Water Treatment Laboratory Workshop

Week 2

Course # 2122

Fleming Training Center
Your Partner in Clean Water

TN Department of Environment & Conservation

Updated September 2020

Water Treatment Laboratory
Week 2
Course # 2122
Instructor: Amanda Carter

Monday

8:30	Lab Safety and Policies
9:30	TSS Filter Prep
10:00	Fluoride
11:00	Lunch
12:00	Total Suspended Solids
1:30	Carbon Dioxide

Tuesday

8:30	Read TSS samples
9:30	Nitrate/Nitrite
11:00	Lunch
12:00	Iron
1:00	Manganese
2:00	Taste and Odor
2:30	Heterotrophic Plate Count

Wednesday

8:30	Tour - K.R. Harrington (Metro Water Services)
11:00	Lunch
12:00	Tour - Omohundro (Metro Water Services)

Thursday

8:30	Stabilization Presentation
9:30	Total Dissolved Solids & Conductivity
11:30	Lunch
12:30	Hardness
2:00	Alkalinity

Friday

8:30	Read TDS results & Calculate LSI
9:00	Marble Test
10:00	Review
11:00	Lunch
12:00	Class Exam and Evaluations

Fleming Training Center
2022 Blanton Dr.
Murfreesboro, TN 37129

Phone: 615-898-6507
Fax: 615-898-8064
E-mail:
Amanda.Carter@tn.gov

Water Treatment Laboratory
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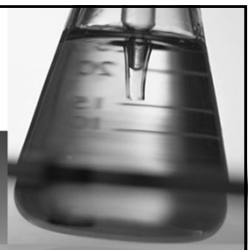
Section 1

Lab Policies

Lab Policies

1. No horse play.
2. No shorts or open-toed shoes.
3. No smoking, eating, dipping or drinking in the lab.
4. Put broken glass in broken glass container, NOT IN THE TRASH.
5. Do not pipet by mouth.
6. Each day after class:
   - All used glassware will be washed in hot soapy water, rinsed in tap water, then distilled water.
   - All counter tops will be wiped clean with disinfectant.
   - Balance room must be clean.
7. Used pipets are placed in containers containing detergent immediately after use, tip up.
8. Acid spills must be cleaned up immediately.
9. Pipet bulbs must be cleaned immediately after overpipeting.
10. Wear safety glasses when performing any experiment.
11. Wear aprons in the lab at all times.
12. Wear gloves when performing any experiment or washing glassware.
13. Wash your hands before leaving the laboratory.
14. Know where the eye wash stations are located and how to use them.
15. Know where the emergency shower is and how to use it.
16. Know where each fire extinguisher is located and how to use them.
17. Read carefully the Safety Data Sheets for all chemicals used in the laboratory.



Lab Safety

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Before Lab Work, Get to Know:

- Hazards of materials and their prescribed safety procedures
- Learn the lay-out of the building
  - location of emergency exits
  - emergency exit routes
  - emergency telephones
  - emergency ventilation system
  - fire-fighting equipment and how it works
  - emergency shower
  - first aid equipment

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Chemical Spill

- Chemical spill kit, cleanup procedures available and training provided if considered necessary by departmental plan
- Safety showers and eyewashes (inspected weekly) easily accessible/ unobstructed

3

First Aid

- First aid box easily accessible and adequately stocked
- First-aider name posted on first aid box
- First aid box contain a copy of first aid instructions
- Medication items not stored in first aid box

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First Aid

- When a major injury occurs:
  - Call the emergency contact number, e.g. 911.
  - Keep the victim warm, lying down, and quiet until medical assistance arrives.
  - It is better NOT to move the injured person unless he or she is immediately threatened by further injury.

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First Aid

- While waiting for the response personnel to arrive:
  - Treat acid and alkali burns with running water for 20-30 minutes
    - Use emergency eyewash/shower if necessary.
    - Do not attempt to neutralize.
    - Take care not to contaminate yourself.
  - Irrigate burned (heat or cryogenic) areas with cold water.

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First Aid

- While waiting for the response personnel to arrive:
  - Remove contact lenses, if present
    - Use eyewash for 15 minutes to cleanse eye after chemical splash.
  - Treat major bleeding with direct compression of the wound using a clean cloth.
  - Expose anyone who has inhaled toxic materials to fresh air.

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Safety Data Sheets

- SDS
- Keep on file for all chemicals purchased
  - According to the Americans with Disabilities Act of 1990, SDS's should be kept for a minimum of 30 years
- Includes all information shown on a chemical label and more

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Lab Hygiene

- Food and drink are not to be stored or prepared in laboratories or chemical storerooms
- Use appropriate personal protective equipment and wash your hands regularly when working with chemical reagents, especially before meals or snacks.
- Smoking in laboratories is prohibited.

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Lab Hygiene

- Loose sleeves are a hazard and should not be worn in the lab.
- If you have long hair, ensure that it is properly tied back.
- Wearing of contact lenses in the lab is strongly discouraged.
  - If it is unavoidable, advise your supervisor and co-workers so that this information is known in the event of a chemical splash in the eyes.

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Personal Practices

- No inappropriate clothing and shoes (shorts, sandals, slippers, etc.)
- Gloves removed before handling telephone, door handle or leaving laboratory
- No pipeting by mouth

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Personal Practices

- Lab coats and safety glasses/ goggles worn by all where necessary
- Proper gloves are used as needed
- Other personal protective equipment used properly as needed

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Lab Work Area

- The work bench is to be kept clean at all times, and free from chemicals and apparatus which are not required.
- Before starting an experiment, make sure you are familiar with all the procedures and the potential hazards of the starting materials and products.
  - Determine the appropriate safeguards and remedies.
  - Know the procedures for emergency shut off as well as the person and phone numbers to contact in case of emergency.
  - If anything unexpected occurs during your experiment, or if you are in any doubt, consult your supervisor immediately.

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Handling Glassware

- Examine all glassware before use.
  - Discard any broken glass apparatus in the appropriate sharps container.
- Never store damaged glassware in cupboards.
  - Damaged glassware should either be sent for repair properly or disposed in a separate labeled container for sharps disposal.
- Use gloves when sweeping up broken glass, do not use bare hands.
  - Pick up fine glass particles with wet paper toweling.

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Handling Glassware

- Cut ends of glass rods and tubing should always be fire-polished before use.
- Use a cloth for protection when inserting glass tubing, rods or thermometers into bungs or tubing
  - Use a lubricant or water where necessary.

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Chemical Spills

- Small spills (generally less than 100 mL) can usually be cleaned up safely by the employees involved.
- The hazardous properties of the material must be considered when deciding whether it is a “small” spill or not, and therefore whether unassisted clean-up should be attempted.
- Employees must be trained in advance to handle cleanup of even small spills

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Section 2

Fluoride

Fluoride

Water Treatment Lab

Fluoride

- A mineral that occurs naturally in water and soil
- May be added to drinking water for the reduction of dental caries (cavities)

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Adjusting Fluoride Levels

- If too little is present, the benefits will not be obtained
- If too much is consumed, staining or pitting of teeth may be present

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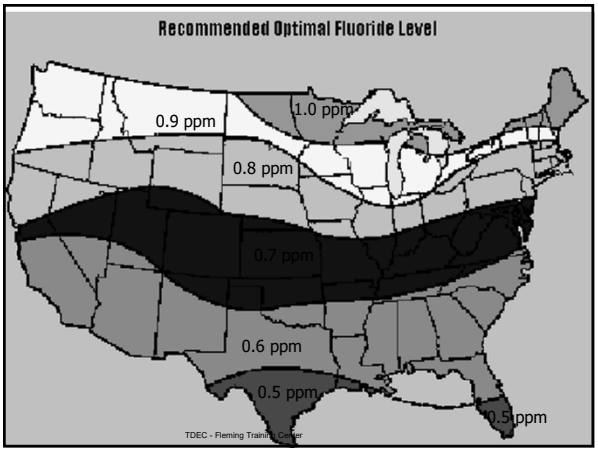

Who, What, Where, Why, How

- Fluoridation is adjustment of water fluoride
- Used for optimum oral health benefits
- One of ten great public health achievements of the twentieth century (CDC)
- Water fluoridation has a 60-year history of success

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Who?

- Dr. Frederick S. McKay initiated a study in 1908 of "Colorado Brown Stain" in Colorado Springs
- Important conclusions…
  - Mottled teeth more resistant to dental decay
  - Life-long residents had stained teeth, more recent residents did not
  - High fluoride content of water identified in 1931

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Who? (continued)

- In 1930s, Dr. H. Trendley Dean conducted the "21 Cities Study"
- Important conclusions:
  - Optimum levels of fluoride for enhancing oral health (natural breakpoint at 1 mg/L)
  - 1.0 mg/L provided best combination of reduction in tooth decay (caries) and low risk of fluorosis
  - Established community fluorosis index (increased incidence at 2 mg/L)

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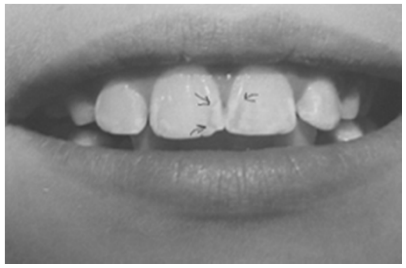
Fluorosis



Mild Fluorosis

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Fluorosis

Moderate Fluorosis w/ stains

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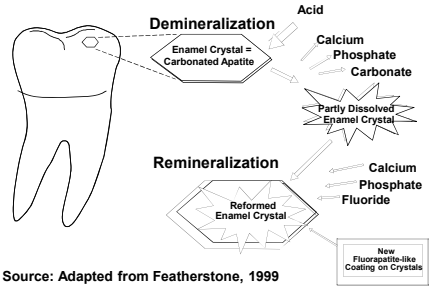
How Fluoride Works



Source: Adapted from Featherstone, 1999

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Alternatives to Fluoridated Water

- Fluoridated water most common vehicle (various estimates of 220-300 million people worldwide)
- Fluoridated salt second most common vehicle (various estimates of 40-300 million people worldwide)
- Dietary fluoride supplements -- drops, tablets, or vitamins (60 million people-WHO 2003)
- Fluoridated milk used in a few places

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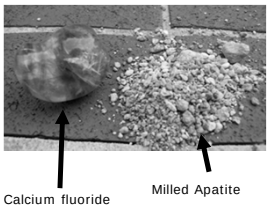
Apatite

- Mixture of calcium compounds
  - Calcium phosphate
  - Calcium carbonates
  - Calcium fluorides (Contains 3 to 7% Fluoride)
- Primary source for fluoridation additives
- Raw material for phosphate fertilizer
- US largest world production; Florida principal location



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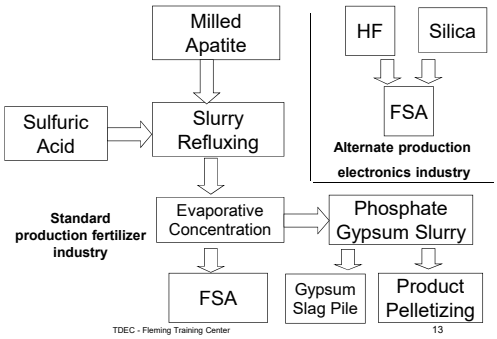
Fluorosilicic Acid (FSA)



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Industrial Waste???

- The hydrogen fluoride and silicon tetrafluoride that otherwise would be released to the atmosphere or left in the gypsum slurry is deliberately recovered from the slurry by evaporators and condensed to FSA used for water fluoridation.
- The recovered fluorosilicic acid is a high-purity, low-cost source of fluoride.
- Some sources may tell you that fluorosilicic acid is hazardous waste material that the industry wants to dispose of, but that is not true.

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Recommended Levels

- For the State of Tennessee the recommended levels are 0.7mg/L
  - Fluoridation of drinking water is not required in the State of Tennesseee
- Primary MCL for the prevention of fluorosis is 4.0 mg/L
- Secondary MCL is 2.0 mg/L

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MCL Exceedance

- 0400-45-1.09(7)(a) – Where the results of sampling for … fluoride … indicate an exceedance of the maximum contaminant level, the state may require that one additional sample be collected as soon as possible after the initial sample was taken (but not to exceed two weeks after the date of the initial sample analysis) at the same sampling point.

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Fluoride Analysis

- Two methods are approved:
  - Colorimetric
    - SPADNS and SPADNS 2
  - Electrode

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Fluoride Analysis

- Fluoride sample collection:
  - Preservative – none
  - Container – plastic or glass
  - Holding time – 1 month

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SPADNS or SPADNS 2

- Bulk SPADNS Method
  - Detection at 0.02 – 2.00 mg/L
  - Pipet 10 mL sample
  - Pipet 2 mL SPADNS
  - Swirl to mix and let 1 minute reaction take place
- AccuVac Method
  - Detection at 0.02 – 2.00 mg/L
  - Vacuum draws correct sample amount into vial with pre-measured SPADNS

SPADNS 2 is Arsenic-free, which means no hazardous waste disposal requirements and is still EPA approved

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SPADNS

- Sodium 2-(parasulfophenylazo)1, 8-dihydroxy-3, 6-naphthalene disulfonate plus zirconium
- Any fluoride present in the water sample removes zirconium from the reaction, therefore decreasing the color intensity

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SPADNS Interferences

Interfering Substances	Interference Levels and Treatment
Alkalinity (as CaCO3)	At 5000 mg/L it causes a -0.1 mg/L F– error.
Aluminum	At 0.1 mg/L it causes a -0.1 mg/L F– error. To check for interferences from aluminum, read the concentration one minute after reagent addition, then again after 15 minutes. An appreciable increase in concentration suggests aluminum interference. Waiting 2 hours before making the final reading will eliminate the effect of up to 3.0 mg/L aluminum.
Chloride	At 7000 mg/L it causes a +0.1 mg/L F– error.

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SPADNS Interferences cont.

Interfering Substances	Interference Levels and Treatment
Chlorine	SPADNS Reagent contains enough arsenite to eliminate interference up to 5 mg/L chlorine. For higher chlorine levels, add one drop of Sodium Arsenite Solution (Cat. No. 1047-32) to 25 mL of sample for each 2 mg/L of Chlorine.
Iron, ferric	At 10 mg/L it causes a -0.1 mg/L F– error.
Phosphate, ortho	At 16 mg/L it causes a +0.1 mg/L F– error.
Sodium Hexametaphosphate	At 1.0 mg/L it causes a +0.1 mg/L F– error.

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Electrode

- Calibrate with a 1 mg/L and 10 mg/L
  - Recommended daily
- Mix in TISAB
- Stir sample and measure with electrode
- Less interferences because of TISAB

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Electrode

- Advantages
  - Greater Range, 0.1 – 10.0 mg/L
  - Fewer Interfering Substances
  - Less Susceptible to Technique Errors
- Disadvantages
  - Expensive

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Electrode

- **T**otal **I**onic **S**trength **A**djusting **B**uffer
  - Adjusts pH 5 – 5.5 to optimize fluoride ion availability
  - Adjusts total ionic strength by swamping background
  - Complexes iron & aluminum
  - Contains CDTA – used to sequester interferences

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Total Ionic Strength Adjusting Buffer (TISAB)

- TISAB II
  - Equal parts TISAB & sample
  - Complexes up to 5 mg/L aluminum or iron
    - CDTA

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References

- CDC's Water Fluoridation Principles and Practices for Water Facility Operators
- CDC's Water Fluoridation – A Manual for Water Plant Operators

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Fluoride Lab Math

1. A water plant produces 2,000 gpm, and the city wants to have 1.1mg/L of fluoride in the finished water. If sodium fluorosilicate were used, what would the fluoride feed rate be in lbs/day?

2. If it is known that the plant rate is 4,000 gpm and the dosage needed is 0.8mg/L, what is the fluoride feed rate in lbs/min using fluorosilicic acid?

3. A water plant produces 1.0 MGD. What would the fluoride feed rate be from a saturator in gpd to obtain 1.0mg/L in the water?

4. A plant uses 65lbs of sodium fluorosilicate in treating 5,540,000 gallons of water in one day. What is the calculated dosage in mg/L?

5. A plant uses 10 gallons of sodium fluoride from a saturator in treating 200,000 gallons of water. What is the calculated dosage in mg/L?

1. 44.2 lb/day 2. 0.15 lb/min 3. 55.6 gpd 4. 0.84 mg/L 5. 0.9 mg/L

4500-F^- FLUORIDE*

4500-F^- A. Introduction

Fluoride may occur naturally in water or it may be added in controlled amounts. Some fluorosis may occur when the fluoride level exceeds the recommended limits. In rare instances, the naturally occurring fluoride concentration may approach 10 mg/L.

Accurate determination of fluoride has increased in importance with the growth of the practice of fluoridation of water supplies as a public health measure. Maintenance of an optimal fluoride concentration is essential in maintaining effectiveness and safety of the fluoridation procedure.

1. Preliminary Treatment

Among the methods suggested for determining fluoride ion (F^-) in water, the electrode and colorimetric methods are the most satisfactory. Because both methods are subject to errors due to interfering ions (Table 4500:F^-:I), it may be necessary to distill the sample as directed in 4500-F^-.B before making the determination. When interfering ions are not present in excess of the tolerance of the method, the fluoride determination may be made directly without distillation.

2. Selection of Method

The electrode methods (4500-F^-.C and G) are suitable for fluoride concentrations from 0.1 to more than 10 mg/L. Adding the prescribed buffer frees the electrode method from most interferences that adversely affect the SPADNS colorimetric method and necessitate preliminary distillation. Some substances in industrial wastes, such as fluoborates, may be sufficiently concentrated to present problems in electrode measurements and will not be measured without a preliminary distillation. Fluoride measurements can be made with an ion-selective electrode and either an expanded-scale pH meter or a specific ion meter, usually without distillation, in the time necessary for electrode equilibration.

The SPADNs method (4500-F^-.D) has a linear analytical range of 0 to 1.40 mg F^-/L. Use of a nonlinear calibration can extend the range to 3.5 mg F^-/L. Color development is virtually instantaneous. Color determinations are made photometrically, using either a filter photometer or a spectrophotometer. A curve developed from standards is used for determining the fluoride concentration of a sample.

Fluoride also may be determined by the automated complexone method, 4500-F^-.E.

Table 4500-F^-:I. Concentration of Some Substances Causing 0.1-mg/L Error at 1.0 mg F^-/L in Fluoride Methods

Substance	4500-F^-.C (Electrode) Conc *mg/L*	4500-F^-.C (Electrode) Type of Error*	4500-F^-.D (SPADNS) Conc *mg/L*	4500-F^-.D (SPADNS) Type of Error*
Alkalinity ($CaCO_3$)	7 000	+	5 000	−
Aluminum (Al^{3+})	3.0	−	0.1†	−
Chloride (Cl^-)	20 000		7 000	+
Chlorine	5 000			Remove completely with arsenite
Color & turbidity				Remove or compensate for
Iron	200	−	10	−
Hexametaphosphate ($[NaPO_3]_6$)	50 000		1.0	+
Phosphate (PO_4^{3-})	50 000		16	+
Sulfate (SO_4^{2-})	50 000	−	200	−

* + = positive error
− = negative error
Blank = no measurable error.
† On immediate reading. Tolerance increases with time: after 2 h, 3.0; after 4 h, 30.

Ion chromatography (Section 4110) is an acceptable method if weaker eluents are used to separate fluoride from interfering peaks or fluoride can be determined by capillary ion electrophoresis (Section 4140).

The flow injection method (4500-F^-.G) is a convenient automated technique for analyzing large numbers of samples.

3. Sampling and Storage

Preferably use polyethylene bottles for collecting and storing samples for fluoride analysis. Glass bottles are satisfactory if previously they have not contained high-fluoride solutions. Always rinse bottle with a portion of sample.

For the SPADNs method, never use an excess of dechlorinating agent. Dechlorinate with sodium arsenite rather than sodium thiosulfate when using the SPADNS method because the latter may produce turbidity that causes erroneous readings.

* Approved by Standard Methods Committee, 1997. Editorial revisions, 2011. Joint Task Group: 20th Edition (4500-F^-.G)—Scott Stieg (chair), Bradford R. Fisher, Owen B. Mathre, Theresa M. Wright.

https://doi.org/10.2105/SMWW.2882.081

4500-F⁻ B. Preliminary Distillation Step

1. Discussion

Fluoride can be separated from other nonvolatile constituents in water by conversion to hydrofluoric or fluosilicic acid and subsequent distillation. The conversion is accomplished by using a strong, high-boiling acid. To protect against glassware etching, hydrofluoric acid is converted to fluosilicic acid by using soft glass beads. Quantitative fluoride recovery is approached by using a relatively large sample. Acid and sulfate carryover are minimized by distilling over a controlled temperature range.

Distillation will separate fluoride from most water samples. Some tightly bound fluoride, such as that in biological materials, may require digestion before distillation, but water samples seldom require such drastic treatment. Distillation produces a distillate volume equal to that of the original water sample, so usually it is not necessary to incorporate a dilution factor when expressing analytical results. The distillate will be essentially free of substances that might interfere with the fluoride determination if the apparatus used is adequate and distillation has been carried out properly. The only common volatile constituent likely to cause interference with colorimetric analysis of the distillate is chloride. When the concentration of chloride is high enough to interfere, add silver sulfate to the sulfuric acid distilling mixture to minimize the volatilization of hydrogen chloride.

