5 mg/L Nitrate: measure 25 mL of 0.5 mg/L Nitrate into a 100 mL volumetric.
- 8) mg/L Nitrate: measure 25 mL of 1.0 mg/L Nitrate into a 100 mL volumetric.
- 9) mg/L Nitrite: measure 25 mL of 1.0 mg/L Nitrite into a 100 mL volumetric.
- 10) Unknown or Sample: measure 25 mL of Unknown into a 100 mL volumetric.
- 11) NOTE: Dilute each to the mark with full strength NH₄Cl-EDTA
- 12) Samples exceeding 1.0 mg/L must be diluted into the working range of the column (0.2 -1.0 mg/L Nitrate). Do this by diluting 10 mL of sample to 100 mL with laboratory pure water in a volumetric flask. Buffer this solution as in step #3 above. The final value will then be multiplied by a factor of ten.
- 13) Prepare the activated column for use by dripping approximately 30 mL of Dilute Ammonium Chloride - EDTA buffer through it. NOTE: You may skip this step if the column has been activated recently.
- 14) Drip each of the standards and samples through the reduction column one at a time starting with the blank and ending with the samples and standards having the highest concentration. Use the following procedure:
- 15) Drain the column until only a few milliliters of solution remain
- 16) Pour in approximately 30 mL of the prepared standard or samples
- 17) Allow the column to drain until only a few milliliters of solution remain - discard this portion
- 18) Pour in the remaining 70 mL of standard or sample all at once and collect the effluent from the column in the same volumetric flask. Cease collection when the amount left in the column is only a few milliliters
- 19) Drip approximately 30 mL of dilute Ammonium Chloride - EDTA through the column to rinse it between samples or standards - discard the column effluent
- 20) Stop column flow with a pinch-clamp if necessary and proceed with the next sample or standard, repeating instruction "a"
- 21) As each of the samples and standards are passed through the column in turn, draw off a 25 mL aliquot and place it in a labeled 50 mL screw-cap centrifuge tube. A single graduated cylinder may be used to do this provided that it is rinsed with laboratory pure water and several 5 mL aliquots of the standard or sample prior to the actual measurement. This should eliminate contamination. "Reduced" samples and standards should not be allowed to stand for longer than 15 minutes prior to the addition of the color reagent in step 6.
- 22) Add 1.0 mL of the Color Reagent to each of the centrifuge tubes, 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.

Alternate Procedure

1. After each of the sample and standards are passed through the column, in turn, draw off a 50 mL aliquot of each and place it in a labeled erlenmeyer flask or beaker. "Reduced" samples and standards should not be allowed to stand for longer than 15 minutes prior to the addition of the color reagent in step 6.

2. Add 2.0 mL of color reagent to each flask and swirl to 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 and standard with a spectrophotometer set at a wavelength of 540 nanometers. Matched cuvettes or a single cuvette which is prerinsed with a small amount of sample between measurements may be used. Follow the instructions on the data sheet, then construct a standard curve on a sheet of rectilinear graph paper by plotting absorbance-versus-concentration.

Sample Source Check

Add 25 mL of sample to a 100 mL volumetric flask, fill to the mark with FULL-STRENGTH Ammonium Chloride - EDTA and mix. Add 2.0 mL of color reagent to a 50 mL aliquot of this 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.

Required Documentation

1. Records must be properly identified and labeled with date and analysts initials and kept on file for 10 years.
2. Calibration curves must be generated at least once per three months.
3. Concentrations and absorbance reading of the blanks and standards for all curve verifications.
4. Expiration dates of the stock nitrate and nitrite standards.
5. Reagent preparation log with reagent, names, date prepared and analyst's initials.
6. Standard concentrations, absorbance readings, correlation coefficients, graph or print-outs associated with the use of a microprocessor spectrophotometer or computer for calculation purposes.
7. Instrument and maintenance log book for spectrophotometer
8. Quality control results if QA samples are used for accuracy and precision.

Nitrate/Nitrite Data Sheet

Procedural Notes

- ▲ Allow spectrophotometer to warm-up for 1 hour, set wavelength to 540 nanometers.
- ▲ Set the absorbance to zero (0.000) with a laboratory pure water blank.
- ▲ Read and record the absorbance of the reagent blank and each of the samples and standards in the first column. Subtract reagent blank result from each absorbance result and record in the second column.
- ▲ Carefully prerinse the cuvettes with a few small aliquots of the substance to be measured prior to the final filling operation; wipe any excess liquid from the outside of the cuvette prior to insertion into the instrument.

Sample/Standard	Absorbance Reading	Absorbance Minus Blank	Concentration/Notes
Dist/Deionized Water	0.0		
Reagent Blank		0.0	
0.2mg/L Standard			
0.6mg/L Standard			
1.0mg/L Standard			
Sample #1			
Sample #2			
1.0mg/L Nitrite			
Sample Source			

Date _____ Analyst _____ Std. Exp Date _____

Wavelength _____ Cuvette pathlength _____

Column Efficiency Check

$$\frac{\text{Mg/L NO}_3}{\text{Mg/L NO}_2} \times 100 = \text{_____}\%$$

The % Must be 90-110%

Nitrate: Electrode Method

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Liquid reagents	Room temperature
	Standards	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Reagents	See procedure
	Diluted Standards	See procedure
	Standards	1 year after receipt
Required Quality Control	Frequency	Required QC
	Quarterly	Construct Graph

Method Reference

ODH Method, (CCF-6A); Standard Methods 18th Edition (4500 - NO₃, D)

Sample Container/Preservation

Collect in a glass or plastic container (250 - 1000 mL)

Concentrated H₂SO₄ to obtain a pH of less than 2 and refrigerate at 2-10 °C. (2.0 mL of concentrated H₂SO₄ per liter should produce the proper pH conditions.)

Maximum Sample Holding Time

28 days - Refrigerated at 2-10 °C, preserved with 2.0 mL H₂SO₄ per liter.