CAUTION: Heating an acid–water mixture can be hazardous if precautions are not taken: Mix acid and water thoroughly before heating. Use of a quartz heating mantle and a magnetic stirrer in the distillation apparatus simplifies the mixing step.

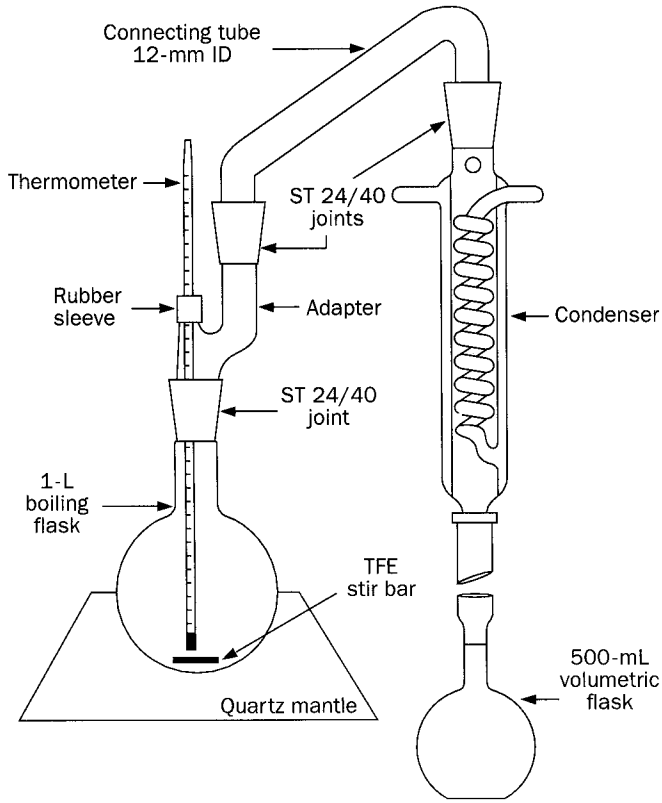

Figure 4500-F⁻:1. Direct distillation apparatus for fluoride.

2. Apparatus

a. Distillation apparatus consisting of a 1-L round-bottom long-neck borosilicate glass boiling flask, a connecting tube, an efficient condenser, a thermometer adapter, and a thermometer that can be read to 200°C. Use standard taper joints for all connections in the direct vapor path. Position the thermometer so the bulb always is immersed in boiling mixture. The apparatus should be disassembled easily to permit adding sample. Substituting a thermoregulator and necessary circuitry for the thermometer is acceptable and provides some automation.

Alternative types of distillation apparatus may be used. Carefully evaluate any apparatus for fluoride recovery and sulfate carryover. The critical points are obstructions in the vapor path and trapping of liquid in the adapter and condenser. (The condenser should have a vapor path with minimum obstruction. A double-jacketed condenser, with cooling water in the outer jacket and the inner spiral tube, is ideal, but other condensers are acceptable if they have minimum obstructions. Avoid using Graham-type condensers.) Avoid using an open flame as a heat source if possible, because heat applied to the boiling flask above the liquid level causes superheating of vapor and subsequent sulfate carryover.

CAUTION: Regardless of apparatus used, provide for thorough mixing of sample and acid; heating a non-homogenous acid–water mixture will result in bumping or possibly a violent explosion.

The preferred apparatus is illustrated in Figure 4500-F⁻:1.

b. Quartz hemispherical heating mantle, for full-voltage operation.

c. Magnetic stirrer, with TFE-coated stirring bar.

d. Soft glass beads.

3. Reagents

a. Sulfuric acid (H_2SO_4), conc, reagent grade.

b. Silver sulfate (Ag_2SO_4), crystals, reagent grade.

4. Procedure

a. Place 400 mL distilled water in the distilling flask and, with the magnetic stirrer operating, carefully add 200 mL conc H_2SO_4. Keep stirrer in operation throughout distillation. Add a few glass beads and connect the apparatus as shown in Figure 4500-F⁻:1, making sure all joints are tight. Begin heating and continue until flask contents reach 180°C (because of heat retention by the mantle, it is necessary to discontinue heating when the temperature reaches 178°C to prevent overheating). Discard distillate. This process removes fluoride contamination and adjusts the acid–water ratio for subsequent distillations.

b. After the acid mixture remaining in the steps outlined in ¶ *a* above, or previous distillations, has cooled to 80°C or below, add 300 mL sample, with stirrer operating, and distill until the temperature reaches 180°C. To prevent sulfate carryover, turn off heat before 178°C. Retain the distillate for analysis.

https://doi.org/10.2105/SMWW.2882.081

c. Add Ag_2SO_4 to the distilling flask at the rate of 5 mg/mg Cl^- when the chloride concentration is high enough to interfere (see Table 4500-F^-:I).

d. Use H_2SO_4 solution in the flask repeatedly until contaminants from samples accumulate to such an extent that recovery is affected or interferences appear in the distillate. Check acid suitability periodically by distilling standard fluoride samples and analyzing for both fluoride and sulfate. After distilling samples containing more than 3 mg F^-/L, flush still by adding 300 mL distilled water, redistill, and combine the two fluoride distillates. If necessary, repeat flushing until the fluoride content of the last distillate is at a minimum. Include additional fluoride recovered with that of the first distillation. After periods of inactivity, similarly flush still and discard distillate.

5. Interpretation of Results

The recovery of fluoride is quantitative within the accuracy of the methods used for its measurement.

6. Bibliography

BELLACK, E. 1958. Simplified fluoride distillation method. *J. Amer. Water Works Assoc.* 50:530.

BELLACK, E. 1961. Automatic fluoride distillation. *J. Amer. Water Works Assoc.* 53:98.

ZEHNPFENNIG, R.G. 1976. Letter to the editor. *Environ. Sci. Technol.* 10:1049.

4500-F^- C. Ion-Selective Electrode Method

1. General Discussion

a. Principle: The fluoride electrode is an ion-selective sensor. The key element in the fluoride electrode is the laser-type doped lanthanum fluoride crystal across which a potential is established by fluoride solutions of different concentrations. The crystal contacts the sample solution at one face and an internal reference solution at the other. The cell may be represented by:

$$\mathrm{Ag}\,|\,\mathrm{AgCl},\ \mathrm{Cl^-}(0.3M),\ \mathrm{F^-}(0.001M)\ |\,\mathrm{LaF_3}\,|\ \text{test solution}\,|\,\text{reference electrode}$$

The fluoride electrode can be used with a standard calomel reference electrode and almost any modern pH meter having an expanded millivolt scale. Calomel electrodes contain both metallic and dissolved mercury; therefore, dispose of them only in approved sites or recycle. For this reason, the Ag/AgCl reference electrode is preferred.

The fluoride electrode measures the ion activity of fluoride in solution rather than concentration. Fluoride ion activity depends on the solution total ionic strength and pH, and on fluoride complexing species. Adding an appropriate buffer provides a nearly uniform ionic strength background, adjusts pH, and breaks up complexes so, in effect, the electrode measures concentration.

b. Interference: Table 4500-F^-:I lists common interferences. Fluoride forms complexes with several polyvalent cations, notably aluminum and iron. The extent to which complexation takes place depends on solution pH, relative levels of fluoride, and complexing species. However, CDTA (cyclohexylenediaminetetraacetic acid), a component of the buffer, preferentially will complex interfering cations and release free fluoride ions. Concentrations of aluminum, the most common interference, up to 3.0 mg/L can be complexed preferentially. In acid solution, F^- forms a poorly ionized HF · HF complex but the buffer maintains a pH above 5 to minimize hydrogen fluoride complex formation. In alkaline solution, hydroxide ion also can interfere with electrode response to fluoride ion whenever the hydroxide ion concentration is greater than one-tenth the concentration of fluoride ion. At the pH maintained by the buffer, no hydroxide interference occurs.

Fluoborates are widely used in industrial processes. Dilute solutions of fluoborate or fluoboric acid hydrolyze to liberate fluoride ion but in concentrated solutions, as in electroplating wastes, hydrolysis does not occur completely. Distill such samples or measure fluoborate with a fluoborate-selective electrode. Also distill the sample if the dissolved solids concentration exceeds 10 000 mg/L.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:I.

2. Apparatus

a. Expanded-scale or digital pH meter or ion-selective meter.

b. Sleeve-type reference electrode: Do not use fiber-tip reference electrodes because they exhibit erratic behavior in very dilute solutions.

c. Fluoride electrode.

d. Magnetic stirrer, with TFE-coated stirring bar.

e. Timer.

3. Reagents

a. Stock fluoride solution: Dissolve 221.0 mg anhydrous sodium fluoride, NaF, in distilled water and dilute to 1000 mL; 1.00 mL = 100 μg F^-.

b. Standard fluoride solution: Dilute 100 mL stock fluoride solution to 1000 mL with distilled water; 1.00 mL = 10.0 μg F^-.

c. Fluoride buffer: Place approximately 500 mL distilled water in a 1-L beaker and add 57 mL glacial acetic acid, 58 g NaCl, and 4.0 g 1,2 cyclohexylenediaminetetraacetic acid (CDTA).* Stir to dissolve. Place beaker in a cool water bath and add slowly 6*N* NaOH (about 125 mL) with stirring, until pH is between 5.0 and 5.5. Transfer to a 1-L volumetric flask and add distilled water to the mark. This buffer, as well as a more concentrated

* Also known as 1,2 cyclohexylenedinitrilotetraacetic acid.

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version, is available commercially. In using the concentrated buffer, follow the manufacturer's directions.

4. Procedure

a. Instrument calibration: No major adjustment of any instrument normally is required to use electrodes in the range of 0.2 to 2.0 mg F^-/L. For those instruments with zero at center scale, adjust calibration control so the 1.0 mg F^-/L standard reads at the center zero (100 mV) when the meter is in the expanded-scale position. This cannot be done on some meters that do not have a millivolt calibration control. To use a selective-ion meter, follow the manufacturer's instructions.

b. Preparation of fluoride standards: Prepare a series of standards by diluting with distilled water 5.0, 10.0, and 20.0 mL of standard fluoride solution to 100 mL with distilled water. These standards are equivalent to 0.5, 1.0, and 2.0 mg F^-/L.

c. Treatment of standards and sample: In 100-mL beakers or other convenient containers, add by volumetric pipet from 10 to 25 mL standard or sample. Bring standards and sample to same temperature, preferably room temperature. Add an equal volume of buffer. The total volume should be sufficient to immerse the electrodes and permit operation of the stirring bar.

d. Measurement with electrode: Immerse electrodes in each of the fluoride standard solutions and measure developed potential while stirring on a magnetic stirrer. Check for air bubbles after immersing electrodes because entrapped air around the crystal can produce erroneous readings or needle fluctuations. Let electrodes remain in the solution 3 min (or until reading is constant) before taking a final millivolt reading. A layer of insulating material between stirrer and beaker minimizes solution heating. Withdraw electrodes, rinse with distilled water, and *blot dry* between readings. (**Caution: Blotting may poison electrode if not done gently.**) Repeat measurements with samples.

When using an expanded-scale pH meter or selective-ion meter, frequently recalibrate the electrode by checking potential reading of the 1.00-mg F^-/L standard and adjusting the calibration control, if necessary, until meter reads as before.

If a direct-reading instrument is not used, plot potential measurement of fluoride standards against concentration on two-cycle semilogarithmic graph paper. Plot milligrams F^- per liter on the logarithmic axis (ordinate), with the lowest concentration at the bottom of the graph. Plot millivolts on the abscissa. From the potential measurement for each sample, read the corresponding fluoride concentration from the standard curve.

The known-additions method may be substituted for the calibration method described. Follow the directions of the instrument manufacturer.

Selective-ion meters may necessitate using a slightly altered procedure, such as preparing 1.00 and 10.0 mg F^-/L standards or some other concentration. Follow the manufacturer's directions. Commercial standards, often already diluted with buffer, frequently are supplied with the meter. Verify the stated fluoride concentration of these standards by comparing them with standards prepared by the analyst.

5. Calculation

$$\text{mg } F^-/\text{L} = \frac{\mu\text{g } F^-}{\text{mL sample}}$$

6. Precision and Bias

A synthetic sample containing 0.850 mg F^-/L in distilled water was analyzed in 111 laboratories by the electrode method, with a relative standard deviation of 3.6% and a relative error of 0.7%.

A second synthetic sample containing 0.750 mg F^-/L, 2.5 mg $(NaPO_3)_6$/L, and 300 mg alkalinity/L added as $NaHCO_3$, was analyzed in 111 laboratories by the electrode method, with a relative standard deviation of 4.8% and a relative error of 0.2%.

A third synthetic sample containing 0.900 mg F^-/L, 0.500 mg Al/L, and 200 mg SO_4^{2-}/L was analyzed in 13 laboratories by the electrode method, with a relative standard deviation of 2.9% and a relative error of 4.9%.

7. Bibliography

Frant, M.S. & J.W. Ross, Jr. 1968. Use of total ionic strength adjustment buffer for electrode determination of fluoride in water supplies. *Anal. Chem.* 40:1169.

Harwood, J.E. 1969. The use of an ion-selective electrode for routine analysis of water samples. *Water Res.* 3:273.

4500-F$^-$ D. SPADNS Method

1. General Discussion

a. Principle: The SPADNS colorimetric method is based on the reaction between fluoride and a zirconium-dye lake. Fluoride reacts with the dye lake, dissociating a portion of it into a colorless complex anion (ZrF_6^{2-}); and the dye. As the amount of fluoride increases, the color produced becomes progressively lighter.

The reaction rate between fluoride and zirconium ions is influenced greatly by the acidity of the reaction mixture. If the proportion of acid in the reagent is increased, the reaction can be made almost instantaneous. Under such conditions, however, the effect of various ions differs from that in the conventional alizarin methods. The selection of dye for this rapid fluoride method is governed largely by the resulting tolerance to these ions.

b. Interference: Table 4500-F$^-$:I lists common interferences. Because these are neither linear in effect nor algebraically additive, mathematical compensation is impossible. Whenever any

one substance is present in sufficient quantity to produce an error of 0.1 mg/L or whenever the total interfering effect is in doubt, distill the sample. Also distill colored or turbid samples. In some instances, sample dilution or adding appropriate amounts of interfering substances to the standards may be used to compensate for the interference effect. If alkalinity is the only significant interference, neutralize it with either hydrochloric or nitric acid. Chlorine interferes and provision for its removal is made.

Volumetric measurement of sample and reagent is extremely important to analytical accuracy. Use samples and standards at the same temperature or at least within 2°C. Maintain constant temperature throughout the color development period. Prepare different calibration curves for different temperature ranges.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:I.

2. Apparatus

Colorimetric equipment: One of the following is required:

a. Spectrophotometer, for use at 570 nm, providing a light path of at least 1 cm.

b. Filter photometer, providing a light path of at least 1 cm and equipped with a greenish yellow filter having maximum transmittance at 550 to 580 nm.

3. Reagents

a. Standard fluoride solution: Prepare as directed in the electrode method, 4500-F⁻.C.3*b*.

b. SPADNS solution: Dissolve 958 mg SPADNS, sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, also called 4,5-dihydroxy-3-(parasulfophenylazo)-2,7-naphthalenedisulfonic acid trisodium salt, in distilled water and dilute to 500 mL. This solution is stable for at least 1 year if protected from direct sunlight.

c. Zirconyl-acid reagent: Dissolve 133 mg zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$, in about 25 mL distilled water. Add 350 mL conc HCl and dilute to 500 mL with distilled water.

d. Acid zirconyl-SPADNS reagent: Mix equal volumes of SPADNS solution and zirconyl-acid reagent. The combined reagent is stable for at least 2 years.

e. Reference solution: Add 10 mL SPADNS solution to 100 mL distilled water. Dilute 7 mL conc HCl to 10 mL and add to the diluted SPADNS solution. The resulting solution, used for setting the instrument reference point (zero), is stable for at least 1 year. Alternatively, use a prepared standard of 0 mg F^-/L as a reference.

f. Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ and dilute to 1 L with distilled water. (**Caution: Toxic—avoid ingestion.**)

4. Procedure

a. Preparation of standard curve: Prepare fluoride standards in the range of 0 to 1.40 mg F^-/L by diluting appropriate quantities of standard fluoride solution to 50 mL with distilled water. Pipet 5.00 mL each of SPADNS solution and zirconyl-acid reagent, or 10.00 mL mixed acid-zirconyl-SPADNS reagent, to each standard and mix well. Avoid contamination. Set photometer to zero absorbance with the reference solution and obtain absorbance readings of standards. Plot a curve of the milligrams fluoride-absorbance relationship. Prepare a new standard curve whenever a fresh reagent is made or a different standard temperature is desired. As an alternative to using a reference, set photometer at some convenient point (0.300 or 0.500 absorbance) with the prepared 0 mg F^-/L standard.

b. Sample pretreatment: If the sample contains residual chlorine, remove it by adding 1 drop (0.05 mL) $NaAsO_2$ solution/0.1 mg residual chlorine and mix. (Sodium arsenite concentrations of 1300 mg/L produce an error of 0.1 mg/L at 1.0 mg F^-/L.)

c. Color development: Use a 50.0-mL sample or a portion diluted to 50 mL with distilled water. Adjust sample temperature to that used for the standard curve. Add 5.00 mL each of SPADNS solution and zirconyl-acid reagent, or 10.00 mL acid-zirconyl-SPADNS reagent; mix well and read absorbance, first setting the reference point of the photometer as above. If the absorbance falls beyond the range of the standard curve, repeat using a diluted sample.

5. Calculation

$$\text{mg } F^-/\text{L} = \frac{A}{\text{mL sample}} \times \frac{B}{C}$$

where:

A = μg F^- determined from plotted curve,
B = final volume of diluted sample, mL, and
C = volume of diluted sample used for color development, mL.

When the prepared 0 mg F^-/L standard is used to set the photometer, alternatively calculate fluoride concentration as follows:

$$\text{mg } F^-/\text{L} = \frac{A_0 - A_x}{A_0 - A_1}$$

where:

A_0 = absorbance of the prepared 0 mg F^-/L standard,
A_x = absorbance of the prepared sample, and
A_1 = absorbance of a prepared 1.0 mg F^-/L standard.

6. Precision and Bias

A synthetic sample containing 0.830 mg F^-/L and no interference in distilled water was analyzed in 53 laboratories by the SPADNS method, with a relative standard deviation of 8.0% and a relative error of 1.2%. After direct distillation of the sample, the relative standard deviation was 11.0% and the relative error 2.4%.

A synthetic sample containing 0.570 mg F^-/L, 10 mg Al/L, 200 mg SO_4^{2-}/L, and 300 mg total alkalinity/L was analyzed in 53 laboratories by the SPADNS method without distillation, with a relative standard deviation of 16.2% and a relative error of 7.0%. After direct distillation of the sample, the relative standard deviation was 17.2% and the relative error 5.3%.

A synthetic sample containing 0.680 mg F^-/L, 2 mg Al/L, 2.5 mg $(NaPO_3)_6$/L, 200 mg SO_4^{2-}/L, and 300 mg total alkalinity/L was analyzed in 53 laboratories by direct distillation and SPADNS methods with a relative standard deviation of 2.8% and a relative error of 5.9%.

7. Bibliography

Bellack, E. & P.J. Schouboe. 1968. Rapid photometric determination of fluoride with SPADNS-zirconium lake. *Anal. Chem.* 30:2032.

https://doi.org/10.2105/SMWW.2882.081

4500-F⁻ E. Complexone Method

1. General Discussion

a. Principle: The sample is distilled in the automated system, and the distillate is reacted with alizarin fluorine blue-lanthanum reagent to form a blue complex that is measured colorimetrically at 620 nm.

b. Interferences: Interferences normally associated with the determination of fluoride are removed by distillation.

c. Application: This method is applicable to potable, surface, and saline waters as well as domestic and industrial wastewaters. The range of the method, which can be modified by using the adjustable colorimeter, is 0.1 to 2.0 mg F^-/L.

d. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:I.

2. Apparatus

An example of the required continuous-flow analytical instrument consists of the interchangeable components in the number and manner indicated in Figure 4500-F^-:2.

3. Reagents

a. Standard fluoride solution: Prepare in appropriate concentrations from 0.10 to 2.0 mg F^-/L using the stock fluoride solution (see 4500-F^-.C.3*a*).

b. Distillation reagent: Add 50 mL conc H_2SO_4 to about 600 mL distilled water. Add 10.00 mL stock fluoride solution (see 4500-F^-.C.3*a*; 1.00 mL = 100 μg F^-) and dilute to 1000 mL.

c. Acetate buffer solution: Dissolve 60 g anhydrous sodium acetate, $NaC_2H_3O_2$, in about 600 mL distilled water. Add 100 mL conc (glacial) acetic acid and dilute to 1 L.

d. Alizarin fluorine blue stock solution: Add 960 mg alizarin fluorine,* $C_{14}H_7O_4 \cdot CH_2N(CH_2 \cdot COOH)_2$, to 100 mL distilled water. Add 2 mL conc NH_4OH and mix until dye is dissolved. Add 2 mL conc (glacial) acetic acid, dilute to 250 mL and store in an amber bottle in the refrigerator.

e. Lanthanum nitrate stock solution: Dissolve 1.08 g $La(NO_3)_3$ in about 100 mL distilled water, dilute to 250 mL, and store in refrigerator.

f. Working color reagent: Mix in the following order: 300 mL acetate buffer solution, 150 mL acetone, 50 mL tertiary butanol, 36 mL alizarin fluorine blue stock solution, 40 mL lanthanum nitrate stock solution, and 2 mL polyoxyethylene 23 lauryl ether.† Dilute to 1 L with distilled water. This reagent is stable for 2 to 4 d.