Common Interferences

Temperature: standards and samples should be analyzed at the same temperature (approximately 20 - 25° C).

pH, Carbonate & Bicarbonate: standards and samples should be analyzed at the same pH (between 3.5 and 4.0). Necessary adjustments should be made with 1.0 or 0.1 N H₂SO₄ or NaOH. Acidifying the samples converts the carbonate and bicarbonate ions to carbon dioxide.

Chloride: chloride concentrations of greater than 20 times the sampled NO₃ concentrate may cause a significant bias (10%) in the electrode method. If chloride is suspected, test prior to each test series, otherwise test for chloride seasonally. Silver Sulfate Solution (add 10 mL per 50 mL of sample) should be added to all standards and samples when samples have significantly high chloride concentrations. See preparation procedures under "Reagents" above. You may forego testing for chloride and add silver sulfate to all samples prior to testing.

Specific Ion General Method Summary

The Specific Ion Electrode method for nitrate determination works very 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 to reduce error in this area. The method is pH and temperature dependent. The pH of the standards and samples must be very consistent after acidifying. Temperature bias can be eliminated by allowing all standards reagents and samples to stabilize at room temperature before starting the procedure.

During procedural practice runs, the necessity of interference suppressor use must be determined by individual analyses of a split sample from each source using interference suppressor added to all standards and sample compared to an analysis not using interference suppressor with all standards and sample. Split sample analysis should agree within 10% for each source to perform analysis without the use of interference suppressor. Documentation for verification is necessary.

A full range curve (0.2 to 10.0 mg/L) must be graphed initially and each time a new sensing module is put into service to verify probe sensitivity and non-linear concentration range.

Thorough rinsing of the probes with laboratory pure water and blotting dry between each standard and sample is imperative to prevent cross contamination. Calibration slope should be checked to verify acceptable sensitivity (between 50-60 mV change/decade of concentration) before continuing with the sample analysis. Record the slope before each use. Both the sensing probe and reference probe can be stored dry if the fill solutions in the reference probe are drained. Increased sensitivity may be obtained by filling the reference probe with fresh solutions before each run.

On-Site Survey Requirements

1. Instrument and electrode performance will be checked for proper functioning.
2. Each analyst must be able to demonstrate the procedure during the survey. A joint effort may be employed to conserve time.
3. Calibration curves, sensitivity curves for new modules, split sample analysis for interference suppressor checks and calibration slope records will be checked.
4. All reagents, standards and solutions used for the test will be checked for proper labeling and dating.
5. Analysts will be required to analyze performance samples during the survey.

Major Equipment

1. A pH meter with expanded millivolt scale or direct reading digital specific ion meter with microprocessor. Millivolt scales must be readable and accurate to 0.1 millivolts.
2. A magnetic stirring device and an adequate number of TFE coated stirring bars.
3. A nitrate ion selective electrode and a double junction reference electrode. (Fill outer chamber with 0.04M ammonium sulfate, ISA).
4. An analytical balance readable to 0.0001g must be used to measure primary standard grade reagents. The balance must be covered by an annual service contract and placed on a stone balance table or stone slab.

Glassware

1. Class A volumetric glassware should be used to prepare all standards and reagents. Glassware should be cleaned with laboratory detergent, tap rinsed, acid rinsed with 20% HCl and then laboratory pure water rinsed before use.
2. Disposable plastic beakers may be used to analyze samples.

Reagents

Potassium Nitrate Stock Solution (100 milligrams per liter as N), commercially available or prepared as follows: dissolve 0.7218 grams of desiccated anhydrous potassium nitrate (KNO_3) in laboratory pure water and dilute to 1.0 liter in a Class A volumetric flask. This solution is stable for 6 months if preserved with 1.0 mL of chloroform per liter and kept under refrigeration when not in use.

Working Standards, Nitrate Nitrogen (use only Class A volumetric glassware for all dilutions). Standard dilutions must be prepared fresh before each test.

(20.0 mg/L as N): dilute 20 mL of 100 mg/L stock to 100 mL.

(10.0 mg/L as N): dilute 10 mL of 100 mg/L to 100 mL.

(5.0 mg/L as N): dilute 5 mL of 100 mg/L stock to 100 mL.

mg/L as N): dilute 1.0 mL of 100 mg/L stock to 100 mL or 10 mL of 10 mg/L standard to 100 mL. (If the sample is below 1.0 mg/L, at least 3 of the following standards must be made to bracket the sample)

(0.75 mg/L as N): dilute 15 mL of 5.0 mg/L standard to 100 mL.

(0.50 mg/L as N): dilute 5 mL of 10 mg/L standard to 100 mL

0.40 mg/L as N): dilute 4.0 mL of 10 mg/L to 100.

(0.30 mg/L as N): dilute 3.0 mL of 10 mg/L to 100.

(0.20 mg/L as N): dilute 2.0 mL of 10 mg/L to 100.

Ionic Strength Adjuster (ISA), 2M ammonium sulfate commercially available or prepared as follows: Add 26.4 g reagent grade ammonium sulfate (NH_4)₂SO₄ to a 100 mL volumetric flask, add approximately 70 mL of laboratory pure water to dissolve the reagent, then bring the solution up to the 100 mL volume with laboratory pure water.

Outer Filling Solution (reference electrode), add 2 mL of 2M ISA to a 100 mL volumetric flask, bring the volume up to 100 mL with laboratory pure water.

Dilute Sulfuric Acid Solution, add 3.00 mL of concentrated H₂SO₄ to 80 mL of laboratory pure water in a volumetric flask, cool and bring the volume up to 100 mL with laboratory pure water.

Silver Sulfate Solution (0.01M), add 0.31 g Ag₂SO₄ to approximately 80 mL of laboratory pure water in a 100 mL volumetric flask. Lightly heat and swirl until dissolved, cool and bring the volume up to 100 mL with laboratory pure water.

Procedure (ODH CCA-6A)

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

1.0 to 20.0 mg/L Range working standards, a, b, c, and d should be used in this range. Samples greater 20 mg/L should be diluted into this range.