4. Procedure

No special handling or preparation of sample is required.

Set up manifold as shown in Figure 4500-F^-:2 and follow the manufacturer's instructions.

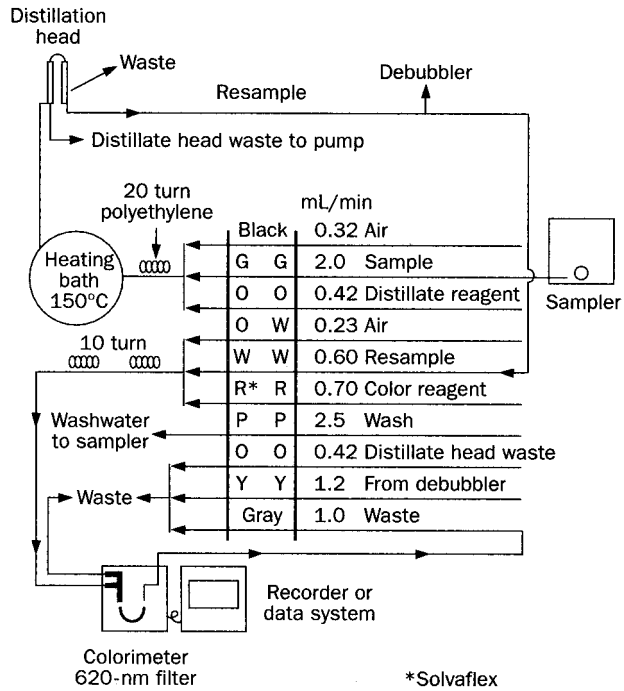


Figure 4500-F^-:2. Fluoride manifold.

5. Calculation

Prepare standard curves by plotting response of standards processed through the manifold against constituent concentrations in standards. Compute sample concentrations by comparing sample response with standard curve.

6. Precision and Bias

In a single laboratory, four samples of natural water containing from 0.40 to 0.82 mg F^-/L were analyzed in septuplicate. Average precision was ± 0.03 mg F^-/L. To two of the samples, additions of 0.20 and 0.80 mg F^-/L were made. Average recovery of the additions was 98%.

7. Bibliography

WEINSTEIN, L.H., R.H. MANDL, D.C. MCCUNE, J.S. JACOBSON & A.E. HITCHCOCK. 1963. A semi-automated method for the determination of fluorine in air and plant tissues. *Boyce Thompson Inst.* 22:207.

* J.T. Baker Catalog No. J-112, or equivalent.
† Brij-35, available from ICI Americas, Wilmington, DE, or equivalent.

https://doi.org/10.2105/SMWW.2882.081

4500-F⁻ F. (Reserved)

4500-F⁻ G. Ion-Selective Electrode Flow Injection Analysis

1. General Discussion

a. Principle: Fluoride is determined potentiometrically by using a combination fluoride-selective electrode in a flow cell. The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions. The reference cell is a Ag/AgCl/Cl^- cell. The reference junction is of the annular liquid-junction type and encloses the fluoride-sensitive crystal.

Also see 4500-F⁻.C and Section 4130, Flow Injection Analysis (FIA).

b. Interferences: Remove large or fibrous particulates by filtering sample through glass wool. Guard against contamination from reagents, water, glassware, and the sample preservation process.

The polyvalent cations Si^{4+}, Al^{3+}, and Fe^{3+} interfere by forming complexes with fluoride. As part of the buffer reagent, 1,2-cyclohexyldiaminetetraacetic acid (CDTA) is added to preferentially complex these cations and eliminate this interference when these concentrations do not exceed 3.0 mg Al^{3+}/L and 20 mg Fe^{3+}/L.

Some interferents are removed by distillation; see 4500-F⁻.B. Drinking water samples generally do not require sample distillation.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:I.

2. Apparatus

Flow injection analysis equipment consisting of:

a. FIA injection valve with sample loop or equivalent.

b. Multichannel proportioning pump.

c. FIA manifold (Figure 4500-F⁻:3) with tubing heater and ion-selective electrode flow cell. In Figure 4500-F⁻:3, relative flow rates only are shown. Tubing volumes are given as an example only; they may be scaled down proportionally. Use manifold tubing of an inert material, such as TFE.

d. Combination ion-selective electrode.

e. Injection valve control and data acquisition system.

3. Reagents

Use reagent water (>10 megohm) for all solutions. To prevent bubble formation, degas carrier and buffer with helium. Pass He at 140 kPa (20 psi) through a helium degassing tube. Bubble He through 1 L solution for 1 min.

a. Carrier, 1.0 mg F⁻/L: Add 10 mL or 10 g stock fluoride standard (¶ *d* below) to 990 mL water and mix well.

b. Buffer: To a tared 1-L polyethylene container add 929.5 g water, 59.8 g glacial acetic acid, 30.0 g sodium hydroxide, NaOH, 58.0 g sodium chloride, NaCl, 0.5 g stock fluoride standard (¶ *d* below), and 4.0 g 1,2-cyclohexyldiaminetetraacetic acid (CDTA) (also called *trans*-1,2-diaminocyclohexane). Stir on a magnetic stir plate until all material has dissolved.

c. Electrode conditioning solution: To a tared 1-L container, add 534 g buffer (¶ *b* above) and 500 g carrier (¶ *a* above). Shake or stir to mix thoroughly. Store fluoride electrode in this solution when it is not in use.

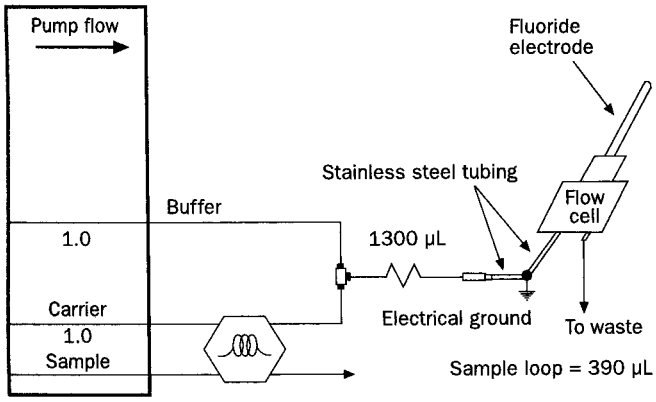


Figure 4500-F⁻:3. FIA fluoride manifold.

d. Stock fluoride standard, 100.0 mg F⁻/L: In a 1-L volumetric flask, dissolve 0.2210 g sodium fluoride, NaF, in approximately 950 mL water. Dilute to mark with water and mix well. Store in a polyethylene bottle.

e. Standard fluoride solutions: Prepare fluoride standards in the desired concentration range, using the stock standard (¶ *d* above), and diluting with water. A blank or zero concentration standard cannot be prepared for this method because it will give an undefined response from the fluoride electrode.

4. Procedure

Set up a manifold equivalent to that in Figure 4500-F⁻:3 and follow method supplied by manufacturer or laboratory standard operating procedure for this method.

5. Calculations

Prepare standard curves by plotting the electrode response to standards processed through the manifold vs. fluoride concentration. Standards greater than 1.0 mg F⁻/L will give positive peaks, standards less than 1.0 mg F⁻/L will give negative peaks, and the 1.0 mg F⁻/L standard having the same concentration as the carrier will give no peak. The calibration curve gives a good fit to a second-order polynomial.

It is not necessary to plot the response versus log[F⁻]; if this is done, the calibration curve will still be a second-order polynomial because there is a concentration-dependent kinetic effect in the flowing stream electrode system.

6. Precision and Bias

The samples used in the studies described below were not distilled.

https://doi.org/10.2105/SMWW.2882.081

a. Recovery and relative standard deviation: The results of single-laboratory studies with various matrices are given in Table 4500-F^-:II.

b. MDL: A 390-μL sample loop was used in the method described above. Ten replicates of a 1.0-mg F^-/L standard were run to obtain an MDL of 0.02 mg F^-/L.

c. Precision: Ten replicate standards of 2.0 mg F^-/L gave a % RSD of 0.5%.

TABLE 4500-F^-:II. RESULTS OF SINGLE-LABORATORY STUDIES WITH SELECTED MATRICES

Matrix	Sample/Blank Designation	Known Addition *mg F^-/L*	Recovery %	Relative Standard Deviation %
Wastewater treatment plant influent	Reference sample*	—	101	—
	Blank†	1.0	91	—
		2.0	97	—
	Site A‡	0	—	4.8
		1.0	93	—
		2.0	82	—
	Site B‡	0	—	6.4
		1.0	96	—
		2.0	86	—
	Site C‡§	0	—	15
		1.0	99	—
		2.0	86	—
Wastewater treatment plant effluent	Reference sample*	—	103	—
	Blank†	1.0	97	—
		2.0	97	—
	Site A‡	0	—	ND
		1.0	ND	—
		2.0	ND	—
	Site B‡	0	—	<0.1
		1.0	80	—
		2.0	78	—
	Site C‡	0	—	<0.1
		1.0	93	—
		2.0	91	—
Landfill leachate‖	Reference sample*	—	99	—
	Blank†	1.0	87	—
		2.0	88	—
	Site A‡	0	—	13
		1.0	74	—
		2.0	68	—
	Site B‡	0	—	10
		1.0	68	—
		2.0	73	—
	Site C‡	0	—	32
		1.0	66	—
		2.0	79	—

ND = not detectable.
* U.S. EPA QC sample, 1.81 mg F^-/L.
† Determined in duplicate.
‡ Samples without known additions determined four times; samples with known additions determined in duplicate. Typical difference between duplicates for influent 5%, for effluent 6%.
§ Mean concentration 0.18 mg F^-/L.
‖ All sites had mean concentration of <0.2 mg F^-/L.

https://doi.org/10.2105/SMWW.2882.081

Fluoride

USEPA SPADNS 2 Method[1]

Method 10225

0.02 to 2.00 mg/L F^-

Reagent Solution or AccuVac® Ampuls

Scope and application: For water, wastewater and seawater; USEPA accepted for reporting for drinking and wastewater analyses (distillation required).[2]

[1] Adapted from Standard Methods for the Examination of Water and Wastewater, 4500-F B & D.
[2] Procedure is equivalent to USEPA Method 340.1 for drinking water and wastewater.

Test preparation

Instrument-specific information

Table 1 shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests. Table 2 shows sample cell and adapter requirements for AccuVac Ampul tests. The tables also show all of the instruments that have the program for this test.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information for reagent addition

Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700 DR 1900	The fill line is to the right.	2495402
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The fill line is toward the user.	2401906

Table 2 Instrument-specific information for AccuVac Ampuls

Instrument	Adapter
DR 6000 DR 5000 DR 900	—
DR 3900	LZV846 (A)
DR 3800 DR 2800 DR 2700	LZV584 (C)
DR 1900	9609900 or 9609800 (C)

Before starting

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
The sample and deionized water must be at the same temperature (±1 °C). Temperature adjustments can be made before or after the reagent addition.
Measure the volume of the reagent accurately. Use a volumetric or high precision pipet if possible.
If the test result is over-range, dilute a fresh sample with a known volume of deionized water and do the test again. Multiply the result by the dilution factor.
Minor variations between lots of reagent become measurable above 1.5 mg/L. While results above 1.5 mg/L are usable for most purposes, for the best accuracy dilute the sample to a lower concentration.
The SPADNS 2 Reagent contains a non-toxic reducing agent to prevent chlorine interference. SPADNS 2 Reagent does not contain sodium arsenite.
The reagent that is used in this test is corrosive. Use protection for eyes and skin and be prepared to flush any spills with running water.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Reagent solution test

Description	Quantity
Pipet filler, safety bulb	1
Pipet, volumetric, Class A, 2.00-mL	1
Pipet, volumetric, Class A, 10.00-mL	1
SPADNS 2 Reagent Solution	4 mL
Thermometer	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific table PPAV.)	2
Water, deionized	10 mL

Refer to Consumable and replacement items on page 6 for order information.

AccuVac Ampuls

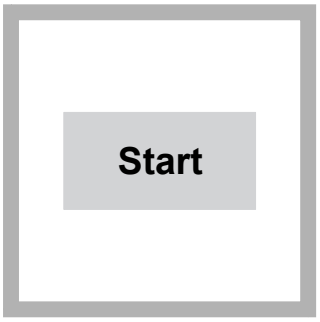
Description	Quantity
Beaker, 50-mL	1
SPADNS 2 Fluoride Reagent AccuVac® Ampuls	1
Stoppers, for 18-mm tubes and AccuVac Ampuls	2
Water, deionized	40 mL

Refer to Consumable and replacement items on page 6 for order information.

Sample collection and storage

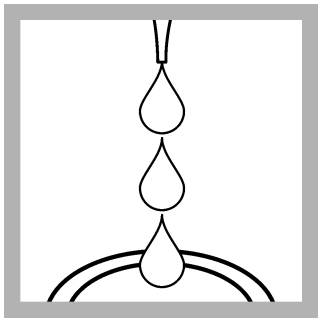
- Collect samples in clean glass or plastic bottles.
- Samples can be kept for up to 28 days.
- Let the sample temperature increase to room temperature before analysis.

Reagent solution test

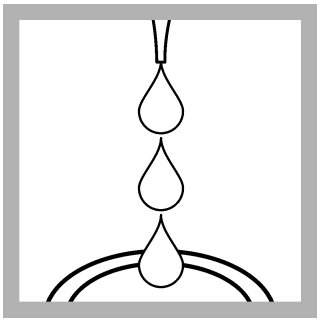


1. Start program **190 Fluoride**. For information about sample cells, adapters or light shields, refer to Instrument-specific table PPAV.

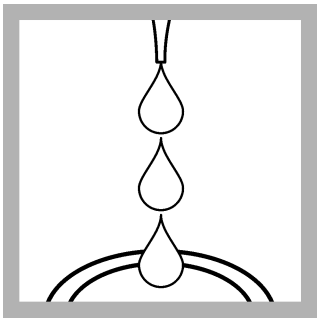
Note: *Although the program name can be different between instruments, the program number does not change.*



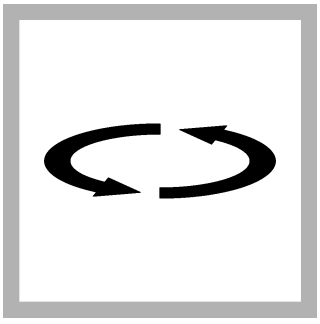
2. Prepare the sample: Use a pipet to add 10.0 mL of sample to a dry sample cell.



3. Prepare the blank: Use a pipet to add 10.0 mL of deionized water to a dry sample cell.

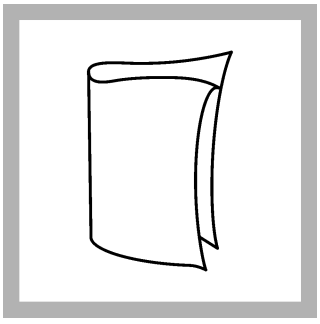


4. Use a pipet to add 2.0 mL of SPADNS 2 reagent to each cell.

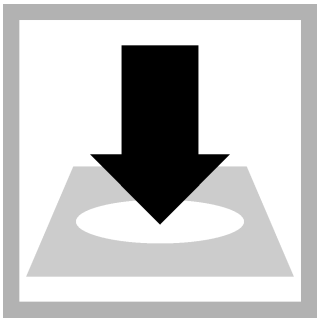


5. Swirl to mix.

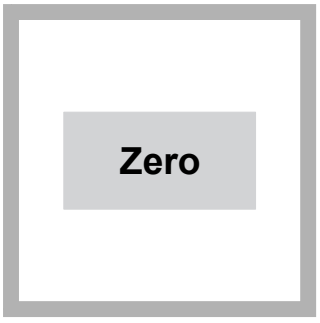
6. Start the instrument timer. A 1-minute reaction time starts.



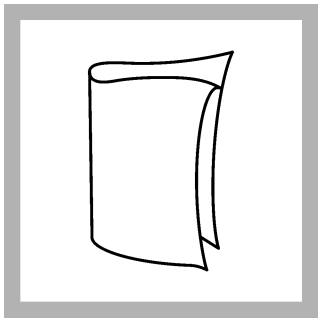
7. When the timer expires, clean the blank sample cell.



8. Insert the blank into the cell holder.



9. Push **ZERO**. The display shows 0.00 mg/L F^-.

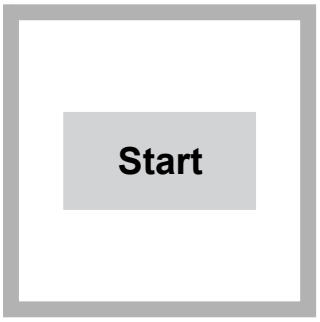


10. Clean the prepared sample cell.

11. Insert the prepared sample into the cell holder.

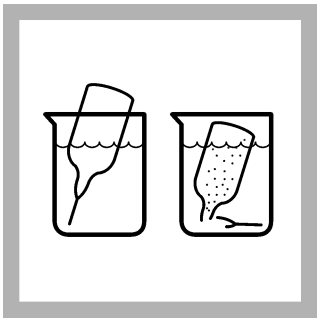
12. Push **READ**. Results show in mg/L F^-.

AccuVac Ampul test

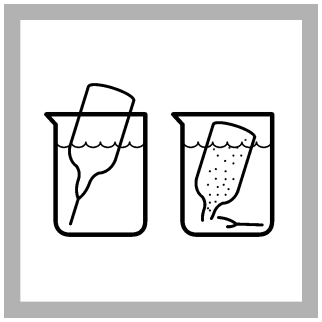


1. Start program **195 Fluoride AV**. For information about sample cells, adapters or light shields, refer to Instrument-specific table PPAV.

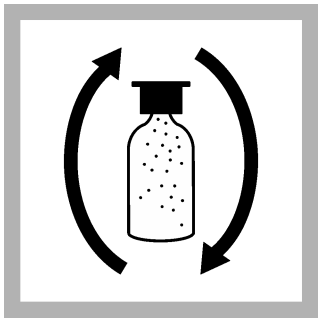
Note: *Although the program name can be different between instruments, the program number does not change.*



2. Prepare the sample: Collect at least 40 mL of sample in a 50-mL beaker. Fill the AccuVac Ampul with sample. Keep the tip immersed while the AccuVac Ampul fills completely.

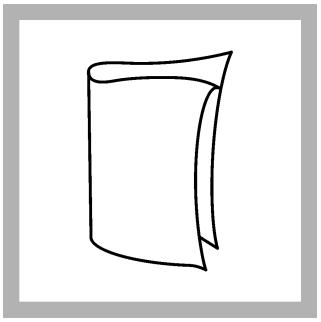


3. Prepare the blank: Pour at least 40 mL of deionized water into a 50-mL beaker. Fill an AccuVac Ampul with deionized water. Keep the tip immersed while the AccuVac Ampul fills completely.

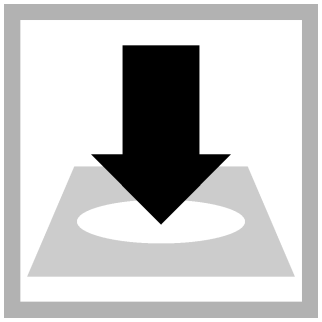


4. Quickly invert the AccuVac Ampuls several times to mix.

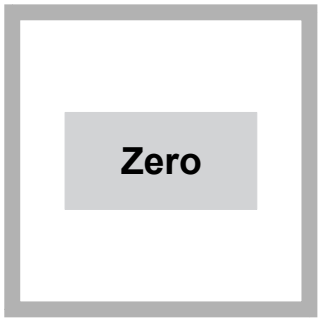
5. Start the instrument timer. A 1-minute reaction time starts.



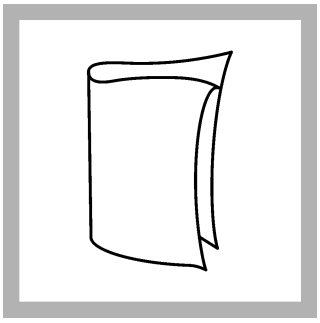
6. When the timer expires, clean the blank AccuVac Ampul.



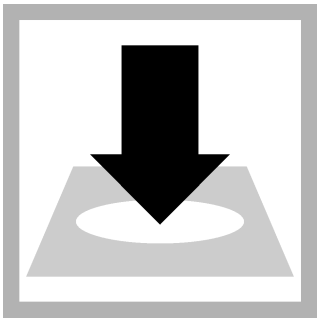
7. Insert the blank AccuVac Ampul into the cell holder.



8. Push **ZERO**. The display shows 0.00 mg/L F^-.



9. Clean the AccuVac Ampul.



10. Insert the prepared sample AccuVac Ampul into the cell holder.

11. Push **READ**. Results show in mg/L F^-.

Interferences

This test is sensitive to small amounts of contamination. Glassware must be very clean (acid rinse before each use). Repeat the test with the same glassware to make sure that the results are accurate.

Interfering substance	Interference level
Alkalinity (as $CaCO_3$)	At 5000 mg/L, it causes a –0.1 mg/L F^- error.
Aluminum	At 0.1 mg/L, it causes a –0.1 mg/L F^- error. To find whether there is an aluminum interference, read the concentration 1 minute after reagent addition, then again after 15 minutes. An appreciable increase in concentration suggests aluminum interference. To remove the effect of up to 3.0 mg/L aluminum, wait 2 hours, then take the final reading.
Chloride	At 7000 mg/L, it causes a +0.1 mg/L F^- error.
Chlorine	SPADNS 2 Reagent contains enough non-toxic reductant to remove interference of up to 5 mg/L chlorine. For higher chlorine levels: **1.** Dilute the sample with deionized water by a factor that will lower the chlorine concentration to below 5 mg/L. **2.** Use the test procedure to measure the fluoride concentration. **3.** Multiply the result by the dilution factor to get mg/L fluoride.
Iron, ferric	At 10 mg/L, it causes a –0.1 mg/L F^- error.
Phosphate, ortho	At 16 mg/L, it causes a +0.1 mg/L F^- error.
Sodium hexametaphosphate	At 1.0 mg/L, it causes a +0.1 mg/L F^- error.
Sulfate	At 200 mg/L, it causes a +0.1 mg/L F^- error.

Distillation

To eliminate most interferences, distill the sample, then use the distilled sample in the test procedure.

Prerequisite—prepare the distillation solution:

1. Measure 60 mL of deionized water into a 250-mL, glass Erlenmeyer flask.
2. With constant stirring, add 120 mL of concentrated sulfuric acid. **Caution: The mixture will become very hot. Put the flask in an ice bath to decrease the temperature of the solution.**

Distillation procedure:

1. Set up the distillation apparatus for general purpose distillation. Refer to the Distillation Apparatus manual for proper assembly.
2. Set up a 125-mL Erlenmeyer flask to collect the distillate.
3. Turn on the water and adjust to maintain a steady flow through the condenser.
4. Use a 100-mL graduated cylinder to add 100 mL of sample into the distillation flask.
5. Add a magnetic stir bar and 5 glass beads.
6. Set the stirrer power to on. Set the stir control to 5.
7. Use a 250-mL graduated cylinder to carefully add 150 mL of distillation solution into the flask.

   Note: *For samples with large amounts of chloride, add 5 mg of silver sulfate to the sample for every mg/L of chloride in the sample.*
8. With the thermometer inserted, set the heat control to 10. The yellow pilot lamp is an indication that the heater is on.
9. When the temperature is 180 °C (356 °F) or when 100 mL of distillate has been collected, turn the still off (takes about 1 hour).
10. Dilute the distillate to a volume of 100 mL, if necessary. Use the diluted distillate in the test procedure.

Accuracy check

Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

Items to collect:

- Standard solution within the test range.

1. Use the test procedure to measure the concentration of the standard solution.
2. Compare the expected result to the actual result.

   Note: *The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are slight variations in the reagents or instruments.*

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% Confidence Interval)	Sensitivity Concentration change per 0.010 Abs change
190	1.00 mg/L F^-	0.97–1.03 mg/L F^-	0.024 mg/L F^- at 1 mg/L
195	1.00 mg/L F^-	0.92–1.08 mg/L F^-	0.03 mg/L F^- at 1 mg/L

Summary of method

The SPADNS 2 Method for fluoride determination involves the reaction of fluoride with a red zirconium-dye solution. The fluoride combines with part of the zirconium to form a colorless complex that bleaches the red color in an amount proportional to the fluoride concentration. This method is equivalent to the EPA method for NPDES and NPDWR reporting purposes when the samples have been distilled. Seawater and wastewater samples require distillation. The measurement wavelength is 580 nm for spectrophotometers or 610 nm for colorimeters.

Consumable and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
SPADNS 2 Reagent Solution	4 mL	500 mL	2947549
OR			
SPADNS 2 Fluoride Reagent AccuVac® Ampuls	2	25/pkg	2527025
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity/Test	Unit	Item no.
Pipet filler, safety bulb	1	each	1465100
Pipet, volumetric, Class A, 2.00-mL	1	each	1451536
Pipet, volumetric, Class A, 10.00-mL	1	each	1451538
Thermometer	1	each	2635700
Beaker, 50-mL	1	each	50041H
Stoppers for 18-mm tubes and AccuVac Ampuls	2	6/pkg	173106

Recommended standards

Description	Unit	Item no.
Fluoride Standard Solution, 0.2-mg/L F^-	500 mL	40502
Fluoride Standard Solution, 0.5-mg/L F^-	500 mL	40505
Fluoride Standard Solution, 0.8-mg/L F^-	500 mL	40508
Fluoride Standard Solution, 1.0-mg/L F^-	1000 mL	29153
Fluoride Standard Solution, 1.0-mg/L F^-	500 mL	29149
Fluoride Standard Solution, 1.2-mg/L F^-	500 mL	40512
Fluoride Standard Solution, 1.5-mg/L F^-	500 mL	40515
Fluoride Standard Solution, 2.0-mg/L F^-	500 mL	40520
Fluoride Standard Solution, 100-mg/L F^-	500 mL	23249
Drinking Water Standard, Mixed Parameter, Inorganic for F^-, NO_3–N, PO_4^{3-}, SO_4^{2-}	500 mL	2833049

Distillation reagents and apparatus

Description	Unit	Item no.
Graduated cylinder, 100-mL	each	50842
Graduated cylinder, 250-mL	each	50846
Distillation apparatus set, general purpose	each	2265300
Distillation heater and support for apparatus set, 115 VAC option	each	2274400
Distillation heater and support for apparatus set, 230 VAC option	each	2274402
Flask, Erlenmeyer, 125-mL	each	2089743
Flask, Erlenmeyer, 250-mL	each	50546
Glass beads	100/pkg	259600
Stir bar, magnetic	each	1076416
Sulfuric Acid, ACS	500 mL	97949

Optional reagents and apparatus

Description	Unit	Item no.
Silver Sulfate	113 g	33414
Balance, analytical, 80 g x 0.1 mg 100–240 VAC	each	2936701
Paper, for weighing, 100 x 100 mm	500/pkg	1473885

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Fluoride

Direct ISE Method

Method 8323

0.1 to 10.0 mg/L F^-

Fluoride ISE

Scope and application: For drinking water[1] and wastewater[2].

[1] The equipment that is specified in this method meets the requirements of the approved EPA Reference Method for NPDWR reporting. Users with NPDWR permits must follow and make a reference to the EPA Reference Method.
[2] This method is USEPA Equivalent for wastewater and can be used for NPDES reporting.

Test preparation

Instrument-specific information

This procedure is applicable to the meters and probes that are shown in Table 1. Procedures for other meters and probes can be different.

Table 1 Instrument-specific information

Meter	Probe
HQ30d portable single input, multi-parameter HQ40d portable dual input, multi-parameter HQ430d benchtop single input, multi-parameter HQ440d benchtop dual input, multi-parameter	IntelliCAL ISEF121 combination fluoride ISE
sensION™+ MM340 lab dual input, pH/mV/ISE sensION™+ MM374 lab dual input, pH/mV/EC/ISE sensION™+ MM378 lab dual input, pH/ISE/EC/DO	sensION+ 9655C combination fluoride ISE
	sensION+ 9655 half-cell fluoride ISE with sensION+ 5044 double junction reference electrode

Before starting

Refer to the meter documentation for meter settings and operation. Refer to probe documentation for probe preparation, maintenance and storage information.
Prepare the probe before initial use. Refer to probe documentation.
When an IntelliCAL™ probe is connected to an HQd meter, the meter automatically identifies the measurement parameter and is prepared for use.
Condition the probe before use. To condition the probe, put the probe in 100 mL of the lowest concentration standard solution for a maximum of 1 hour.
Calibrate the probe before initial use. Refer to Calibration procedure on page 3.
During calibration, measure the standard solutions from lowest to highest concentration for best results.
For USEPA reporting, use fluoride standard solutions of 0.5-mg/L, 1.0-mg/L and 2.0-mg/L to calibrate the electrode.
Make sure that the calibration solutions and the samples are at the same temperature (± 2 °C (± 3.6 °F)) for best results.
Stir the standards and samples at a slow and constant rate to prevent the formation of a vortex.
Air bubbles under the sensor tip can cause slow response or measurement errors. To remove the bubbles, carefully shake the probe.
Small differences in concentration between samples can increase the stabilization time. Make sure to condition the probe correctly. Try different stir rates to see if the stabilization time decreases.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.

Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.
This procedure is specified for the HQd meters. The sensION+ meters can be used, but the menus and navigation will be different.

Items to collect

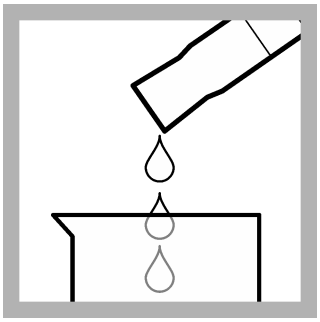
Description	Quantity
Fluoride ISA (TISAB)—powder pillow or solution (1 pillow or 5.0 mL per 25 mL solution)	1
Fluoride Standard Solutions, 1.00 and 10.0 mg/L or 0.5, 1.00 and 2.00 mg/L (USEPA)	varies
Beaker, polypropylene, 50 mL, low form	3 or 4 (USEPA)
Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.)	3 or 4 (USEPA)
Stirrer, magnetic	1
Wash bottle with deionized water	1
Lint-free cloth	1

Refer to Consumables and replacement items on page 6 for order information.

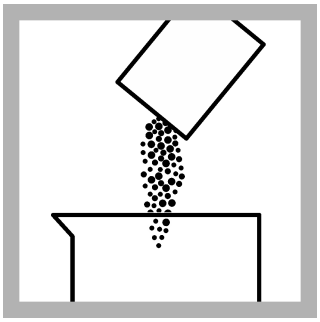
Sample collection

- Collect samples in clean polyethylene bottles.
- If immediate analysis is not possible, keep the samples at room temperature for a maximum of 28 days.

Test procedure

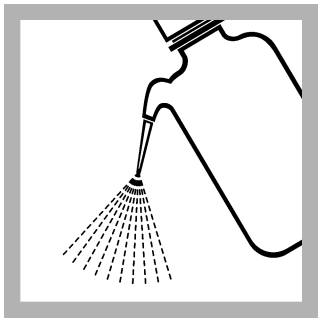


1. Add 25 mL of sample to a beaker.

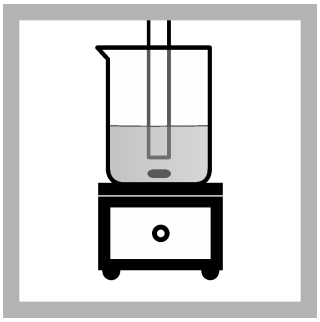


2. Add the contents of one Fluoride ISA Powder Pillow. ***Note:*** *As an alternative, add 5 mL of Fluoride ISA Solution.*

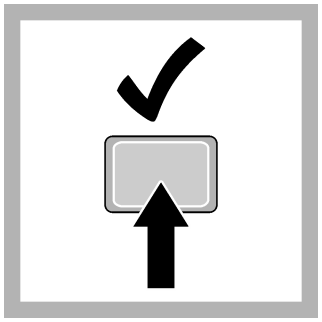
3. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



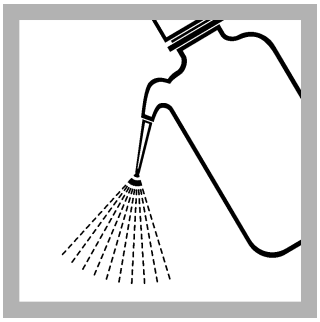
4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



5. Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.

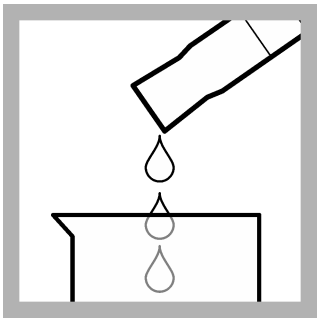


6. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.

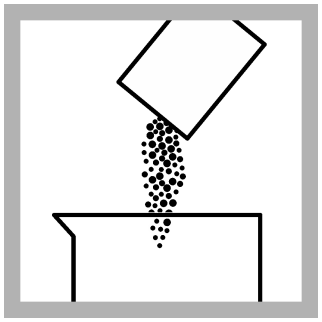


7. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

Calibration procedure

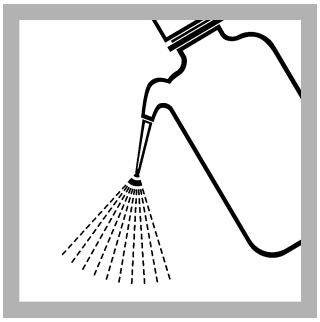


1. Add 25 mL of the lowest concentration standard solution to a beaker.

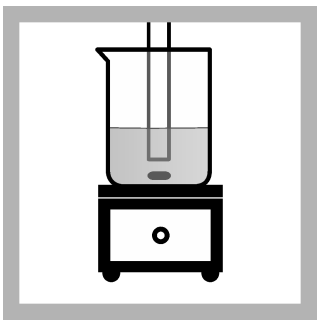


2. Add the contents of one Fluoride ISA Powder Pillow. ***Note:*** *As an alternative, add 5 mL of Fluoride ISA Solution.*

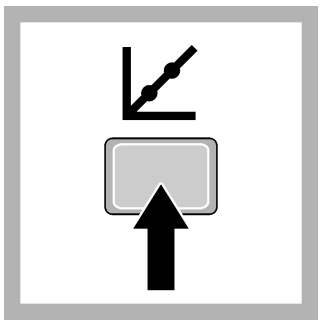
3. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



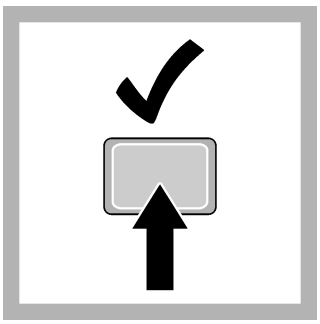
4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



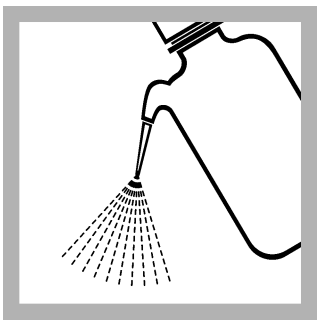
5. Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.



6. Push **Calibrate**. The standard solution value is shown.

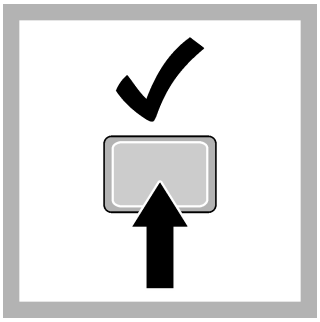


7. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.

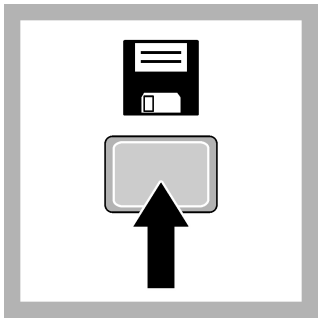


8. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

9. Measure the remaining standard solutions.



10. Push **Done**. A calibration summary is shown when the minimum number of calibration standards are measured.



11. Push **Store** to accept the calibration.

Low-level measurements

Use the techniques that follow for measurements at low concentrations (<1 mg/L).

- Use plastic containers during calibration and measurements. Glass containers can cause inaccurate measurements.
- Clean the probe regularly. Refer to Clean the probe on page 5.
- Soak the probe in the lowest concentration standard solution for a maximum of 1 hour before calibration and measurement.
- Set the stability criteria in the settings menu to a low value (for applicable meters and probes).
- Use a dilute ionic strength adjustor (ISA) solution for calibration and measurements:

  1. Dissolve the contents of one ionic strength adjustor powder pillow in 50 mL of deionized water.
  2. Add 5 mL of this solution to every 25 mL of standard or sample that is used.

  Note: *The use of the ISA is optional when the conditions that follow are true:*

  - *The sample does not contain interferences.*
  - *The sample pH is in the range that is given in the electrode specifications.*
  - *Omission of the ISA is accepted by the regulatory reporting agency (if applicable).*

Interferences

Interfering substance	Interference level
Cations	Do not interfere.
Cl^-, Br^-, SO_4^{2-}, HCO_3^-, PO_4^{3-}, acetate	Do not interfere.
OH^- (hydroxyl ions)	Interferes when the sample pH is 8 or more. The ISA adjusts the sample pH to 5.0–5.5.
CO_3^{2-} or PO_4^{3-}	Do not interfere but can increase the OH^- interference.

Accuracy check

Slope method

Use the slope method to validate the electrode response.

1. Prepare two standard solutions that are one decade apart in concentration (e.g., 1 mg/L and 10 mg/L or 10 mg/L and 100 mg/L). The minimum concentration is 0.2 mg/L.
2. Use the test procedure to measure the mV value of each standard solution.
3. Compare the mV value of each standard solution. The expected difference is 58 (± 3) mV at 25 °C (77 °F).

Standard solution method

Use the standard solution method to validate the test procedure, the reagents (if applicable) and the instrument.

Items to collect:

- Standard solution within the test range

1. Use the test procedure to measure the concentration of the standard solution.
2. Compare the expected result to the actual result.

Standard additions method

Use the standard additions method to validate the test procedure, reagents and instrument and to find if there is an interference in the sample.

Items to collect:

- Fluoride Standard Solution, 100-mg/L
- Graduated cylinder, 25-mL, polypropylene
- TenSette pipet
- Pipet tips

1. Use a graduated cylinder to measure 25 mL of sample into a beaker.
2. Use the test procedure to measure the concentration of the sample.
3. Use the TenSette pipet to add 0.5 mL of the standard solution to the sample.
4. Measure the concentration of the spiked sample.
5. Compare the results before and after the standard solution addition. The concentration should increase by 1.96 mg/L F^-.

Temperature check

For probes that do not have a temperature sensor, measure the temperature of the standard solutions and samples. Make sure that the calibration solutions and the samples are at the same temperature (± 2 °C (± 3.6 °F)) for best results.

Clean the probe

Clean the probe when:

- Drifting/inaccurate readings occur as a result of contamination on the sensing element or incorrect storage conditions.
- Slow response time occurs as a result of contamination on the sensing element.
- The slope is out of range as a result of contamination on the sensing element.

For general contamination, complete the steps that follow.

1. Rinse the probe with deionized water. Blot dry with a lint-free cloth.
2. If harsh contaminants are attached to the probe, use a small amount of plain fluoride toothpaste on a soft toothbrush or cloth (no teeth whiteners or abrasives) and gently rub it into the crystal with a circular motion. Continue to rub until the toothpaste film is removed. When finished, rinse with deionized water to clean the probe.
3. Soak for 30 minutes in 1 mg/L Fluoride Standard Solution.

Method performance

The method performance data that follows was derived from laboratory tests during ideal test conditions. Users can get different results under different test conditions.

System	Standard	Precision (95% confidence interval)
HQd meter and ISEF121 ISE probe	1.00 mg/L	± 0.01 mg/L
sensION+ meter and 9655C/9655 ISE probe	1.00 mg/L	± 0.01 mg/L

Summary of method

The fluoride electrode consists of a sensing Lanthanum Fluoride element bonded into an epoxy body. When the sensing element contacts fluoride ions in a solution, a potential develops across the sensing element. The potential is proportional to the level of fluoride ions in the sample. The potential is measured against a constant reference potential with a pH/mV meter or ISE meter.

Consumables and replacement items

HQd meters and probes

Description	Unit	Item no.
HQ30d portable single input, multi-parameter meter	each	HQ30D53000000
HQ40d portable dual input, multi-parameter meter	each	HQ40D53000000
HQ430d benchtop single input, multi-parameter meter	each	HQ430D
HQ440d benchtop dual input, multi-parameter meter	each	HQ440D
IntelliCAL™ ISEF121 digital combination fluoride ISE probe, 1 m cable	each	ISEF12101
IntelliCAL™ ISEF121 digital combination fluoride ISE probe, 3 m cable	each	ISEF12103

sensION+ meters and probes

Description	Unit	Item no.
sensION™+ MM340 lab dual input, pH/mV/ISE meter	each	LPV2200.97.0002
sensION™+ MM374 lab dual input, pH/mV/EC/ISE meter	each	LPV4110.97.0002
sensION™+ MM378 lab dual input, pH/ISE/EC/DO meter	each	LPV4130.97.0002
sensION™+ 9655C combination fluoride ISE probe	each	LZW9655C.97.002
sensION™+ 9655 fluoride half-cell ISE probe	each	LZW9655.97.0002
sensION™+ 5044 reference electrode	each	LZW5044.97.0002

Recommended reagents and standards

Description	Unit	Item no.
Fluoride Ionic Strength Adjustor (ISA) Powder Pillows	100/pkg	258999
Fluoride Ionic Strength Adjustor (ISA) Solution	3.78 L	2829017
Fluoride Standard Solution, 0.5-mg/L F^-	500 mL	40505
Fluoride Standard Solution, 1.0-mg/L F^-	500 mL	29149
Fluoride Standard Solution, 2.0-mg/L F^-	500 mL	40520
Fluoride Standard Solution, 5.0-mg/L F^-	500 mL	2797149
Fluoride Standard Solution, 10-mg/L F^-	500 mL	35949

Accessories

Description	Unit	Item no.
Beaker, polypropylene, 50 mL, low form	each	108041
Bottle, wash, 500 mL	each	62011
Graduated cylinder, polypropylene, 25 mL	each	108140
Pipet, TenSette®, 0.1–1.0 mL	each	1970001

Accessories (continued)

Description	Unit	Item no.
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Probe clips, color-coded, for IntelliCAL probes	50/pkg	5818400
Probe holder, 3 probes, for sensION+ benchtop meters	each	LZW9321.99
Probe stand, universal	each	8508850
Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.)	each	4531500
Stirrer, electromagnetic, 120 VAC, with electrode stand	each	4530001
Stirrer, electromagnetic, 230 VAC, with electrode stand	each	4530002

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Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

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WORLD HEADQUARTERS
Telephone: (970) 669-3050
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TNT 878 Fluoride

0.1–2.5 mg/L F^-

TNTplus®—Method 10275

Scope and application: For water, wastewater and seawater. USEPA accepted for reporting for drinking and wastewater analyses (distillation required). Procedure is equivalent to USEPA Method 340.1 for drinking water and wastewater.