0.2 to 1.0 mg/L Range working standards, b, d, f, and at least three other working standards with less than 1.0 mg/L should be used in this range. Choose working standards which will "bracket" the sample concentration (at least two standards below and two above the sample concentration, if possible).

Standard Curve (Concentration Mode)

Two Standard Calibration Meters: Sample Concentrations greater than 1.0 mg/L: Calibrate at 1.0 and 10.0 mg/L and analyze a third standard in the sample concentration range (2.0 or 5.0 mg/L). Midrange standard should be within 10% of its nominal value to accept the calibration (Records must be kept of the midrange standard readout).

Sample Concentrations less than 1.0 mg/L: Two standard calibration meter cannot be used on the concentration mode if the sample concentration is less than 1.0 mg/L. The mV mode must be used in this range as in 1b above.

Multi-Standard Calibration Meters: Sample Concentrations greater than 1.0 mg/L: Calibrate using at least three standards. A 1.0 and a 10.0 mg/L must be included in the calibration for proper slope determination.

Sample Concentrations less than 1.0 mg/L: Calibrate at 1.0 and 10.0 mg/L per slope determination. Recalibrate using four or five standard concentrations between 1.0 and 0.2 mg/L.

Standard and Sample Preparation

Using a 50 mL graduate (TD), carefully measure 50 mL of the lowest standard to be used and pour it into a properly labeled 100 mL beaker.

Rinse the graduate with laboratory pure water, then rinse it with 5 mL of the next highest standard in the curve and discard.

Carefully measure 50 mL of the next highest standard and pour it into a properly labeled 100 mL beaker.

Repeat b and c until all the standards in the curve and the samples are in their respective beakers.

Add magnetic stir bars to each of the beakers.

Using volumetric pipets, add to each of the beakers: 1 mL of the 2M ISA solution; 10 mL of the Ag_2SO_4 solution (if needed).

While gently stirring with a magnetic stirrer, add the dilute sulfuric acid or NaOH solution drop wise to adjust the pH of each of the solutions to between 3.5 and 4.0.

Specific Ion Measurements: (mV vs Concentration.)

While gently stirring, lower the electrodes into the 5.0 mg/L standard (for the 1.0 to 20.0 range) or the 1.0 mg/L standard (for the 0.2 to 1.0 range). Allow the mv reading to stabilize (approximately 1 minute) and set the mV reading to a convenient number (e.g., 0.0 or 100.0), record this reading. NOTE: Meters must have the capacity to set a specific mV value. If your meter does not, you must obtain a new meter.

While gently stirring, lower the electrodes into the lowest standard, allow the mV reading to stabilize (approximately 1 minute), record the result.

Rinse the electrodes with laboratory pure water and blot dry with a soft paper towel (tissue). While gently stirring,

lower the electrodes into the next highest standard, wait for stabilization, and record the results. Repeat this step until all standards and samples have been tested.

Specific Ion Measurement (Concentration Mode):

Sample Concentrations Less Than 1.0

While gently stirring standards, calibrate at 1.0 and 10.0mg/L. Use microprocessor for slope determination, record slope value.

Clear calibration, set instrument to multi-standard calibration. While gently stirring standard, lower the probes into the lowest standard concentration (0.2 mg/L). Allow the mV reading to stabilize (approximately 1 min) and calibrate the meter to the standard concentrate.

Properly rinse and blot dry probes. Lower probes into the next highest standard concentration (while stirring). Allow mV reading to stabilize and calibrate the meter to the standard concentration.

Repeat step (iii) with the remaining standards using four or five different standard concentrations.

Rinse probes and blot dry. While gently stirring, lower into sample, allow to stabilize (approx. 1 min) and record concentration. Repeat this step for additional samples with concentrations less than 1.0 mg/L.

Sample Concentrations Greater Than 1.0 mg/L

While gently stirring the sample lower the probes into the 1.0 mg/L standard. Allow the mV reading to stabilize (approx. 1 min) and calibrate the meter to the standard concentration.

Rinse probes and blot dry. Repeat step (i) using up to a total of five standard concentrations. Always include the 10.0 mg/L standard in the calibration for proper slope determination.

Rinse probes and blot dry. While gently stirring, lower probes into the sample, allow to stabilize, and record concentration. Repeat this step for additional samples with concentrations greater than 1.0 mg/L.

Treatment of Data

Standard Curve Construction:

Using two cycle semi logarithmic graph paper, construct a standard curve by plotting concentration on the logarithmic axis in mg/L nitrate-nitrogen and the corresponding electrode potential readings in mV on the linear axis.

Sample concentration is determined by relating the millivolt reading previously recorded, to the concentration indicated on the standard curve.

Slope Determination - The slope of the electrode must be determined each time the test is run by finding the difference in mV between a decade of change in concentration. An acceptable slope will be between 50 and 60 mV change/decade of concentration. Use 1.0 and 10.0 mg/L to determine the slope. A low slope indicates poor electrode performance. Rejuvenation or replacement of the sensing module is required.

Documentation

Date of Analysis

Analyst's Name

Expiration of Nitrate stock standard solution

mV readings for calibration standards mV vs Concentration.

Graph of standard curve and sample concentrations

Slope reading in mV/decade difference in concentration mode

Slope read out (using 1.0 and 10.0 mg/L standards)

A full range mV vs concentration graph (0.2 - 10.0 mg/L). Initially and whenever the electrode or sensing module is replaced.

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Liquid reagents	Room temperature
	Standards	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Reagents	See procedure
	Diluted Standards	See procedure
	Standards	1 year after receipt
Required Quality Control	Frequency	Required QC
	Quarterly	Construct Graph

NOTE: This method is to be used only on samples that have never been chlorinated.