Test preparation

Reagent storage

Storage temperature: 15–25 °C (59–77 °F)

pH/Temperature

The pH of the water sample must be between pH 1–11.

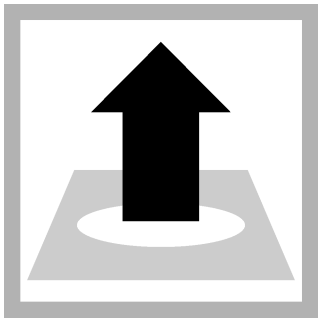
The temperature of the water sample and reagents must be 20 °C (68 °F).

Before starting

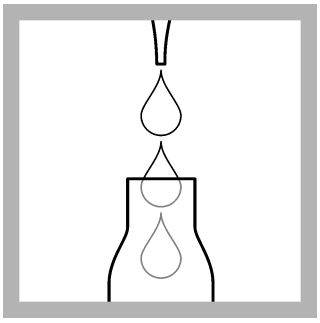
In case of not working at the correct recommended temperature an incorrect result may be obtained.
Measurements can be made at aluminium concentrations of more than 0.1 mg/L if the vial is allowed to stand after the reaction until there is no change in the measured value.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment. Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.
Review safety information and expiration date on the package.

Procedure

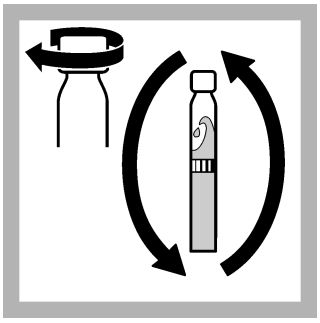
1. Insert the vial into the cell holder.
DR 1900: Select the test, push **READ 1**.



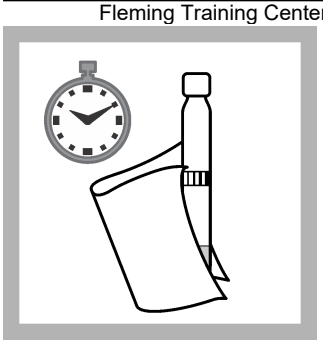
2. Remove the vial.



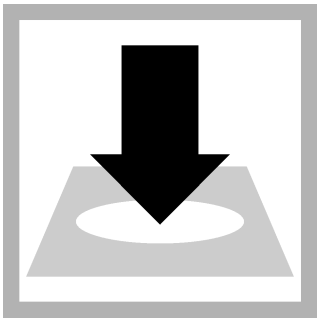
3. Carefully pipet **3.0 mL** of **sample**.



4. Close the vial and invert a few times.



5. After **1 minute**, thoroughly clean the outside of the vial and evaluate.



6. Insert the vial into the cell holder.
DR 1900: Push **READ 2**.

Interferences

The ions listed in the table have been individually checked against the given concentrations and do not cause interference. The cumulative effects and the influence of other ions have not been determined.

The measurement results must be subjected to plausibility checks (dilute and/or spike the sample).

Interference level	Interfering substance
7000 mg/L	Cl^-
200 mg/L	SO_4^{2-}
35 mg/L	Cl_2
30 mg/L	Mn^{2+}
16 mg/L	PO_4^{3-}
10 mg/L	Fe^{2+}, Fe^{3+}
1 mg/L	Sodium metaphosphate
0.1 mg/L	Al^{3+}

Summary of method

Fluoride ions react with zirconium to form a colorless zirconium fluoride complex. This causes the red zirconium lake which is present to lose color.

TNTplus®

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Fluoride Bench Sheet

	Tap	A	B
Probe			
SPADNS 2			

Section 3

Carbon Dioxide

CO_2 Analysis

Fleming Training Center

TN Department of Environment & Conservation

1

CO_2 Analysis

- Surface waters normally contain less than 10 mg/L free carbon dioxide (CO_2)
  - Some ground waters may easily exceed that concentration
- CO_2 content of water may contribute significantly to corrosion
- Recarbonation of a supply during the last stages of water softening is a recognized treatment process

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2

Titrimetric Method for Free Carbon

- Principle:
  - Carbon reacts with sodium carbonate or sodium hydroxide to form sodium bicarbonate
- Completion of reaction indicated by:
  - pH end point OR
  - pink color change if using phenolphthalein indicator
- A 0.01N sodium bicarbonate solution is a suitable color standard

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3

Sampling & Storage

- Until tested, keep sample at a temperature lower than that at which water was collected
- Make laboratory examination as soon as possible to minimize the effect of CO_2 changes
- Some loss is to be expected in storage & transit

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4

Titration using Phenolphthalein

- Reagents
  - Sodium Hydroxide titrant, 0.1N
  - Phenolphthalein indicator solution, pH 8.3 indicator
  - Sodium thiosulfate, 0.1 M
- Apparatus
- Titration vessel

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5

Titration using Phenolphthalein

- Procedure:
  - Adjust sample to room temperature, if necessary
  - If free residual chlorine is present add 0.05mL (1 drop) 0.1M sodium thiosulfate
  - Add 0.2mL (5 drops) indicator solution & titrate over a white surface to a persistent color change characteristic of the equivalence point

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6

Calculation

- mg/L CO_2 = $\frac{A \times N \times 44{,}000}{\text{mL sample}}$

- where: A = mL titrant
  N = normality of NaOH

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7

Carbon Dioxide

Sodium Hydroxide Method — Method 8223

0 to 250 mg/L CO_2 — Buret Titration

Scope and application: For water and seawater.

Test preparation

Before starting

To prevent agitation of the sample, pour the sample directly into the Erlenmeyer flask. As a reference, fill a graduated cylinder with the sample volume of deionized water or sample. Pour the water into the Erlenmeyer flask. Make a mark on the Erlenmeyer flask at the water level to identify the sample volume level.
As an alternative to the Phenolphthalein Indicator Powder Pillow, use 4 drops of Phenolphthalein Indicator Solution.
Color or turbidity in the sample can make it difficult to see the color change at the endpoint. For these samples, use a pH meter to determine the titration endpoint. The endpoint for phenolphthalein acidity is pH 8.3.
The optional TitraStir Titration Stand can hold the buret and stir the sample.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

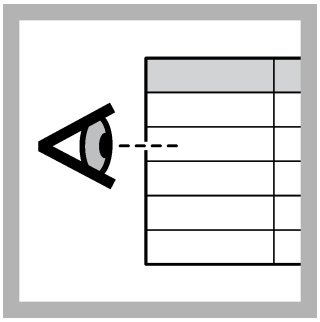
Description	Quantity
Phenolphthalein Indicator Powder Pillow	1
Sodium Hydroxide Standard Solution, 0.0227 N	varies
pH meter and probe (for samples that have a lot of color or turbidity)	1
Buret, Class A, 25 mL	1
Graduated cylinder (use a size that is applicable to the selected sample volume), or TenSette pipet with tips	1
Erlenmeyer flask, 250 mL	1
Funnel, micro	1
Support stand with buret clamp	1
Water, deionized	varies

Refer to Consumables and replacement items on page 3 for order information.

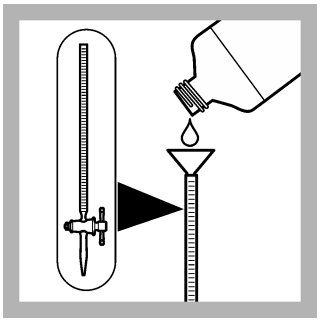
Sample collection

- Collect samples in clean glass or plastic bottles with tight-fitting caps. Completely fill the bottle and immediately tighten the cap.
- Prevent agitation of the sample and exposure to air.
- Analyze the samples as soon as possible for best results.
- If immediate analysis is not possible, keep the samples at or below 6 °C (43 °F) for a maximum of 24 hours.
- Let the sample temperature increase to room temperature before analysis.

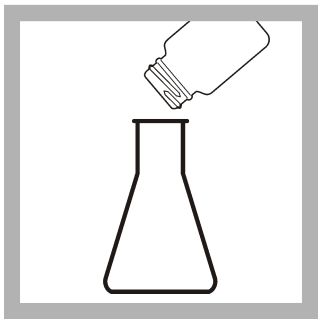
Test procedure



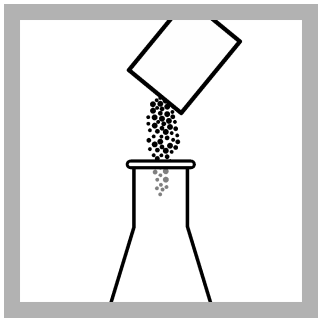
1. Select a sample volume, titrant and flask from Table 1 on page 2.



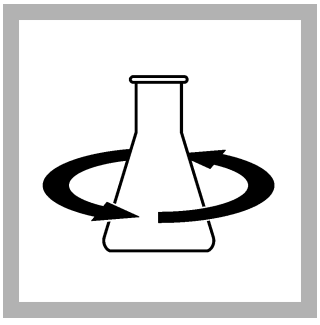
2. Fill a 25-mL buret to the zero mark with the titrant.



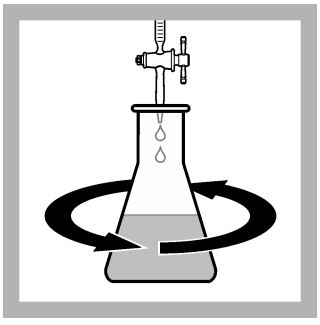
3. Pour the sample volume in Table 1 on page 2 in the Erlenmeyer flask. When possible, collect the sample directly in the Erlenmeyer flask to prevent agitation of the sample.



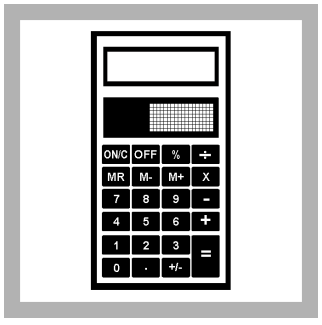
4. Add the contents of one Phenolphthalein Indicator Powder Pillow. The indicator is not necessary if a pH meter is used.



5. Swirl to mix. If a pink color forms, no carbon dioxide is in the sample.



6. Put the flask under the buret. Swirl the flask. Add titrant until the color changes from colorless to a light pink color for a minimum of 30 seconds (pH 8.3).



7. Use the multiplier in Table 1 on page 2 to calculate the concentration. mL of titrant × multiplier = mg/L CO_2.

Sample volumes and multipliers

Select a range in Table 1, then read across the table row to find the applicable information for this test. Use the multiplier to calculate the concentration in the test procedure.

Example: A 100-mL sample was titrated with 0.0227 N titrant and 12 mL of titrant was used at the endpoint. The concentration is 12 mL × 10 = 120 mg/L CO_2.

Table 1 Sample volumes and multipliers

Range (mg/L)	Sample volume (mL)	Titrant—sodium hydroxide	Flask size	Multiplier
0–125	200	0.0227 N	250 mL	5
100–250	100	0.0227 N	125 mL	10

Interferences

Interfering substance	Interference level
Other acids	Interferes directly and is included in the test result.
Color and turbidity	Color or turbidity in the sample can make it difficult to see the color change at the endpoint. For these samples, use a pH meter to determine the titration endpoint. The endpoint is pH 8.3.

Summary of method

A phenolphthalein indicator is added to the sample. Carbonic acid formed by carbon dioxide in the sample is titrated with a sodium hydroxide standard solution until the indicator changes color at the endpoint pH of 8.3. Strong acids cannot be in the sample at concentration levels that will have an effect on the results.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Phenolphthalein Indicator Powder Pillows	1 pillow	100/pkg	94299
Sodium Hydroxide Standard Solution, 0.0227 N	varies	1 L	19253

Required apparatus

Description	Quantity/test	Unit	Item no.
Buret clamp, double	1	each	32800
Buret, Class A, 25 mL	1	each	2636540
Support stand	1	each	56300
Funnel, micro	1	each	2584335
Flask, Erlenmeyer, 125 mL	1	each	50543
Flask, Erlenmeyer, 250 mL	1	each	50546

Optional reagents and apparatus

Description	Unit	Item no.
Phenolphthalein Indicator Solution, 5-g/L	100 mL MDB	16232
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
Bottle, sampling, with cap, low density polyethylene, 250 mL	12/pkg	2087076
Clippers	each	96800
Water, deionized	500 mL	27249
Stir bar, octagonal	each	2095352
TitraStir® Titration Stand, 115 VAC	each	1940000
TitraStir® Titration Stand, 230 VAC	each	1940010

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Section 4

Solids

Analysis of Solids

1

Solids Testing

- Why should I care about solids tests?
  - Assessment of compliance
  - Control of Biological and Physical treatment process
    - Poor data = Poor decisions

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Definitions

- Total Solids-all residue left after drying
- Dissolved Solids-the portion of TS which pass through a 2.0um filter
- Suspended Solids- that portion retained on the 2.0um filter

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Standard Methods 2540B-G

- Sources of error
  - Sampling
  - Sub sampling
  - Measuring
  - Filter/Bowl preparation
  - Filter/Bowl handling
- Remedies
  - MIX WELL
  - Measure quickly

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Standard Methods 2540B-G

- Temperatures
  - Each Method has a specified drying Temp.
  - Minimize opening desiccator
  - Weigh quickly, dry samples attract moisture
- Rinse Water
  - Type III, distilled or deionized water

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Standard Methods 2540B-G

- Sampling
  - Glass or plastic containers, watch for particles adhering to container walls especially plastic.
- Begin test ASAP is preferred.
- Sampling Holding
  - Preserve at 4°C to minimize bio. decomp.
  - Hold <24 hours preferred
  - Never hold over 7 days

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Total Solids 2540-B

- Temperature 103-105°C
- Calculations based on sample volume

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Dissolved Solids 2540-C

- Temperature 180°C
- Non-regulatory at 103-105°C

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Total Suspended Solids 2540-D

- Temperature 103-105°C
- Interferences
  - Limit sample size to 200mg of residue, small filter
  - Avoid prolonged filtration times >5-7 min.
- Glass fiber filter 22-125mm diameter.
  - Whatman 934AH 1.5um
  - Gelman A/E 1.0um
  - Millipore AP40
  - E-D Scientific Grade 161

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Total Suspended Solids 2540-D

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TSS 2540-D

- Filter preparation:
  - Pre wash approved glass fiber filter by rinsing three times with 20mL of deionized (DI) water
  - Dry in weighing pans at 103 – 105° C for 1 hour and cool in desiccator
  - Record the initial weight of the filter & pan after drying
  - Repeat this cycle of drying, desiccating and weighing until a constant weight has been reached

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TSS 2540-D

- Sample Analysis:
  - Choose a sample volume to yield between 2.5 - 200 mg dried residue
  - Assemble filtering apparatus and filter
  - Wet filter with small amount of distilled water to seal before applying the sample
  - Sample must be well mixed before applying to filter

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TSS 2540-D

- Sample Analysis – continued:
  - Wash filter and apparatus three times with 10 mL of DI water
  - Transfer filter into support pans
  - Dry in oven at 103-105 ° C for 1 hr and cool in desiccator
  - Weigh filter until a constant weight is obtained

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TSS 2540-D

- Uses
  - Clarifier Suspended Solids
  - Stream samples
  - Some digester solids tests

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TSS Calculations

- TSS in mg/L is equal to the amount of residue retained on the filter in mg per liter of sample
- Formula: TSS mg/L = $\frac{(A - B)}{1000 \text{ mg/g}}$
- Where: A = wt. of filter + dried residue (g)
  B = initial wt. of filter (g)
  1,000 = conversion factor
  (1 g = 1000 mg)

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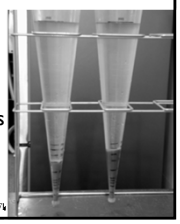
Settleable Solids 2540-F

- Important process control test for rates and volume of sedimentation
- Report as mL/L
  - Minimum Detection Limit 0.1mL/L
  - Adjust for water layers if present
- Basin control: Imhoff cone
  - Sample volume: 1 L
  - Solids settle 45 min
  - Gently stir sides
  - Solids settle another 15 minutes
  - Read after a total of 60 min



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Total Solids 2540-G

- For solid and semisolid materials
  - Required or Biosolids per 40 CFR 503
- Calculations based on wet and dry weight.

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Balance Operation

- Key to quality solids tests
- Care of Balance
  - Vibration, heat, sunlight
  - Dust, dirt, moisture
- Calibration
  - Outside contractor
  - In house, "S" class weights

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40CFR136

Method Update Rule
For Backwash Lagoons that have Discharge Permits
May 10, 2013
Fleming Training Center

40 CFR 136 05-21-2012 Table 1B

Parameter	Methodology	EPA	Standard Methods	ASTM	USGS/AOAC /Other
Residue – Non-filterable (TSS), mg/L	**Gravimetric, 103-105° post washing of residue**	……	**2540 D-1997**	D5907-03	I-3765-85.[2]
Residue – Settleable, mg/L	**Volumetric, (Imhoff cone) or gravimetric**	……	**2540 F-1997**		
Temperature, °C	**Thermometric**	……	**2550 B-2000**	……	See Footnote.[32]

12 Quality Control Elements

1. DOC – demonstration of capability
2. MDL – method detection level
3. LRB/MB – method blank
4. LFB – laboratory fortified blank (standard)
5. LFM/LFMD – laboratory fortified matrix/duplicate (spike)
6. Internal standards, surrogate standards or tracer – ***only applies to organic analysis and radiochemistry***
7. Calibration- initial and continuing
8. Control charts or other trend analysis
9. Corrective action – root cause analysis
10. QC acceptance criteria
11. Definition of a batch (preparation and analytical)
12. Minimum frequency for conducting all QC elements
13. Unwritten 13th Step – SOP – Standard Operating Procedures need to be written and followed for all lab sampling and analyses

Not all of these items apply to all tests, there are many exceptions!

TSS SM2540 D – 1997 Dried at 103-105°C

- DOC
- LRB
- LFB
- Dup
- ICAL
- Corrective Action
- QC Acceptance
- Batch Size
- QC Frequency

TSS SM2540 D – 1997 Dried at 103-105°C

- Demonstration of Capability (DOC)
  - Run a laboratory-fortified blank (LFB) at least four times and compare to the limits listed in the method
  - Real people language: each operator running this test need to analyze 4 samples of an Total Suspended Solids Standards
  - Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.
  - Recommend backup analyst do this once a year.

TSS SM2540 D – 1997 Dried at 103-105°C

- Blanks
  - Filter 100 mL of deionized/distilled water through a pre-washed/pre-dried/pre-weighed filter with each batch of 20 or fewer samples
    - Run on a 5% basis, one for every 20 samples **(or day of for monthly reporting purposes)**
- Laboratory Fortified Blank
  - Real people language: analyze a TSS standard that can be prepared from recipe (next slide) or bought premade
    - Run on a 5% basis, one for every 20 samples **(or day of for monthly reporting purposes)**

TSS SM2540 D – 1997 Dried at 103-105°C

- To prepare TSS check samples from dry reference material:
  - Dry the reference material* in the desiccator
  - On an analytical balance, weigh 0.1000 gram of the dry powder, put it in a 1000 mL volumetric flask, bring it to the mark with distilled or deionized water and shake well until well suspended.
  - Measure 100 mL and process as usual for environmental samples.
  - A difference of 10 mg should be obtained.
  - Calculation: $\frac{(A - B)(1000)}{\text{Vol. used}} = \frac{(10\text{ mg})(1000)}{100\text{ mL}} = 100\text{ g/L}$

*Example of material available from Fisher

- Celite 545 Filter Aid (Powder), Fisher Chemical, 500 gram bottle – Cat#C212-500

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TSS SM2540 D – 1997 Dried at 103-105°C

- Initial Calibration
  - Check balances daily with at least 2 working weights that bracket the normal usage range and record results on bench sheet or separate log book
- Duplicates
  - Run on a 10% basis, one for every 10 samples **(or day of for monthly reporting purposes)**
  - Calculate %RPD
  - Duplicates must agree within 5% of their average weight

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Total Suspended Solids Analysis
Procedure to Omit Re-drying/Re-cooling/Re-weighing

How to acquire acceptable results for the total suspended solids comparability data:

- The maximum holding time for a total suspended solids sample prior to analysis is 7 days if stored at temperatures of 6°C and below (not 0°C). (*40CFR part 136, Table II*)
- EPA recommends that 4-7 different samples, in duplicate, be collected and analyzed for this procedure in order to prove that the step for "reheating, recooling, and reweighing" is unnecessary. "Different" could mean samples collected 4-7 consecutive days or 4-7 samples run in one day. These 4-7 samples are dried ***overnight*** at 103-105°C.
- The next morning, the filters are removed from the oven, allowed to cool in the desiccator and weighed.
- The samples are then returned to the drying oven for one hour, recooled and reweighed.
- The resulting data should be examined to determine if the difference between the overnight values and the redried values are less than 4% or 0.5 mg, whichever is less. If so, the redrying step may be omitted for a normal set of samples.
- This procedure excludes atypical samples. (i.e. high fat, oil and grease samples).
- The operator may choose not to perform this study and continue to follow the procedure for redrying/recooling/reweighing as stated the method (Std Methods, 2540 D).