Method Reference

Standard Methods 18th Edition (4500 - NO₂, B); (4500 - NO₃, E, F); Ion Chromatography

Sample Container/Preservation

Collect in a glass or plastic container (250 - 1000 mL)

No preservative is used

Maximum Sample Holding Time

48 hours - Refrigerated at 2-10°C, must not be preserved

Sample Source Check

Add 25 mL of sample to a 100 mL volumetric flask, fill to the mark with full-strength Ammonium Chloride EDTA and mix. Add 2.0 mL of color reagent to a 50 mL aliquot of this sample to check for the presence of nitrite; this sample is not passed through the column. Read absorbance and subtract any significant nitrite results from nitrate results.

Documentation

1. Records must be properly identified and labeled with date and analysts initials and kept on file for 10 years.
2. Calibration curves must be generated at least once per three months.
3. Concentrations and absorbance reading of the blanks and standards for all curve verifications.

4. Expiration dates of the stock nitrate and nitrite standards.
5. Reagent preparation log with reagent names, date prepared and analyst's initials.
6. Standard concentrations, absorbance readings, correlation coefficients, graph or print-outs associated with the use of a microprocessor spectrophotometer or computer for calculation purposes.
7. Instrument and maintenance log book for spectrophotometer
8. Quality control results if QC samples are used for accuracy and precision.

Please refer to the nitrate section in addition to this information.

Total Dissolved Solids

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	KCl	Room temperature
	1000 mg/L check sample solution	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	1000 mg/L check sample solution	1 year
	KCl	Six years after receipt
Required Quality Control	Frequency	Required QC
	Each Run (or batch of 10)	Duplicate samples run
	Each Run (or batch of 10)	Low range control
	Each Run (or batch of 10)	Blank

Method Reference

Standard Methods 19th Edition (SM 2540C)

Equipment

1. An analytical balance with the a capability of measuring to at least 0.0001 g.
2. A steam bath, or a drying oven capable of maintaining a temperature of 98-105 °C,
3. A drying oven capable of maintaining a temperature of 180 ± 2 °C.
4. Desiccator with a humidity indicator.
5. Evaporating dishes with a capacity of 50-100 mL.
6. 50 mL volumetric delivery flask, or pipet.
7. Filtering flask, holder, funnel, and vacuum pump.
8. Glass fiber filters, Whatman GF/C or equivalent.
9. Tongs capable of holding evaporation dishes.

Sample Container/Preservative

A clean plastic or glass screw top container (250-1000mL)

No preservative should be added.

Maximum sample holding time

7 days in the refrigerator at 2-10 °C.

General method summary

A known volume of sample is filtered through a 0.45 μ m glass fiber filter. The filtered sample is placed into an evaporating dish, then evaporated to a specific dryness on a steam bath, or a 98 °C oven. The sample is then placed in a 180 °C oven for at least one hour and then desiccated until constant weight is obtained. The method measures the amount of minerals and other substances that are dissolved in the sample.

Choose sample volume (50-100 mL) to yield between 10 and 200 mg dried solids.

On-site Survey Requirements

1. At least one total solids test must be prepared prior to the survey so that it can be completed at the time of the survey.
2. Each analyst must be familiar with the procedure if asked questions during the survey.

Reagents

1. Lab pure water: Lab pure water used for blanks, rinsing, and standards should be free of all dissolved substances and suspended material.
2. A laboratory control sample can be prepared by dissolving 1.000 g pre-dried KCl (heated and desiccated) into 1 liter of lab pure water. This provides a 1000 mg/L check solution.

Test 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. When sample is at room temperature filter enough sample to rinse the filter flask with two aliquots of 50-100 mL of water. Then filter enough sample to supply approximately 100 mL of water. Always use tweezers when handling filters.
5. Volumetrically deliver 50 mL of each sample to its assigned dish.
6. Place evaporation dishes over steam bath and allow the sample to evaporate to dryness. An oven set at 98-105 °C may also be used to evaporate sample.
7. Oven dry the evaporating dishes at 180 °C for at least one hour after they have evaporated to dryness.
8. Allow the dishes to cool in desiccator for 1 hour or until room temperature is reached.

9. Weigh the dishes and record weight. Balance should be monitored for drift and re-zeroed as necessary. Repeat drying cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained, or until the weight change is less than 0.5 mg.

QC Requirements

1. Blanks must be run with every batch or every 10 samples. Blanks water must be less than 10 mg/L in total dissolved solids.
2. Duplicate samples must be run with every batch or every 10 samples. Duplicate determinations must agree within 5% of their average.
3. A laboratory control sample must be run for each range with every batch or every 10 samples (low range 10-200mg/L). Laboratory control sample must be within 10% acceptance criteria.

<i>Quick Reference</i>	Standard/Reagent	Condition
Standard/Reagent/Equipment Storage Conditions	Liquid reagents	Room temperature
	Standards	Refrigerated
Standard/Reagent Storage Times	Standard/Reagent	Maximum Storage Time
	Reagents	See procedure
	Chloramine-T Solution	One week
	Standards	1 year after receipt
Required Quality Control	Frequency	Required QC
	Quarterly	Standardization

Method Reference

Standard Methods 18th Edition 4500CN-C,E,F,G; MCAWW 335.4

The following approved methods for total cyanide must always include a manual distillation as a first step:

1. The spectrophotometric method SM 4500 CN-E (total).
2. The semi-automated spectrophotometric method - MCAWW 335.4.
3. Selective ion method: Total Cyanide - SM 4500 CN-F.
4. Amenable spectrophotometric method (free) is acceptable when total cyanide results are >0.2 mg/L. The approved method, **only** when used in conjunction with 4500 CN E, 4500 CN F or 335.4 is: SM 4500CN-G

Distillation methods which are acceptable include:

1. The full volume method, or macro distillation method, which uses 500 mL of sample.
2. The midi distillation method which uses 25 mL or another adjusted sample volume. Approved midi systems are available. **Note: The mini distillation method is unacceptable.**

Sample Container/Preservative

A clean plastic or glass screw top container (1000 mL)

Must be kept refrigerated at 2-10 °C; Raise pH to ≥ 12.0 with 10 N - NaOH, adding NaOH drop-by-drop

Maximum Sample Holding Time

Fourteen Days

General Summary

Drinking water may be monitored at levels <0.2 mg/L for total cyanide. If concentrations are >0.2 mg/L then the amenable to chlorination procedures (as outlined) are performed.