The study should be re-evaluated at least once per year or whenever a change in sample characteristics occurs and kept on file at the treatment plant.

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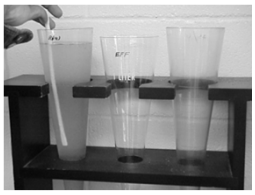
SS SM2540 F – 1997 Settleable Solids

- Dup
- Corrective Action
- Batch Size
- QC Frequency



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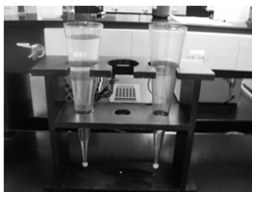
SS SM2540 F – 1997 Settleable Solids

- Duplicates of the sample
  - Run on a 5% basis, one for every 20 samples **(or day of for monthly reporting purposes)**
- Calculate %RPD, ≤ 20%



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2540 SOLIDS*

2540 A. Introduction

Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Waters with high dissolved solids generally are of inferior palatability and may induce an unfavorable physiological reaction in the transient consumer. For these reasons, a limit of 500 mg dissolved solids/L is desirable for drinking waters. Highly mineralized waters also are unsuitable for many industrial applications. Waters high in suspended solids may be esthetically unsatisfactory for such purposes as bathing. Solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limitations.

1. Definitions

"Total solids" is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids includes "total suspended solids," the portion of total solids retained by a filter, and "total dissolved solids," the portion that passes through the filter.

The type of filter holder, the pore size, porosity, area, and thickness of the filter and the physical nature, particle size, and amount of material deposited on the filter are the principal factors affecting separation of suspended from dissolved solids. "Dissolved solids" is the portion of solids that passes through a filter of 2.0 μm (or smaller) nominal pore size under specified conditions. "Suspended solids" is the portion retained on the filter.

"Fixed solids" is the term applied to the residue of total, suspended, or dissolved solids after heating to dryness for a specified time at a specified temperature. The weight loss on ignition is called "volatile solids." Determinations of fixed and volatile solids do not distinguish precisely between inorganic and organic matter because the loss on ignition is not confined to organic matter. It includes losses due to decomposition or volatilization of some mineral salts. Better characterization of organic matter can be made by such tests as total organic carbon (Section 5310), BOD (Section 5210), and COD (Section 5220).

"Settleable solids" is the term applied to the material settling out of suspension within a defined period. It may include floating material, depending on the technique (2540F.3*b*).

2. Sources of Error and Variability

Sampling, subsampling, and pipeting two-phase or three-phase samples may introduce serious errors. Make and keep such samples homogeneous during transfer. Use special handling to insure sample integrity when subsampling. Mix small samples with a magnetic stirrer. If suspended solids are present, pipet with wide-bore pipets. If part of a sample adheres to the sample container, consider this in evaluating and reporting results. Some samples dry with the formation of a crust that prevents water evaporation; special handling is required to deal with this. Avoid using a magnetic stirrer with samples containing magnetic particles.

The temperature at which the residue is dried has an important bearing on results, because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating. Each sample requires close attention to desiccation after drying. Minimize opening desiccator because moist air enters. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

Residues dried at 103 to 105°C may retain not only water of crystallization but also some mechanically occluded water. Loss of CO_2 will result in conversion of bicarbonate to carbonate. Loss of organic matter by volatilization usually will be very slight. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow.

Residues dried at 180 ± 2°C will lose almost all mechanically occluded water. Some water of crystallization may remain, especially if sulfates are present. Organic matter may be lost by volatilization, but not completely destroyed. Loss of CO_2 results from conversion of bicarbonates to carbonates and carbonates may be decomposed partially to oxides or basic salts. Some chloride and nitrate salts may be lost. In general, evaporating and drying water samples at 180°C yields values for dissolved solids closer to those obtained through summation of individually determined mineral species than the dissolved solids values secured through drying at the lower temperature.

To rinse filters and filtered solids and to clean labware use Type III water. Special samples may require a higher quality water; see Section 1080.

Results for residues high in oil or grease may be questionable because of the difficulty of drying to constant weight in a reasonable time.

To aid in quality assurance, analyze samples in duplicate. Dry samples to constant weight if possible. This entails multiple drying-cooling-weighing cycles for each determination.

Analyses performed for some special purposes may demand deviation from the stated procedures to include an unusual constituent with the measured solids. Whenever such variations of technique are introduced, record and present them with the results.

3. Sample Handling and Preservation

Use resistant-glass or plastic bottles, provided that the material in suspension does not adhere to container walls. Begin analysis as soon as possible because of the impracticality of preserving the sample. Refrigerate sample at 4°C up to the time of analysis to minimize microbiological decomposition of solids. Preferably do not hold samples more than 24 h. In no case hold sample more than 7 d. Bring samples to room temperature before analysis.

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* Approved by Standard Methods Committee, 1997.
Joint Task Group: 20th Edition—Brannon H. Wilder (chair), Harold S. Costa, Christine M. Kosmowski, William E. Purcell.

4. Selection of Method

Methods B through F are suitable for the determination of solids in potable, surface, and saline waters, as well as domestic and industrial wastewaters in the range up to 20 000 mg/L.

Method G is suitable for the determination of solids in sediments, as well as solid and semisolid materials produced during water and wastewater treatment.

5. Bibliography

THERIAULT, E.J. & H.H. WAGENHALS. 1923. Studies of representative sewage plants. *Pub. Health Bull.* No. 132.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Methods for Chemical Analysis of Water and Wastes. Publ. 600/4-79-020, rev. Mar. 1983. Environmental Monitoring and Support Lab., U.S. Environmental Protection Agency, Cincinnati, Ohio.

2540 B. Total Solids Dried at 103–105°C

1. General Discussion

a. Principle: A well-mixed sample is evaporated in a weighed dish and dried to constant weight in an oven at 103 to 105°C. The increase in weight over that of the empty dish represents the total solids. The results may not represent the weight of actual dissolved and suspended solids in wastewater samples (see above).

b. Interferences: Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Exclude large, floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result. Disperse visible floating oil and grease with a blender before withdrawing a sample portion for analysis. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue (see 2540A.2).

2. Apparatus

a. Evaporating dishes: Dishes of 100-mL capacity made of one of the following materials:

1) Porcelain, 90-mm diam.
2) Platinum—Generally satisfactory for all purposes.
3) High-silica glass.*

b. Muffle furnace for operation at 550°C.

c. Steam bath.

d. Desiccator, provided with a desiccant containing a color indicator of moisture concentration or an instrumental indicator.

e. Drying oven, for operation at 103 to 105°C.

f. Analytical balance, capable of weighing to 0.1 mg.

g. Magnetic stirrer with TFE stirring bar.

h. Wide-bore pipets.†

i. Graduated cylinder.

j. Low-form beaker.‡

3. Procedure

a. Preparation of evaporating dish: If volatile solids are to be measured ignite clean evaporating dish at 550°C for 1 h in a muffle furnace. If only total solids are to be measured, heat clean dish to 103 to 105°C for 1 h. Store and cool dish in desiccator until needed. Weigh immediately before use.

b. Sample analysis: Choose a sample volume that will yield a residue between 2.5 and 200 mg. Pipet a measured volume of well-mixed sample, during mixing, to a preweighed dish. For homogeneous samples, pipet from the approximate midpoint of the container but not in the vortex. Choose a point both middepth and midway between wall and vortex. Evaporate to dryness on a steam bath or in a drying oven. Stir sample with a magnetic stirrer during transfer. If necessary, add successive sample portions to the same dish after evaporation. When evaporating in a drying oven, lower temperature to approximately 2°C below boiling to prevent splattering. Dry evaporated sample for at least 1 h in an oven at 103 to 105°C, cool dish in desiccator to balance temperature, and weigh. Repeat cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained, or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. When weighing dried sample, be alert to change in weight due to air exposure and/or sample degradation. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight.

4. Calculation

$$\text{mg total solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of dried residue + dish, mg, and
B = weight of dish, mg.

5. Precision

Single-laboratory duplicate analyses of 41 samples of water and wastewater were made with a standard deviation of differences of 6.0 mg/L.

6. Bibliography

SYMONS, G.E. & B. MOREY. 1941. The effect of drying time on the determination of solids in sewage and sewage sludges. *Sewage Works J.* 13:936.

* Vycor, product of Corning Glass Works, Corning, NY, or equivalent.
† Kimble Nos. 37005 or 37034B, or equivalent.
‡ Class B or better.

2540 C. Total Dissolved Solids Dried at 180°C

1. General Discussion

a. Principle: A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids. This procedure may be used for drying at other temperatures.

The results may not agree with the theoretical value for solids calculated from chemical analysis of sample (see above). Approximate methods for correlating chemical analysis with dissolved solids are available.[1] The filtrate from the total suspended solids determination (Section 2540D) may be used for determination of total dissolved solids.

b. Interferences: See 2540A.2 and 2540B.1. Highly mineralized waters with a considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Samples high in bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

2. Apparatus

Apparatus listed in 2540B.2*a-h* is required, and in addition:

*a. Glass-fiber filter disks** without organic binder.

b. Filtration apparatus: One of the following, suitable for the filter disk selected:

1) *Membrane filter funnel.*

2) *Gooch crucible,* 25-mL to 40-mL capacity, with Gooch crucible adapter.

3) *Filtration apparatus* with reservoir and coarse (40- to 60-μm) fritted disk as filter support.†

c. Suction flask, of sufficient capacity for sample size selected.

d. Drying oven, for operation at 180 ± 2°C.

3. Procedure

a. Preparation of glass-fiber filter disk: If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up into filtration apparatus. Apply vacuum and wash disk with three successive 20-mL volumes of reagent-grade water. Continue suction to remove all traces of water. Discard washings.

b. Preparation of evaporating dish: If volatile solids are to be measured, ignite cleaned evaporating dish at 550°C for 1 h in a muffle furnace. If only total dissolved solids are to be measured, heat clean dish to 180 ± 2°C for 1 h in an oven. Store in desiccator until needed. Weigh immediately before use.

c. Selection of filter and sample sizes: Choose sample volume to yield between 2.5 and 200 mg dried residue. If more than 10 min are required to complete filtration, increase filter size or decrease sample volume.

d. Sample analysis: Stir sample with a magnetic stirrer and pipet a measured volume onto a glass-fiber filter with applied vacuum. Wash with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Transfer total filtrate (with washings) to a weighed evaporating dish and evaporate to dryness on a steam bath or in a drying oven. If necessary, add successive portions to the same dish after evaporation. Dry evaporated sample for at least 1 h in an oven at 180 ± 2°C, cool in a desiccator to balance temperature, and weigh. Repeat drying cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight. If volatile solids are to be determined, follow procedure in 2540E.

4. Calculation

$$\text{mg total dissolved solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of dried residue + dish, mg, and
B = weight of dish, mg.

5. Precision

Single-laboratory analyses of 77 samples of a known of 293 mg/L were made with a standard deviation of differences of 21.20 mg/L.

6. Reference

1. Sokoloff, V.P. 1933. Water of crystallization in total solids of water analysis. *Ind. Eng. Chem.,* Anal. Ed. 5:336.

7. Bibliography

Howard, C.S. 1933. Determination of total dissolved solids in water analysis. *Ind. Eng. Chem.,* Anal. Ed. 5:4.

U.S. Geological Survey. 1974. Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases. Techniques of Water-Resources Investigations, Book 5, Chap. A1. U.S. Geological Surv., Washington, D.C.

* Whatman grade 934AH; Gelman type A/E; Millipore type AP40; E-D Scientific Specialties grade 161; Environmental Express Pro Weigh; or other products that give demonstrably equivalent results. Practical filter diameters are 2.2 to 12.5 cm.
† Gelman No. 4201 or equivalent.

2540 D. Total Suspended Solids Dried at 103–105°C

1. General Discussion

a. Principle: A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids. If the suspended material clogs the filter and prolongs filtration, it may be necessary to increase the diameter of the filter or decrease the sample volume. To obtain an estimate of total suspended solids, calculate the difference between total dissolved solids and total solids.

b. Interferences: See 2540A.2 and 2540B.1. Exclude large floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not representative. Because excessive residue on the filter may form a water-entrapping crust, limit the sample size to that yielding no more than 200 mg residue. For samples high in dissolved solids thoroughly wash the filter to ensure removal of dissolved material. Prolonged filtration times resulting from filter clogging may produce high results owing to increased colloidal materials captured on the clogged filter.

2. Apparatus

Apparatus listed in Sections 2540B.2 and 2540C.2 is required, except for evaporating dishes, steam bath, and 180°C drying oven. In addition:

Aluminum weighing dishes.

3. Procedure

a. Preparation of glass-fiber filter disk: If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up in filtration apparatus. Apply vacuum and wash disk with three successive 20-mL portions of reagent-grade water. Continue suction to remove all traces of water, turn vacuum off, and discard washings. Remove filter from filtration apparatus and transfer to an inert aluminum weighing dish. If a Gooch crucible is used, remove crucible and filter combination. Dry in an oven at 103 to 105°C for 1 h. If volatile solids are to be measured, ignite at 550°C for 15 min in a muffle furnace. Cool in desiccator to balance temperature and weigh. Repeat cycle of drying or igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of the previous weighing or 0.5 mg, whichever is less. Store in desiccator until needed.

b. Selection of filter and sample sizes: Choose sample volume to yield between 2.5 and 200 mg dried residue. If volume filtered fails to meet minimum yield, increase sample volume up to 1 L. If complete filtration takes more than 10 min, increase filter diameter or decrease sample volume.

c. Sample analysis: Assemble filtering apparatus and filter and begin suction. Wet filter with a small volume of reagent-grade water to seat it. Stir sample with a magnetic stirrer at a speed to shear larger particles, if practical, to obtain a more uniform (preferably homogeneous) particle size. Centrifugal force may separate particles by size and density, resulting in poor precision when point of sample withdrawal is varied. While stirring, pipet a measured volume onto the seated glass-fiber filter. For homogeneous samples, pipet from the approximate midpoint of container but not in vortex. Choose a point both middepth and midway between wall and vortex. Wash filter with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Samples with high dissolved solids may require additional washings. Carefully remove filter from filtration apparatus and transfer to an aluminum weighing dish as a support. Alternatively, remove the crucible and filter combination from the crucible adapter if a Gooch crucible is used. Dry for at least 1 h at 103 to 105°C in an oven, cool in a desiccator to balance temperature, and weigh. Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until the weight change is less than 4% of the previous weight or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight. If volatile solids are to be determined, treat the residue according to 2540E.

4. Calculation

$$\text{mg total suspended solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of filter + dried residue, mg, and
B = weight of filter, mg.

5. Precision

The standard deviation was 5.2 mg/L (coefficient of variation 33%) at 15 mg/L, 24 mg/L (10%) at 242 mg/L, and 13 mg/L (0.76%) at 1707 mg/L in studies by two analysts of four sets of 10 determinations each.

Single-laboratory duplicate analyses of 50 samples of water and wastewater were made with a standard deviation of differences of 2.8 mg/L.

6. Bibliography

DEGEN, J. & F.E. NUSSBERGER. 1956. Notes on the determination of suspended solids. *Sewage Ind. Wastes* 28:237.

CHANIN, G., E.H. CHOW, R.B. ALEXANDER & J. POWERS. 1958. Use of glass fiber filter medium in the suspended solids determination. *Sewage Ind. Wastes* 30:1062.

NUSBAUM, I. 1958. New method for determination of suspended solids. *Sewage Ind. Wastes* 30:1066.

SMITH, A.L. & A.E. GREENBERG. 1963. Evaluation of methods for determining suspended solids in wastewater. *J. Water Pollut. Control Fed.* 35:940.

WYCKOFF, B.M. 1964. Rapid solids determination using glass fiber filters. *Water Sewage Works* 111:277.

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT. 1975. A Preliminary Review of Analytical Methods for the Determination of Suspended Solids in Paper Industry Effluents for Compliance with EPA-NPDES Permit Terms. Spec. Rep. No. 75-01. National Council of the Paper Industry for Air & Stream Improvement, New York, N.Y.

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT. 1977. A Study of the Effect of Alternate Procedures on

Effluent Suspended Solids Measurement. Stream Improvement Tech. Bull. No. 291, National Council of the Paper Industry for Air & Stream Improvement, New York, N.Y.

TREES, C.C. 1978. Analytical analysis of the effect of dissolved solids on suspended solids determination. *J. Water Pollut. Control Fed.* 50: 2370.

2540 E. Fixed and Volatile Solids Ignited at 550°C

1. General Discussion

a. Principle: The residue from Method B, C, or D is ignited to constant weight at 550°C. The remaining solids represent the fixed total, dissolved, or suspended solids while the weight lost on ignition is the volatile solids. The determination is useful in control of wastewater treatment plant operation because it offers a rough approximation of the amount of organic matter present in the solid fraction of wastewater, activated sludge, and industrial wastes.

b. Interferences: Negative errors in the volatile solids may be produced by loss of volatile matter during drying. Determination of low concentrations of volatile solids in the presence of high fixed solids concentrations may be subject to considerable error. In such cases, measure for suspect volatile components by another test, for example, total organic carbon (Section 5310). Highly alkaline residues may react with silica in sample or silica-containing crucibles.

2. Apparatus

See Sections 2540B.2, 2540C.2, and 2540D.2.

3. Procedure

Ignite residue produced by Method 2540B, C, or D to constant weight in a muffle furnace at a temperature of 550°C. Ignite a blank glass fiber filter along with samples. Have furnace up to temperature before inserting sample. Usually, 15 to 20 min ignition are required for 200 mg residue. However, more than one sample and/or heavier residues may overtax the furnace and necessitate longer ignition times. Let dish or filter disk cool partially in air until most of the heat has been dissipated. Transfer to a desiccator for final cooling in a dry atmosphere. Do not overload desiccator. Weigh dish or disk as soon as it has cooled to balance temperature. Repeat cycle of igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight. Weight loss of the blank filter is an indication of unsuitability of a particular brand or type of filter for this analysis.

4. Calculation

$$\text{mg volatile solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

$$\text{mg fixed solids/L} = \frac{(B - C) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of residue + dish before ignition, mg,
B = weight of residue + dish or filter after ignition, mg, and
C = weight of dish or filter, mg.

5. Precision

The standard deviation was 11 mg/L at 170 mg/L volatile total solids in studies by three laboratories on four samples and 10 replicates. Bias data on actual samples cannot be obtained.

2540 F. Settleable Solids

1. General Discussion

Settleable solids in surface and saline waters as well as domestic and industrial wastes may be determined and reported on either a volume (mL/L) or a weight (mg/L) basis.

2. Apparatus

The volumetric test requires only an Imhoff cone. The gravimetric test requires all the apparatus listed in Section 2540D.2 and a glass vessel with a minimum diameter of 9 cm.

3. Procedure

a. Volumetric: Fill an Imhoff cone to the 1-L mark with a well-mixed sample. Settle for 45 min, gently agitate sample near the sides of the cone with a rod or by spinning, settle 15 min longer, and record volume of settleable solids in the cone as milliliters per liter. If the settled matter contains pockets of liquid between large settled particles, estimate volume of these and subtract from volume of settled solids. The practical lower limit of measurement depends on sample composition and generally is in the range of 0.1 to 1.0 mL/L. Where a separation of settleable and floating materials occurs, do not estimate the floating material as settleable matter. Replicates usually are not required.

Where biological or chemical floc is present, the gravimetric method (3*b*) is preferred.

b. Gravimetric:

1) Determine total suspended solids as in Section 2540D.

2) Pour a well-mixed sample into a glass vessel of not less than 9 cm diam using not less than 1 L and sufficient sample to

give a depth of 20 cm. Alternatively use a glass vessel of greater diameter and a larger volume of sample. Let stand quiescent for 1 h and, without disturbing the settled or floating material, siphon 250 mL from center of container at a point halfway between the surface of the settled material and the liquid surface. Determine total suspended solids (milligrams per liter) of this supernatant liquor (Section 2540D). These are the nonsettleable solids.

4. Calculation

mg settleable solids/L

= mg total suspended solids/L − mg nonsettleable solids/L

5. Precision and Bias

Precision and bias data are not now available.

6. Bibliography

FISCHER, A.J. & G.E. SYMONS. 1944. The determination of settleable sewage solids by weight. *Water Sewage Works* 91:37.