Cyanide is highly toxic: fumes must not be inhaled. Inhalation of fumes can result in death. Perform all analysis in a fume hood.

Cyanide is measured as CNCl. The conversion reaction is completed with chloramine-T at a pH of <8. Absorbance of the solution can be determined at wavelengths between 578-582 nm inclusive, after the addition of pyridine-barbituric.

During the distillation process, a blank and a calibration verification and one duplicate are used to verify the recovery.

Perform standardizations once every three months (quarterly). In the interim, Quality Control (QC) samples are used to verify the standard curve. The QC for method 4500 CN - E includes a reagent blank and a midrange standard. These controls must be within 10% of standard curve values. If the standard is outside of control limits, a new curve must be prepared.

On Site Requirements

1. Each analyst must be able to demonstrate the procedure during the survey. Just prior to the survey a standard curve and a sample should be used for analysis during the survey. A joint effort may be employed to conserve time.
2. The spectrophotometer will be checked for proper operation. Records of the calibration curves, absorbance readings, standard curve verifications instrument log and related information will be checked.
3. All reagents, standards and solutions used for the test will be checked for proper labeling and dating.
4. Analysts may be required to analyze a performance sample during the survey.

Equipment (Method 4500 CN C)

1. Boiling Flasks, 1 liter with inlet tube and provision for a water cooled condenser.
2. Distillation apparatus (Use ground glass ST joints and the appropriate lubricant or TFE sleeved for the boiling flask and the condenser)
3. Heating Element, adjustable
4. Hood (used during the entire analysis)
5. Timer
6. Gas Absorber, with gas dispersion tube and medium porosity fritted outlet
7. Consult Standard Methods (4500CN-C) for a complete listing of required equipment.

Reagents

1. 1 N NaOH - 40g NaOH diluted to 1 liter of deionized water
2. Magnesium Chloride - 510g $MgCl_2 \cdot 6H_2O$ diluted to 1 liter of deionized water
3. Sulfuric Acid - one-to-one dilution of deionized water and concentrated H_2SO_4
4. Lead Carbonate - $PbCO_3$
5. Sulfamic Acid - NH_2SO_3H
6. Lead acetate paper.

Distillation Procedures

1. Collect 500 mL of sample, transfer to a boiling flask.
2. Add 10 mL of the NaOH solution into the absorber.
3. Dilute with laboratory pure water to obtain an adequate volume, if necessary. Do not exceed 225 mL total volume of absorber solution.
4. Check samples for the presence of sulfur with lead acetate paper. If present, add 50 mg or more of lead carbonate in order to precipitate sulfur if its presence is suspected.
5. Set up the apparatus as illustrated in SM 4500CN-C.
6. Adjust the suction so that the air rate is approximately 1 air bubble/sec entering the flask. During the analysis the flow rate may be adjusted so that there is not an reverse flow.
7. Add 2g of sulfamic acid through the air inlet tube and rinse it down with DI water.
8. Add 50 mL of H_2SO_4 through the air inlet tube. Rinse with DI and air mix for **3 minutes**.
9. Add 20 mL of $MgCl_2$ reagent through the air inlet tube and rinse with DI.
10. Heat with rapid boiling and maintain vapors one half of the way into the condenser. **Reflux (boil) for 1hr.**
11. Discontinue heat and maintain the air flow **15 minutes**.
12. If incomplete recovery is expected distill again by refilling the gas washer with fresh NaOH solution. **Reflux (boil) for 1hr**. The cyanide from the second reflux will indicate the completeness of the recovery.

Colorimetric Procedures (SM 4500 CN E)

Follow procedures as listed in Standard Methods 4500CN-E.

Equipment

1. Spectrophotometer - Set on 578 nm
2. Pipets - Class A

3. Volumetric Flasks - Class A

Reagents

1. Chloramine-T Solution - 1.0g in 100 mL deionized water. Prepare weekly, store in the refrigerator.
2. Stock Cyanide Solution - prepared as outlined in Standard methods, 4500 CN-E.
3. Standard Cyanide Solution - prepared as outlined in Standard methods, 4500 CN-E.
4. Pyridine-barbituric Acid - prepared as outlined in Standard methods, 4500 CN-E.
5. Acetate Buffer - 410g of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ in 500 mL of deionized water. Add glacial acetic acid to bring the pH to 4.5. This will take about 500 mL of acid.
6. Sodium Hydroxide - 1.6g of NaOH to 1 liter of deionized water.

Procedure

Follow the procedure outlined in Standard Methods, 4500 CN-E.; Calculate the values as outlined in Standard Methods 4500 CN-E.

Documentation

1. Records must be properly identified and labeled with date and analyst's initials and kept on file.
2. Calibration curves displaying concentration and absorbance readings must be generated at least once per three months. Correlation coefficients must be recorded or print outs kept on file. Graphs or printouts associated with the use of a microprocessor spectrophotometer or computer for calculation purposes are to be recorded or printed out and kept on file.
3. Concentrations and absorbance reading of the blanks and standards for all curve verifications.
4. Expiration dates of the stock standards.
5. Reagent preparation log with reagent name, date prepared and analyst's initials.
6. Instrument and maintenance log book for spectrophotometer.
7. Quality control results for QC samples.

Ion Chromatography

Method Reference: US-EPA 300.0 Revision 2.1

Analytes

Method A Bromide
 Chloride
 Fluoride

	Nitrate
	Nitrite
	Ortho-Phosphate
	Sulfate
Method B	Bromate
	Chlorite
	Chlorate

Summary of Method

A small volume of sample is introduced into an ion chromatography instrument. The anions-of-interest are separated and measured. A typical system uses a guard column, analytical column, conductivity detector, and data collection software for interpretation of results.