2540 G. Total, Fixed, and Volatile Solids in Solid and Semisolid Samples

1. General Discussion

a. Applicability: This method is applicable to the determination of total solids and its fixed and volatile fractions in such solid and semisolid samples as river and lake sediments, sludges separated from water and wastewater treatment processes, and sludge cakes from vacuum filtration, centrifugation, or other sludge dewatering processes.

b. Interferences: The determination of both total and volatile solids in these materials is subject to negative error due to loss of ammonium carbonate and volatile organic matter during drying. Although this is true also for wastewater, the effect tends to be more pronounced with sediments, and especially with sludges and sludge cakes. The mass of organic matter recovered from sludge and sediment requires a longer ignition time than that specified for wastewaters, effluents, or polluted waters. Carefully observe specified ignition time and temperature to control losses of volatile inorganic salts if these are a problem. Make all weighings quickly because wet samples tend to lose weight by evaporation. After drying or ignition, residues often are very hygroscopic and rapidly absorb moisture from the air. Highly alkaline residues may react with silica in the samples or silica-containing crucibles.

2. Apparatus

All the apparatus listed in Section 2540B.2 is required except that a magnetic stirrer and pipets are not used and a balance capable of weighing to 10 mg may be used.

3. Procedure

a. Total solids:

1) Preparation of evaporating dish—If volatile solids are to be measured, ignite a clean evaporating dish at 550°C for 1 h in a muffle furnace. If only total solids are to be measured, heat dish at 103 to 105°C for 1 h in an oven. Cool in desiccator, weigh, and store in desiccator until ready for use.

2) Sample analysis

a) Fluid samples—If the sample contains enough moisture to flow more or less readily, stir to homogenize, place 25 to 50 g in a prepared evaporating dish, and weigh. Evaporate to dryness on a water bath, dry at 103 to 105°C for 1 h, cool to balance temperature in an individual desiccator containing fresh desiccant, and weigh. Repeat heating, cooling, desiccating, and weighing procedure until the weight change is less than 4% or 50 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight.

b) Solid samples—If the sample consists of discrete pieces of solid material (dewatered sludge, for example), take cores from each piece with a No. 7 cork borer or pulverize the entire sample coarsely on a clean surface by hand, using rubber gloves. Place 25 to 50 g in a prepared evaporating dish and weigh. Place in an oven at 103 to 105°C overnight. Cool to balance temperature in a desiccator and weigh. Repeat drying (1 h), cooling, weighing, and desiccating steps until weight change is less than 4% or 50 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight.

b. Fixed and volatile solids: Transfer the dried residue from 2)a) above to a cool muffle furnace, heat furnace to 550°C, and ignite for 1 h. (If the residue contains large amounts of organic matter, first ignite it over a gas burner and under an exhaust hood in the presence of adequate air to lessen losses due to reducing conditions and to avoid odors in the laboratory.) Cool in desiccator to balance temperature and weigh. Repeat igniting (30 min), cooling, desiccating and weighing steps until the weight change is less than 4% or 50 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight.

4. Calculation

$$\%\ \text{total solids} = \frac{(A - B) \times 100}{C - B}$$

$$\%\ \text{volatile solids} = \frac{(A - D) \times 100}{A - B}$$

$$\%\ \text{fixed solids} = \frac{(D - B) \times 100}{A - B}$$

where:

A = weight of dried residue + dish, mg,
B = weight of dish,
C = weight of wet sample + dish, mg, and
D = weight of residue + dish after ignition, mg.

5. Precision and Bias

Precision and bias data are not now available.

6. Bibliography

GOODMAN, B.L. 1964. Processing thickened sludge with chemical conditioners. Pages 78 et seq. *in* Sludge Concentration, Filtration and Incineration. Univ. Michigan Continued Education Ser. No. 113, Ann Arbor.

GRATTEAU, J.C. & R.I. DICK. 1968. Activated sludge suspended solids determinations. *Water Sewage Works* 115:468.

2550 TEMPERATURE*

2550 A. Introduction

Temperature readings are used in the calculation of various forms of alkalinity, in studies of saturation and stability with respect to calcium carbonate, in the calculation of salinity, and in general laboratory operations. In limnological studies, water temperatures as a function of depth often are required. Elevated temperatures resulting from discharges of heated water may have significant ecological impact. Identification of source of water supply, such as deep wells, often is possible by temperature measurements alone. Industrial plants often require data on water temperature for process use or heat-transmission calculations.

* Approved by Standard Methods Committee, 2000.

2550 B. Laboratory and Field Methods

1. Laboratory and Other Non-Depth Temperature Measurements

Normally, temperature measurements may be made with any good mercury-filled Celsius thermometer. As a minimum, the thermometer should have a scale marked for every 0.1°C, with markings etched on the capillary glass. The thermometer should have a minimal thermal capacity to permit rapid equilibration. Periodically check the thermometer against a precision thermometer certified by the National Institute of Standards and Technology (NIST, formerly National Bureau of Standards)* that is used with its certificate and correction chart. For field operations use a thermometer having a metal case to prevent breakage.

A total immersion thermometer is designed to indicate temperatures correctly when the bulb and the entire liquid column are exposed to the temperature being measured, except for a minimal emergent length. A partial-immersion thermometer has a line around it at the immersion distance from the bottom. It indicates correctly when the bulb and the liquid column to that line are exposed to the temperature being measured and the emergent stem is at ambient temperature.

* Some commercial thermometers may be as much as 3°C in error.

2. Depth Temperature Measurements

Depth temperature required for limnological studies may be measured with a reversing thermometer, thermophone, or thermistor. The thermistor is most convenient and accurate; however, higher cost may preclude its use. Calibrate any temperature measurement devices with a NIST-certified thermometer before field use. Make readings with the thermometer or device immersed in water long enough to permit complete equilibration. Report results to the nearest 0.1 or 1.0°C, depending on need.

The thermometer commonly used for depth measurements is of the reversing type. It often is mounted on the sample collection apparatus so that a water sample may be obtained simultaneously. Correct readings of reversing thermometers for changes due to differences between temperature at reversal and temperature at time of reading. Calculate as follows:

$$\Delta T = \left[\frac{(T^1 - t)(T^1 + V_0)}{K}\right] \times \left[1 + \frac{(T^1 - t)(T^1 + V_0)}{K}\right] + L$$

where:

ΔT = correction to be added algebraically to uncorrected reading,
T^1 = uncorrected reading at reversal,

Solids, Non-filterable Suspended, Total and Volatile

USEPA Gravimetric Method[1, 2] Method 8158 and Method 8164

Scope and application: For water and wastewater.

[1] USEPA accepted.
[2] Adapted from *Standard Methods for the Examination of Water and Wastewater*, Section 2540B.

Test preparation

Before starting

Analyze samples as soon as possible for best results.
For the best accuracy, use as much filtered sample as possible (step 11). Samples that contain more than 15 mg of solids will clog the fiber filter disc. Adjust the correct volume of the water sample to get accurate results. Some completed tests will show if adjustments are necessary.
Always use tweezers with fiber filter discs. Moisture from fingers can add moisture to the fiber filter disc and cause a weighing error.
For Volatile Non-filterable Solids (or Residue) (VNR) preheat the muffle furnace below the recommended temperature. Do not put the watch glass directly in a 550 °C (1022 °F) muffle furnace because it can break. Put the watch glass in a 100 °C (212 °F) preheated muffle furnace and then increase the temperature to 550 °C (1022 °F) for 15 minutes.
The Total Non-filterable Solids (or Residue) (TNR) are the same as the Total Suspended Solids (TSS).

Items to collect

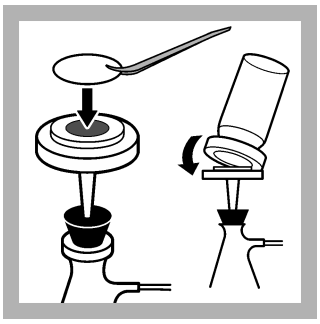
Description	Quantity
Analytical balance	1
Cylinder, graduated, 100 mL	1
Desiccator with desiccant	1
Drying oven	1
Filter flask	1
Filter holder	1
Filter, 47-mm	1
Furnace, muffle	1
Rubber policeman for 3/16 in. rod (user-supplied)	1
Tongs	1
Tweezers	1
Watch glass	1
Watch glass	1
Water, deionized	varies

Refer to Consumables and replacement items on page 5 for order information.

Sample collection and storage

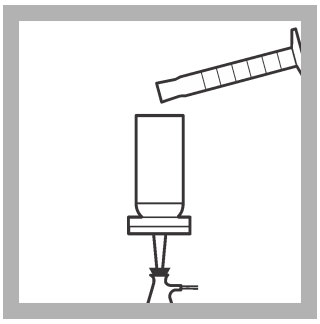
- Collect samples in clean glass or plastic bottles.
- To preserve samples for later analysis, keep the samples at or below 6 °C (43 °F) for up to 7 days.
- Let the sample temperature increase to room temperature before analysis.

Test procedure—Total Non-filterable Solids, Method 8158

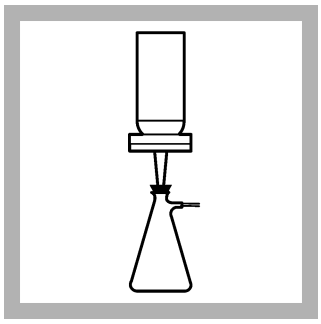


1. Use tweezers to put a fiber filter disc in the filter holder.

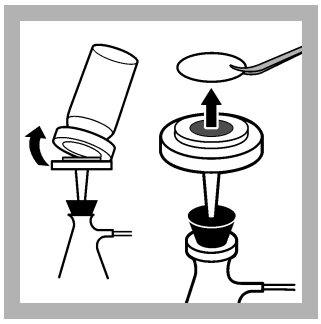
Put the filter holder assembly in the filtering flask.



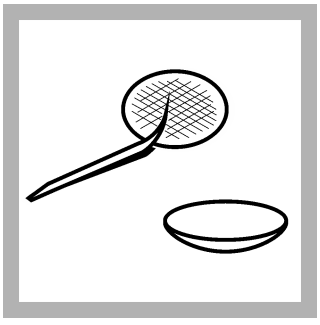
2. Use a graduated cylinder to add 100 mL of deionized water to the filtering flask.



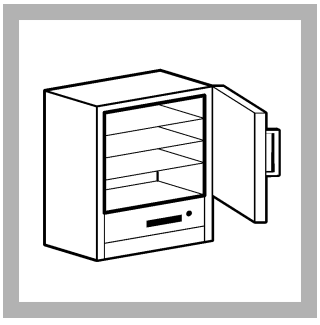
3. Apply vacuum to the flask until all of the water is pulled through the filter.



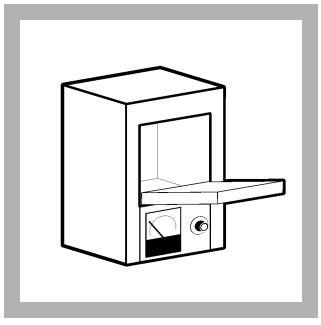
4. Slowly release the vacuum from the filtering system. Remove the fiber filter disc from the filter holder.



5. Put the fiber filter disc in a watch glass.



6. Put the watch glass with the fiber filter disc in a preheated drying oven at 103–105 °C (217–221 °F) for 1 hour.

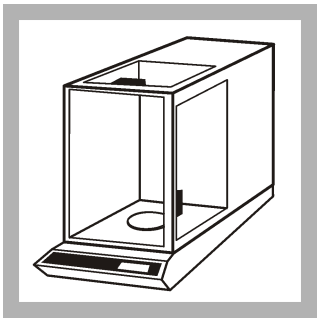


7. If Volatile Non-filterable Solids are also measured, use tongs to put the watch glass with the fiber filter disc into a preheated muffle furnace at 550 °C (1022 °F) for 15 minutes. Discard this step if Volatile Non-filterable Solids are not measured.

Note: *Do not put the watch glass directly in a 550 °C (1022 °F) muffle furnace because it can break. Put the watch glass in a 100 °C (212 °F) preheated muffle furnace and then increase the temperature to 550 °C (1022 °F) for 15 minutes.*

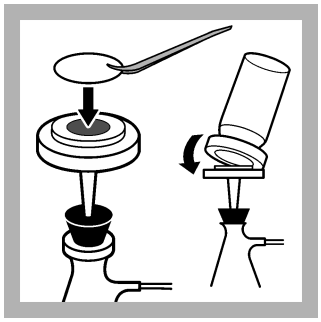
8. Use metal tongs to remove the watch glass with the fiber filter disc from the drying oven or muffle furnace and put in a desiccator. Immediately cover the desiccator. Do not seal the desiccator until the watch glass temperature has decreased a little, because pressure from the hot air inside can push the cover off.

Let the fiber filter disc and watch glass temperature decrease to room temperature.

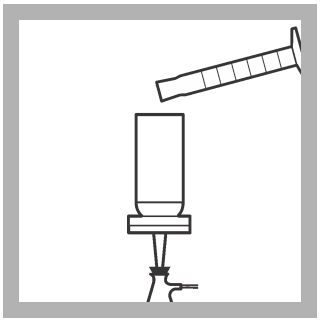


9. Remove the watch glass with the fiber filter disc from the desiccator and put it adjacent to the analytical balance.

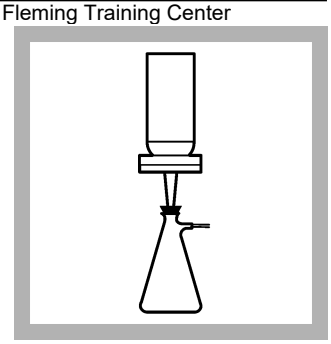
Use tweezers to remove the fiber filter disc from the watch glass. Weigh the fiber filter disc to the nearest 0.1 mg (0.0001 g). Record this mg value as B.



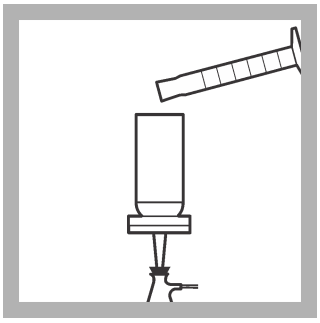
10. Put the fiber filter disc in the filter holder/filtering system again. Use deionized water to bond the fiber filter disc to the filter holder.



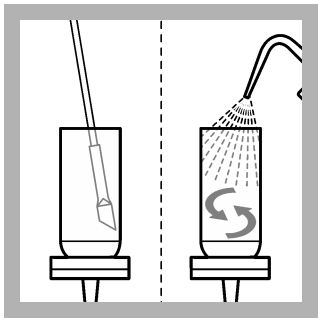
11. Use a graduated cylinder to add 100 mL (or more, if the solids content is low) of well-mixed, representative water sample.



12. Apply vacuum to the flask until all of the water is pulled through the filter.



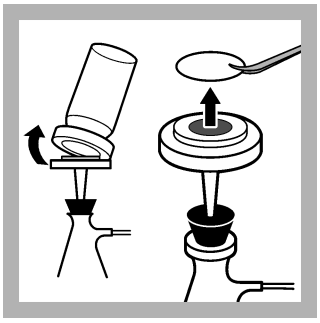
13. Add three different 10-mL aliquots of deionized water. Wait until each aliquot is pulled through the filter before the next one is added.



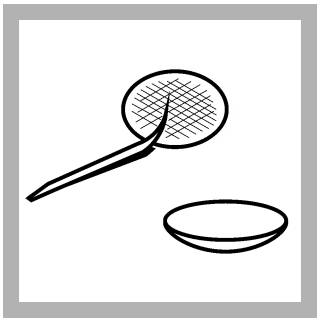
14. Move all of the remaining material that stays on the sides or bottom lip of the filter holder on the filter.

Use a rubber policeman on the end of a stirring rod as a scraper to remove the solids.

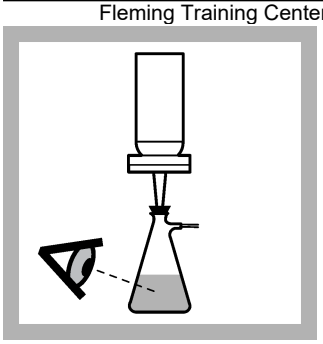
Use small amounts of deionized water to pull the solids down on the fiber filter disc.



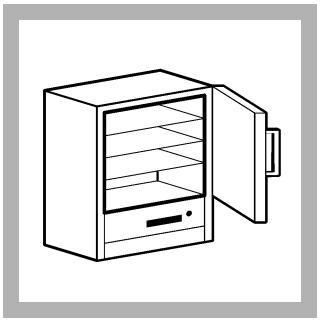
15. Slowly release the vacuum from the filtering system. Remove the fiber filter disc from the filter holder.



16. Put the fiber filter disc in a watch glass.



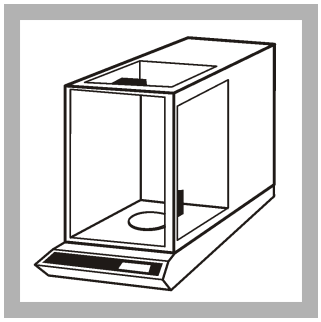
17. Examine the filtrate (filtered water in flask) to make sure that the solids are caught on the fiber filter disc.



18. Put the watch glass with the fiber filter disc in a preheated drying oven at 103–105 °C (217–221 °F) for 1 hour.

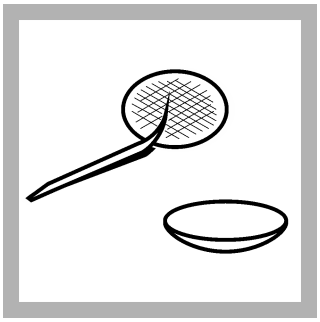
19. Use metal tongs to remove the watch glass with the fiber filter disc from the drying oven or muffle furnace and put in a desiccator. Immediately cover the desiccator. Do not seal the desiccator until the watch glass temperature has decreased a little, because pressure from the hot air inside can push the cover off.

Let the fiber filter disc and watch glass temperature decrease to room temperature.

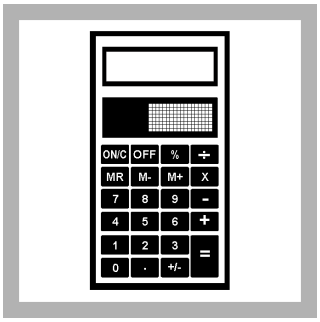


20. Remove the watch glass with the fiber filter disc from the desiccator and put it adjacent to the analytical balance.

Use tweezers to remove the fiber filter disc from the watch glass. Weigh the fiber filter disc to the nearest 0.1 mg (0.0001 g). Record this mg value as A.



21. Put the fiber filter disc back on the watch glass to measure Volatile Nonfilterable Residue. If not, discard the disc. If Volatile Nonfilterable Residue is measured, make sure to not lose any of the suspended matter on the disc.



22. Calculate the test results:

(A – B) ÷ L sample = mg/L Total Non-filterable Residue (TNR)

Where:
A = Weight (mg)[1] of fiber filter disc with solids

B = Weight (mg) of empty fiber filter disc

Example:

A = 95.5 mg

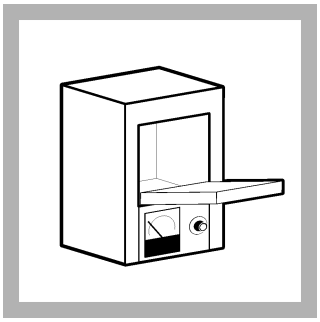
B = 81.5 mg

Volume of sample = 0.100 L

(95.5 mg – 81.5 mg) ÷ 0.100 = 140 mg/L TNR

[1] Weight in mg = grams × 1000

Test procedure—Volatile Non-filterable Solids, Method 8164

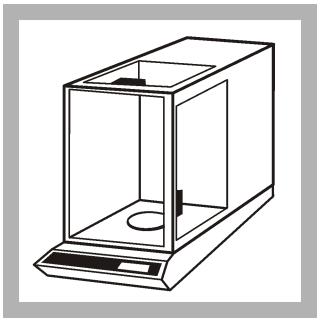


1. Put the watch glass and filter disc from the Total Non-filterable Solids procedure (step 21) in a preheated muffle furnace at 550 °C (1022 °F) for 15 minutes.

Note: *Do not put the watch glass directly in a 550 °C (1022 °F) muffle furnace because it can break. Put the watch glass in a 100 °C (212 °F) preheated muffle furnace and then increase the temperature to 550 °C (1022 °F) for 15 minutes.*

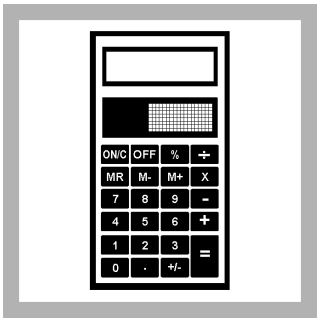
2. Use metal tongs to remove the watch glass with the fiber filter disc from the drying oven or muffle furnace and put in a desiccator. Immediately cover the desiccator. Do not seal the desiccator until the watch glass temperature has decreased a little, because pressure from the hot air inside can push the cover off.

Let the fiber filter disc and watch glass temperature decrease to room temperature.



3. Remove the watch glass with the fiber filter disc from the desiccator and put it adjacent to the analytical balance.

Use tweezers to remove the fiber filter disc from the watch glass. Weigh the fiber filter disc to the nearest 0.1 mg (0.0001 g). Record this mg value as C.