On Site Requirements

1. Each analyst must be able to demonstrate the procedure during the survey.
2. All reagents and standards used will be checked for proper labeling and dating.
3. Analysts may be required to analyze a performance sample during the survey.
4. Documentation, quality control and analyst training records will be checked.

Documentation

1. Reagent log with reagent name and concentration, date received or prepared, expiration date, and analyst initials.
2. Instrument logbook.
3. Maintenance logbook.
4. Annual Method Detection Limits (MDL) studies.
5. Initial demonstration of capabilities for all analysts.
6. Control charts of the LFB and LFM must meet acceptable control limits.

Quality Control

1. Quality control samples analyzed quarterly from an approved PT suppliers.
2. A Laboratory Reagent Blank (LRB) with each batch of samples.
3. A Laboratory Fortified Blank (LFB) with each batch of samples. Control limits for the LFB are 90%-110% or better.
4. A reporting limit check (RLC) must be analyzed after the daily calibration. Control limits for the RLC are 90-110% or better. The analyte concentrations in the RLC must all be at the laboratory's reporting limit for each of the analytes.

5. An Instrument Performance Check (IPC) must be analyzed after daily calibration and every tenth sample. Control limits for the IPC are 90%-110% or better. Retention times for analytes must be within 10% of that days initial IPC. If the calibration cannot be verified a second IPC may be analyzed. If a second IPC fails to meet control limits sample analysis must be discontinued and all samples analyzed since the last acceptable IPC must be reanalyzed.
6. A Laboratory Fortified Sample Matrix (LFM) every tenth sample. Control limits for the LFM are 80%-120% or better for Method A and 75%-125% or better for Method B.
7. Duplicate samples must be run every batch or tenth sample. Duplicates must agree within 10% of each other.

Parameter Group/Primary Metals: Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Selenium, Thallium

Method References

Standard Methods 18th & 19th Edition, USEPA Methods

General Requirements

Laboratory plans must be approved in writing by the Ohio EPA. If the plans have never been approved a survey cannot be conducted until such time that approval is granted. Submit scale drawings, equipment lists and other required material to the Ohio EPA. Contact the Ohio EPA, DES for further details.

All applicable Ohio EPA fees will be required for laboratory certification.

All equipment used in the analyses must be acceptable to the Ohio EPA/DES Laboratory Certification Section. When a laboratory submits floor plans, equipment lists are also forwarded to the Ohio EPA for acceptance.

Primary metals testing laboratories must successfully complete a PT study for the primary metal parameter group.

Primary metals testing laboratories must use an approved USEPA method for each primary metal. Methods are included in the final page of this section.

The following quality control procedures must be performed:

1. Instrument/equipment calibration and/or standardization as required by the manufacturer and Ohio EPA.
2. Routine instrument performance checks.
3. A reporting limit check (RLC) must be analyzed once daily at the beginning of the run or may be included as part of the calibration curve.
4. One matrix spike per sample for graphite furnace analysis.
5. Validation of calibration curves using a high and a low concentration prepared from second standard source. These QC standards are run at the beginning of analyses with others at the end of the analyses. Curve acceptance criteria should be maintained at ± 2 SD or 90-110%.
6. Duplicates must be run at a 10% sample frequency.
7. Matrix spiking is required at a 10% sample frequency for other than graphite furnace analysis.
8. Continuing Calibration Verifications (CCV) are required at a 10% sample frequency.
9. Preventive maintenance schedules and procedures must be performed at regular intervals.
10. Required matrix spike recoveries must be calculated and monitored for each run. If the sample is negative the matrix spike recovery must be 80-120% ; and 85-115% if it is positive.
11. Corrective actions must be documented whenever QC standards, precision & accuracy data, RLCs or CCVs are

outside of limits.

12. Real time control charts must be maintained for the QC standards in order to monitor for shifts and trends.

Prior to the survey for renewal, each laboratory must submit to the Ohio EPA , the laboratory's Laboratory Quality Assurance Plan QAP, including all Standard Operating Procedures, (SOPs) and Method Detection Limit (MDL) studies for each parameter. The MDLs must be as low or lower than Ohio's reporting limits for each test parameter. An MDL study must comply with OAC 3745-89-03. The QAP must contain the following:

1. Sampling procedures: An example of the written sampling instructions that must accompany each sample kit.
2. Sample handling procedures including:
3. Procedures used to maintain the integrity of the samples, that is, the procedures used to track samples from receipt to testing and finally to disposal.
4. Chain of custody forms and other special requirements used for enforcement or litigation
5. The procedure and frequency of instrument/equipment calibration and/or standardization.
6. The standard operating procedures used when performing the analyses.
7. Data validation and reporting procedures, including:
8. Procedures used to convert raw data to standard units.
9. Validation of data procedures by the laboratory's QC Officer including the procedures used to ensure transcription accuracy and accurate calculations.
10. Reporting limit checks criteria.
11. Methods used to ensure that all reporting is performed within reasonable turnaround time limits and that the data format is as prescribed by the Ohio EPA.
12. A procedure and a blank log page for use in recording standard and reagent preparation.
13. The specific Quality Control procedures used by the laboratory must include:
14. The preparation and frequency of calibrations and the creation of calibration curves.
15. Routine instrument performance checks.
16. One matrix spike per sample for graphite furnace analysis.
17. Validation criteria for calibration curves using a second standard source.
18. Duplicates at 10% sample frequency.
19. Matrix spiking at a 10% sample frequency for other than graphite furnace analysis.
20. Continuing calibration verifications at a 10% sample frequency.
21. Preventive maintenance schedules and procedures.
22. The routine practices that are used to ensure the accuracy and precision of the generated data.

23. Precision is based on the conclusions drawn from the results of duplicate analyses.
24. Accuracy determined by the results of matrix spike recoveries.
25. Procedures to implement corrective action whenever:
26. RLCs are unacceptable.
27. QC standards are outside of limits.
28. Precision & accuracy data is outside of limits.
29. Laboratory fortified blank (LFB) recoveries are not acceptable.
30. PT samples are out of limits.
31. Any other problem that may impede the accuracy and precision of the testing.
32. If the continuing calibration verification is outside of limits.
33. Shifts or trends are observed on control charts.
34. A table of organization of the laboratory that delineates responsibilities of all personnel.

The procedure used for daily required Ohio EPA RLCs.

1. During, or prior to the survey an actual performance sample or unknown supplied by the survey officer must be run.
2. At least once each three months a blind performance sample from an outside source, covering each analytical technique, must be analyzed and recorded. PT samples may be substituted for two quarters.
3. At least once each three months a minimum of one actual drinking water sample must be analyzed for each test parameter, to maintain certification.

The following are requirements for metals analyses by Flame Atomic Absorption (FLAA), Graphite Furnace Atomic Absorption (GFAA), Stabilized Temperature Graphite Furnace Atomic Absorption (STGFAA), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma - Mass Spectrophotometry (ICP-MS):

1. Samples are to be preserved with nitric acid either at collection or in the laboratory to a pH of <2.0.
2. If the samples are received by the laboratory unpreserved they must be acid preserved by the laboratory and held for 16 hours prior to testing.
3. Samples must not be filtered prior to preservation or testing.
4. The pH of samples must be checked prior to testing. The pH must be recorded. pH paper in a suitable range may be used for this. The pH must be <2 or additional preservative must be used.
5. Turbidity must be checked prior to analyses. All approved method steps for turbidity analysis must be performed. All turbidity QC requirements must be followed and documented.
6. If the turbidity is <1 NTU the sample must be digested.
7. If the sample registers <1 NTU on turbidity, but particulate matter is seen in the sample, the sample must be

digested.

8. If the sample shows <1 NTU on turbidity and is free from particulates, direct analysis may be made. All samples analyzed by cold vapor atomic absorption or when testing for antimony, arsenic or selenium by gaseous hydride atomic absorption, must be digested. The only exception to this is when performing the gaseous hydride method for arsenic and selenium, in which case the perchloric digestion is never used. Please consult the method and method addenda for details.

Additional Metals Test Information

Autosampler spiking is acceptable provided that the calculations are based on the volume of sample not including the volume of the spike. Manual spiking should be kept at a 10% dilution ratio (to total sample volume).

Reporting limit check (RLC) protocol must be followed. Either use a standard with a concentration that is less than or equal to the Ohio EPA's reporting limit value as part of the calibration curve or prepare a standard with a concentration that is less than or equal to the Ohio EPA's reporting limit value. Analyze it after calibration. Use a value of $\pm 30\%$ for acceptance of the RLC.

Consult the method for acceptable digestion techniques. The previously acceptable method of autoclaving samples is no longer acceptable. Perform digestion with a hot plate in an acceptable fume hood.

Use the following guidelines for furnace digestions:

Sb - 1 mL of concentrated HNO_3 + 0.5 mL of concentrated HCl/100 mL

As, Se, Cr - 1 mL of concentrated HNO_3 + 5.0 mL of 30% H_2O_2 /100 mL. (H_2O_2 addition for As and Se are only necessary in the presence of nickel nitrate.)

Others - 1 mL of concentrated HNO_3 /100 mL.

Quarterly (1/three months) blind performance samples may be purchased through a commercial supplier or may be laboratory generated by the Quality Control Officer.

Laboratory generated limits for QC knowns (Initial calibration verification [ICV], CCV, etc.) should be established at ± 3 standard deviation (SD) for control and ± 2 SD for warning. The true value must be used for quality control charts, not the mean. Acceptable spike recoveries for positive samples are 85-115%.

A laboratory may elect to maintain certification for one or all of the regulated metals group provided that:

The elected metals are analyzed at least once every three months on a "real" drinking water sample, as noted above.

PT samples are analyzed for all of the regulated metals group. Acceptable results must be achieved on at least every other study. Two consecutive unacceptable results for the group will result in invalidation of certification. All applicable quality control must be followed to maintain certification.

Lead and copper certification may be obtained separately without certification for primary metals.

Primary Metal Methods and Limits

<i>Test Parameter</i>	<i>Methods</i>	<i>MCL ppb</i>	<i>MDL ppb</i>	<i>Reporting Limit ppb</i>
Antimony	200.8, 200.9, SM 3113, ASTM D-3697-87	6.0	1.2	4.0
Arsenic	200.9, 206.3, 206.4, 200.7, SM 3113	50.0	5.0	5.0
Barium	200.7, SM 3113, 3120	2000.0	200.0	300.0
Beryllium	200.7, 200.8, 200.9, SM 3120	4.0	0.5	1.0
Cadmium	200.7, 200.8, 200.9, SM 3113	5.0	0.5	1.0
Chromium	200.7, 200.8, 200.9, SM 3113, 3120	100.0	10.0	10.0
Copper	200.7, 200.8, 200.9, SM 3113, 3113B	1000.0	50.0	50.0
Lead	200.8, 200.9, SM 3113	LCR 15	3.0	5.0
Mercury	245.1, 245.2, SM 3112	2.0	0.4	0.5
Nickel	200.7, 200.8, 200.9, SM 3113, 3111B, 3120	100.0	10.0	20.0
Selenium	200.8, 200.9, SM 3113, 3114B	50.0	5.0	5.0
Thallium	200.8, 200.9	2.0	1.0	1.5
	LCR 1300			

Parameters/Parameter Groups

Trihalomethanes (THMs), Haloacetic acids (HAAs), Volatile Organic Chemicals (VOCs), Vinyl Chloride, Synthetic Organic Chemicals (SOCs)

Method References

Standard Methods (latest edition), USEPA 500 Series

General Requirements

Laboratory plans must be approved in writing by the Ohio EPA/DES. If the plans have never been approved a survey cannot be conducted until such time that approval is granted. Submit scale drawings, equipment lists and other required material to the Ohio EPA. Contact the Ohio EPA, DES for further details.

All applicable Ohio EPA fees will be required for laboratory certification.

All equipment used in the analyses must be acceptable to the Ohio EPA/DES Laboratory Certification Section. When a laboratory submits floor plans, equipment lists must also be forwarded to the Ohio EPA/DDAGW.

Organic testing laboratories must successfully complete a proficiency test (PT) study for all desired parameters or parameter groups.

Organic testing laboratories must use the Ohio EPA approved method for each type of analyses, methods as listed above.

Prior to the survey for renewal, each laboratory must submit to the Ohio EPA, the laboratory's Quality Assurance Plan (QAP) which includes, all Standard Operating Procedures (SOPs), and Method Detection Limit (MDL) studies for each parameter. The MDLs must be as low or lower than Ohio's reporting limits for each parameter or parameter group. An MDL study must comply with OAC 3745-89-03. A QAP must contain the following:

Sampling procedures: An example of the written sampling instructions that must accompany each sample kit.

Sample handling procedures including:

1. Procedures used to maintain the integrity of the samples, that is, the procedures used to track samples from receipt to testing and finally to disposal.
2. The procedure used and the documentation required to verify proper preservation/dechlorination of each sample prior to analyses.
3. Chain of custody forms and other special requirements used for enforcement or litigation
4. The procedure and frequency of instrument/equipment calibration/standardization.
5. The standard operating procedures used when performing the analyses.
6. Data validation and reporting procedures as outlined in OAC 3745-89-03, including:
7. Procedures used to convert raw data to standard units.

8. Validation of data procedures by the laboratory's QC officer including the procedures used to ensure transcription accuracy and accurate calculations.
9. Methods used to ensure that all reporting is performed within reasonable turnaround time limits and that the data format is as prescribed by the Ohio EPA.
10. A procedure and a blank log page for use in recording standard and reagent preparation.
11. The specific Quality Control procedures used by the laboratory, all of which are required for certification, including:
12. The frequency of reporting limit checks (RLC). RLCs are to be analyzed each day of testing. The RCL value must be equal to or less than to the Ohio EPA reporting limit. RLC recoveries must be within 60-140% before sample analysis can begin. RLC samples are not necessary if the calibration concentrations are less than or equal to the Ohio EPA reporting limit value.
13. The preparation and frequency of calibrations and the creation of calibration curves.
14. GC/MS tuning frequency requirements.
15. The frequency of continuing calibrations and criteria.
16. The procedure for using Laboratory fortified matrix (LFM) spikes or matrix spike duplicates as required in the 500 series approved methods. Some methods such as HPLC require 10% LFM.
17. Matrix duplicate analyses requirements.
18. Procedures for the use of calibration standards and calibration curves.
19. Laboratory Fortified Blank (LFB) analysis requirements.
20. Laboratory fortified matrix analysis requirements.
21. Field and trip blank requirements.
22. Charting procedures for surrogates for extractables and purgables when required as well as LFB QCs.
23. Initial demonstration of capability with documentation for each new analyst applying for initial method approval. MDL studies may be substituted for this.
24. Preventive maintenance schedules and procedures.
25. The routine practices that are used to ensure the accuracy and precision of the generated data.
26. Precision is based on the conclusions drawn from the results of matrix duplicate analyses.
27. Accuracy determined by the results of matrix spike and LFM and LFB analyses.
28. Procedures to implement corrective action whenever:
29. LFB's are out of limits.

30. Matrix spikes show poor recovery.
31. PT samples are out of limits.
32. Tuning criteria is unacceptable.
33. Blank contamination is present.
34. Calibration or continuing calibration criteria are not met.
35. Surrogate recoveries are too low.
36. Any other problem that may impede the accuracy and precision of the testing.
37. A table of organization of the laboratory that delineates responsibilities of all personnel.
38. The procedure used for RLCs whenever analyses are run.

During, or prior to the survey an actual performance sample will be supplied by the survey officer for on-site analysis.

At least once each three months, blind performance samples from an outside source must be analyzed and recorded.

At least once each three months a minimum of one actual drinking water sample must be analyzed to maintain certification.

RLCs must be analyzed daily in conjunction with continuing calibration verifications.

Special Considerations for PCB's

As stated in the Federal Register, either method 508, 508.1 or 505 must be used to screen for the presence of seven individual aroclors. If method either 508, 508.1 or 505 shows no detects, analysis is complete and the laboratory is not to perform method 508A. In this case the test is reported as <0.1 mg/L. If any of the PCB aroclors are detected with either methods 508, 508.1 or 505, then method 508A is performed in order to quantify PCBs as decachlorobiphenyl.

With methods 508, 508.1 or 505, results are not to be quantified. A detect with methods 508, 508.1 or 505 is based on the ability to recognize a chromatogram pattern.

Method 508A can sometimes yield false positives. Both the screening test (508, 508.1 or 505) and 508A must show positive results before results can be reported as decachlorobiphenyl. In addition, when a "positive" aroclor pattern is identified via screening method (508, 508.1 or 505), it is required that the same sample be analyzed via method 508A (this does not mean a resample). Therefore, it is necessary that a laboratory performing screens for PCBs via methods 508, 508.1 or 505 also be certified for method 508A.

Additional Quality Control Forms

Calibration/Standardization Schedule: Wet Chemistry Tests

Laboratory Name _____

Month →	1	2	3	4	5	6	7	8	9	10	11	12
Weekly Test												
Fluoride Slope												
Monthly Tests												
Chloride Titrant												
PAO Titrant												
FAS Titrant												
pH Linearity												
Alkalinity Titrant												
Hardness Titrant												
Quarterly (1/three months) Tests												
Nitrate Curve/Probe/Efficiency												
Turbidity - Secondary Std												
Curve - PO ₄ /Fe												
Curve - Cu/Mn												
Curve - NO ₃ Cadmium Red												
Curve - DPD												
Chlorine Colorimeter Calibration												