4. Calculate the test results:

(A – C) ÷ sample volume in L = mg/L Volatile Non-filterable Residue (VNR)

Where:
A = Weight (mg) of fiber filter disc with solids (step 20)

C = Weight (mg) of fiber filter disc with solids

Example:

A = 95.5 mg

C = 91.2 mg

Volume of sample = 0.100 L

(95.5 mg – 91.2 mg) ÷ 0.100 = 43 mg/L VNR

Summary of method

A glass fiber filter disc is used as a filter in a filtering flask. Deionized water is pulled with vacuum through the filter. The fiber filter disc is dried to a constant weight in an oven at 102-105 °C (217–221 °F) to determine the weight of the empty disc. A well-mixed filtered sample is dried in the same fiber filter disc to a constant weight in an oven at 102-105 °C (217–221 °F). The weight difference between the empty disc and the disc with the remaining materials shows the Total Non-filterable Solids. To measure the Volatile Non-filterable Solids, the fiber filter disc is put in a muffle furnace at 550 °C (1022 °F) to remove all of the volatile material. The weight difference between the disc and the disc with remaining materials shows the Volatile Non-filterable Solids.

Consumables and replacement items

Required reagents and apparatus

Description	Quantity/test	Unit	Item no.
Aspirator, vacuum pump	1	each	213100
Balance, analytical, 80 g x 0.1 mg, 100–240 VAC	1	each	2936701
Bottle, wash, 500 mL	1	each	62011
Cylinder, graduated, 100 mL	1	each	50842
Desiccant, indicating Drierite	1	each	2088701
Desiccator, without stopcock	1	each	1428500
Desiccator plate, ceramic	1	each	1428400
Filter discs, glass fiber, 47 mm	1	100/pkg	253000
Filter holder, 47-mm, magnetic base	1	each	1352900

Required reagents and apparatus (continued)

Description	Quantity/test	Unit	Item no.
Flask, filtering, glass, 1000 mL	1	each	54653
Furnace, muffle 240 VAC, 50/60 Hz	1	each	1429624
Furnace, muffle, 120 VAC, 50/60 Hz	1	each	1429600
Oven, laboratory, 240 VAC/50 Hz	1	each	1428902
Oven, laboratory, 120 VAC/60 Hz	1	each	1428900
Stopper, rubber, one-hole, number 8	1	6/pkg	211908
Tongs	1	each	56900
Tubing, rubber, 7.9 mm x 2.4 mm	varies	12 ft	56019
Tweezers, plastic	1	each	1428200
Watch glass, 100 mm	1	each	57870
Water, deionized	varies	4 L	27256

Optional reagents and apparatus

Description	Unit	Item No.
Ammonium Hydroxide, 58%	500 mL	10649
Sampling bottle with cap, low density polyethylene, 500-mL	12/pkg	2087079
Brush	each	68700
Pump, vacuum, hand-operated	each	1428300
Pump, vacuum, 1.2 CFM, 220 VAC	each	2824801
Pump, vacuum, 1.2 CFM 115 V	each	2824800
Stirring rod, glass	3/pkg	177001

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Total Suspended Solids, SM 2540 D, 22nd edition (1997)

Initial Demonstration of Capability (DOC)

- 2020 B.1 - each analyst must run a known standard concentration at least four times and compare limits listed in the method (under Precision). Table 2020:II lists duplicates and MB for QC only.
- Recommend running replicates and compare results and calculate the standard deviation to compare with that reported in 2540 D.5.
- **Real people language - *each* operator running this test needs to analyze 4 samples of a TSS Standard**
    - **Keep a folder for each analyst, keep a copy here**
    - **Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.**
    - **Recommend backup analyst do this once a year.**

Method Detection Limit (MDL)

- NONE

Initial Calibration Verification (ICV)

- 2020 B.2.a.– check instrument balance daily as stated below.
- 9020.B.4.b. Service balances annually or more often as conditions change or problems occur…

  Check balance routinely, preferably daily before use, with at least two working weights that bracket the normal usage range. (e.g., ANSI/ASTM Class 1 or NIST Class S accompanied by appropriate certificate) for accuracy, precision, and linearity. Record results along with date and technician's initials.

  Recertify reference weights as specified in the certificate of calibration or at least every 5 years.
- 2540 B.2. analytical balance, with a sensitivity of 0.1 mg
- **Real people language – check balance *daily* with at least 2 working weights that bracket the normal usage range and record results on bench sheet or separate log book.**

Method Blank

- 2020 B.2.d.– include at least 1 method blank (MB) daily or with each batch of 20 or fewer samples, whichever is more frequent.
- **Real people language – on a 5% basis (1 for every 20 samples) filter 100 mL of distilled water with each batch of 20 or fewer samples.**

Laboratory Fortified Blank (LFB)

- 1020 B.6.– A laboratory-fortified blank is a reagent water sample to which a known concentration of the analyte of interest has been added.
    - Sample batch = 5% basis = 1 every 20 samples
    - Use an added concentration of at least 10 times the MDL, less than or equal to the midpoint of the calibration curve.

- 2020 B.2.e. – Using stock solutions, prepare fortified concentrations so they are within the calibration curve.
- **Real people language – analyze TSS Standard sample that can be prepared from recipe below or bought premade.**
    - **Run on a 5% basis, see batch size for more information**

TSS Standard Samples

To prepare TSS check samples from dry reference material:

1. Dry the reference material* in the desiccator
2. On an analytical balance, weigh 0.1000 gram of the dry powder, put it in a 1000 mL volumetric flask, bring it to the mark with distilled or deionized water and shake well until well suspended.
3. Measure 100 mL and process as usual for environmental samples.
4. A difference of 10 mg should be obtained.
5. Calculation:

$$\frac{(A - B)\ (1000)}{\text{Vol. used}} = \frac{(10\ \text{mg})\ (1000)}{100\ \text{mL}} = 100\ \text{mg/L}$$

*Example of material available from Fisher

- Celite 545 Fitler Aid (Powder), Fisher Chemical, 500 gram bottle – Cat#C212-500

Procedure to Omit Re-drying/Re-cooling/Re-weighing Cycle

How to acquire acceptable results for the total suspended solids comparability data:

- The maximum holding time for a total suspended solids sample prior to analysis is 7 days if stored at temperatures of 6°C and below (not 0°C). (*40CFR part 136, Table II*)
- EPA recommends that 4-7 different samples, in duplicate, be collected and analyzed for this procedure in order to prove that the step for "reheating, recooling, and reweighing" is unnecessary. "Different" could mean samples collected 4-7 consecutive days or 4-7 samples run in one day. These 4-7 samples are dried ***overnight*** at 103-105°C.
- The next morning, the filters are removed from the oven, allowed to cool in the desiccator and weighed.
- The samples are then returned to the drying oven for one hour, recooled and reweighed.
- The resulting data should be examined to determine if the difference between the overnight values and the redried values are less than 4% or 0.5 mg, whichever is less. If so, the redrying step may be omitted for a normal set of samples.
- This procedure excludes atypical samples. (i.e. high fat, oil and grease samples).
- The operator may choose not to perform this study and continue to follow the procedure for redrying/recooling/reweighing cycle as stated the method (SM 2540 D.3.c.).

  The study should be re-evaluated at least once per year or whenever a change in sample characteristics occurs and kept on file at the treatment plant.

Duplicate

- 1020 B.8. states as a minimum to include one duplicate sample with each sample set or on a 5% basis whichever is more frequent.
- 2020 B.2.f. states to include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples.
- 2540 A.2. "*To aid in quality assurance, analyze samples in duplicate. Dry samples to constant weight if possible. This entails multiple drying-cooling-weighing cycles for each determination.*"
- 2540 D.3.c. Analyze at least 10% of all samples in duplicate.
    - Duplicates must agree within 5% of their average weight.

- **Real people language – analyze 2 samples for TSS.**
  - **For example, filter 100 mL of effluent through filter pad A then filter another 100 mL of effluent through filter pad B. Dry, cool and weigh. Figure RPD for both samples.**
  - **Target value is to get close to the first value and have a small RPD, less than 15%**
  - **Analyze a duplicate at a 10% rate or with each batch of 10 or fewer samples.**

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD)

- NONE

Control Charts

- NONE

Corrective Action - 1020 B.5., B.8,. & B.15.

QC Acceptance Criteria

- Blanks < reporting limits
- LFB ± 15%
- RPD± 15%

Batch Size

- *Influent and Effluent are 2 different samples*
- For samples that need to be analyzed on a 10% basis or once for every 10 samples follow these criteria:
  - If a permit stated that 3 analyses per week, that would be 6 samples per week, we would allow for a duplicate to be analyzed at least twice a month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!
  - If a permit stated 5 analyses per week, that would be 10 samples per week, we would suggest once a week.
    - Pick a date and be consistent, every Monday. Mark your calendar!!

Calculations

- % Recovery for LFB
  - $= \frac{\text{LFB concentration}}{\text{Expected concentration}} \times 100\%$
- Samples agreeing within 5% of their average weight
  - Average $= \frac{\text{Sample Conc + Dup Conc}}{2}$
  - 5% of Average = (Average Concentration)(0.05)
  - Acceptable Range = (Avg. – 5% of Avg) & (Avg + 5% of Avg)
- RPD – relative percent differences for duplicates and LFM/LFMD
  - $= \frac{\text{Difference between sample and duplicate}}{\text{Average of the sample and duplicate}} \times 100\%$

Ex: Sample = 78 mg/L ; Dup = 85 mg/L
Avg = (78+85)/2 = 81.5
5% of Avg = (81.5)(0.05) = 4.075
Range = 81.5 – 4.075 = 77.425
= 81.5 + 4.075 = 85.575

Solids, Settleable Matter

Direct Measurement[1] — Method 8165

Scope and application: For sewage and wastewater.

[1] Adapted from *Standard Methods for the Examination of Water and Wastewater*, Section 2540E.

Test preparation

Before starting

Make sure that the sample is fully mixed before analysis.
Keep samples refrigerated until the time of analysis to keep to a minimum the microbiological decomposition of solids.

Items to collect

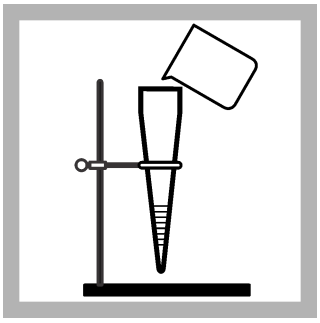
Description	Quantity
Imhoff cone	2
Imhoff cone brush	1
Imhoff cone support	1

Refer to Consumables and replacement items on page 2 for order information.

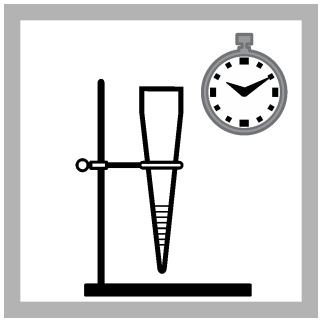
Sample collection and storage

- Collect samples in clean glass or plastic bottles.
- To preserve samples for later analysis, keep the samples at or below 6 °C (43 °F) for up to 24 hours.
- Let the sample temperature increase to room temperature before analysis.

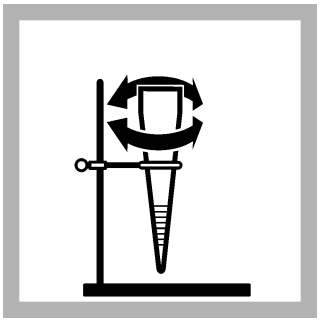
Test procedure



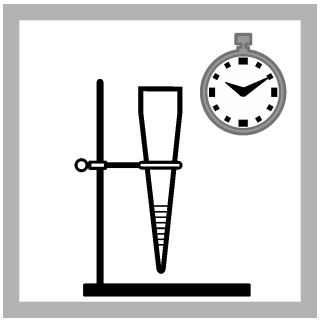
1. Fill an Imhoff cone to the 1-L mark with a mixed sample.



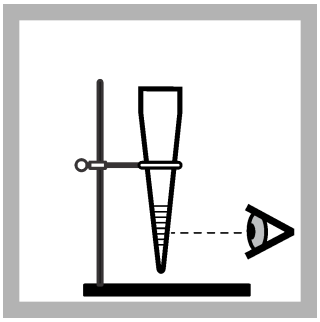
2. Do not move for 45 minutes to let the sample become stable.



3. Turn the cone forward and back to remove materials on the sloped side of the cone.



4. Do not move for 15 minutes to let the sample become stable.



5. Read the graduated scale on the Imhoff cone at the top of the solids layer as mL/L settleable matter.

Summary of method

The quantity of settleable matter in sewage treatment plant influent and effluent gives an empirical estimate of the type and intensity of treatment required. The quantity of settleable matter also gives the general quality of the water being discharged.

Consumables and replacement items

Required apparatus

Description	Quantity/test	Unit	Item no.
Imhoff cone	2	each	206700
Imhoff cone brush	1	each	68800
Imhoff cone support	1	each	57200

Optional apparatus

Description	Unit	Item no.
Beaker, glass, low form 2000 mL	each	50054
Gloves, chemical resistant, size 9–9.5	pair	2410104[1]
Pitcher, graduated 2000 mL	each	2612854
Sampler, dipper 3–9 ft handle	each	2929501

[1] Other sizes available

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Settleable Solids, SM 2540 F, 22nd edition (1997)

Initial Demonstration of Capability (DOC)

- Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.

Method Detection Limit (MDL)

- NONE

Initial Calibration Verification (ICV)

- NONE

Method Blank

- NONE

Laboratory Fortified Blank (LFB)

- NONE

Duplicate –

- 2540 A.2. "*To aid in quality assurance, analyze samples in duplicate.*
- **Real people language – analyze 2 samples for Sett. Solids.**
    - **For example, pour up 1000 mL of effluent into Imhoff then pour up another 1000 mL of effluent in another Imhoff. Wait 45 min, stir, wait 15 min, read. Figure RPD for both samples.**
    - **Target value is to get close to the first value and have a small RPD, less than 20%**
    - **Analyze a duplicate at a 5% rate or with each batch of 20 or fewer samples.**

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD)

- NONE

Control Charts

- NONE

Corrective Action - 1020 B.5., B.8,. & B.15.

Batch Size

- For samples that need to be analyzed on a 5% basis or once for every 20 samples follow these criteria:
    - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
        - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
    - If a permit stated 5 analyses per week, we would suggest twice a month.
        - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

Calculations

- RPD – relative percent differences for duplicates and LFM/LFMD
  - $= \frac{\text{Difference between sample and duplicate}}{\text{Average of the sample and duplicate}} \times 100\%$

TSS Sample Worksheet

Sample	Dish Number	Filter Weight, g (B)	Sample Volume, mL (C)	Filter + dried sample, g (A)	Filter + dried sample, g (2nd weighing)	Total Suspended Solids (TSS), mg/L
Duplicate						
Blank			100			

$$\mathbf{TSS, mg/L} = \frac{\mathbf{A - B}}{\mathbf{C}} \times \mathbf{1{,}000{,}000}$$

$$\mathbf{RPD} = \frac{\mathbf{range}}{\mathbf{average}} \times \mathbf{100}$$

$$\mathbf{range} = \mathbf{Sample\ wt} - \mathbf{Duplicate\ wt}$$

$$\mathbf{average} = \frac{\mathbf{Sample\ wt} + \mathbf{Duplicate\ wt}}{\mathbf{2}}$$

Section 5

Water Stability

WATER STABILITY

1

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STABILITY

- Water is considered stable when it is just saturated with calcium carbonate
- It will neither deposit nor dissolve calcium carbonate

2

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STABILITY

Langelier Saturation Index

- Used to indicate how close the water is to the equilibrium point
- Langelier Index = pH - pH_S
  - pH = actual pH of water
  - pH_S = determined by calcium carbonate saturation point
    - $pH_S = A + B - \log(Ca^{2+}) - \log(\text{alkalinity})$
      - A = determined from temperature
      - B = determined from TDS

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STABILITY

Langelier Index

- If the Langelier Index is **zero**, the water is **stable**
- If the Langelier Index is **positive**, the water will be **scale-forming**
- If the Langelier Index is **negative**, the water will be **corrosive**

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CORROSIVITY CHARACTERISTICS AS ADDRESSED BY INDICES

Corrosive Characteristics	Langelier Saturation Index (LSI)	Aggressive Index
Highly Aggressive	< -2.0	< 10.0
Moderately Aggressive	-2.0 to 0.0	10.0 to 12.0
Non-aggressive	> 0.0	> 12.0

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ALKALINITY, HARDNESS, TDS & CONDUCTIVITY

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ALKALINITY

7

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ALKALINITY

- The measure of water's ability to neutralize acids.
- Result of carbonates, bicarbonates and hydroxides
- Needed for coagulation to stabilize the water against a pH change
- Expressed as mg/L $CaCO_3$

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ALKALINITY

- Measured by determining the amount of acid needed to drop the pH of a sample to a certain endpoint
  - Color indicators can be used instead of a pH probe
- Phenolphthalein alkalinity is measure by titrating to a pH of 8.3
  - Phenolphthalein color indicator may be used
- Total alkalinity is determined by titrating to a pH value of 4.5
  - Bromcresol Green-Methyl Red color indicator may be used

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ACCURACY CHECK – SAMPLE SPIKE

- According to Hach's method 8221
  1. Snap the neck off an Alkalinity Voluette Ampule Standard Solution, 0.500 N.
  2. Use the TenSette Pipet to add 0.1 mL of standard to the sample titrated. Resume titration back to the same end point. Record the volume of titrant needed.
  3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.
  4. The mL of titrant required should increase by 5.0 mL for each 0.1 mL increment of standard added in a 100 mL sample.

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INTERFERENCES

- Chlorine at levels above 3.5 mg/L cause a yellow-brown color upon addition of the Bromcresol Green-Methyl Red indicator powder pillow
- Residual chlorine interference with the indicator may be removed by adding a drop of 0.1 N sodium thiosulfate

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ACCURACY CHECK

- How do I know I'm reaching the correct end point with color indicators?
  - You can purchase pH buffers at the pH end point you are wanting to reach.
  - Buy a pH 8.3 and add the phenolphthalein indicator, this should be the resulting end point color you are trying to achieve.

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HARDNESS

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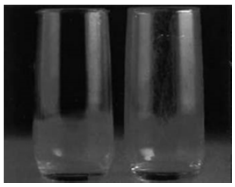
HARDNESS

- A quality of water caused by divalent metallic cations
- The principal hardness-causing cations are calcium and magnesium



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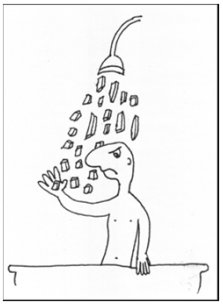
HARDNESS

- Hard water usually requires more soap to produce a foam or lather
- Hard water also produces scale in hot water pipes, heaters, boilers and other units where the temperature of the water is increased



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HARDNESS

- 0-25 mg/L as $CaCO_3$ is very soft
- 25-75 mg/L as $CaCO_3$ is soft
- 75-150 mg/L as $CaCO_3$ is moderately hard
- 150-300 mg/L as $CaCO_3$ is hard
- 300 mg/L and up as $CaCO_3$ is very hard

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ACCURACY CHECK – SAMPLE SPIKE

- According to Hach's method 8226
  1. Snap the neck off an Hardness Voluette Ampule Standard Solution, 10,000-mg/L as $CaCO_3$.
  2. Use the TenSette Pipet to add 0.1 mL of standard to the sample titrated. Swirl to mix.
  3. Titrate the spiked sample to the end point. Record the volume of titrant needed.
  4. Use the TenSette Pipet to add 0.2 mL of standard to the titrated sample. Swirl to mix.
  5. Titrate the spiked sample to the end point. Record the volume of titrant needed.

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ACCURACY CHECK – SAMPLE SPIKE

- According to Hach's method 8226 – continued
  6. Use the TenSette Pipet to add 0.3 mL of standard to the titrated sample. Swirl to mix.
  7. Titrate the spiked sample to the end point. Record the volume of titrant needed.
  8. Each 0.1 mL of standard that was added should use 1.0 mL of titrant to reach the endpoint. If more or less titrant was used, there can be an interference or the concentration of the titrant has changed.

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Total Dissolved Solids

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Total Dissolved Solids (TDS)

- Sources
  - Any minerals, salts, metals, cations or anions dissolved in water
  - TDS comprises inorganic salts principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulfates
  - Originate from natural sources, sewage, urban run-off, industrial waste waters and chemicals used in water treatment process
  - In the US elevated TDS has been due to natural environmental features such as mineral springs, carbonate deposits, salt deposits, agricultural run-off, storm water, point/non-point wastewater discharges

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Potential Effects of Elevated TDS

- Not necessarily a health, however, an aesthetic hazard for taste
- Concentration of TDS ions may cause corrosive, salty, brackish taste, result in scale formation
- Elevations of nitrates, arsenic, aluminum, copper, lead, etc if high TDS
- At 500 mg/L one will get the "barn yard trots"

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Conductivity

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Conductivity

- Current is carried by inorganic dissolved solids: Sodium, calcium, magnesium, iron, aluminum, chloride, nitrate, etc.
- Some anions and cations are toxic and a high measurement warrants looking at causes
- Conductivity is the reciprocal of resistance of the solution tested

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Lab Conductivity Measurements

- Establish degree of mineralization to assess effect of ions on chemical equilibrium, physiological effect on plants, animals, and corrosion rates
- Evaluate variations in dissolved mineral concentration of raw water or wastewater
- Determine amount of ionic reagent needed in certain precipitation and neutralization reactions
- Estimate total dissolved solids in a sample

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Why Electrical Conductivity is Important

- Estimates the amount of total dissolved solids (TDS) in your effluent water
- Or, total amount of dissolved ions in the water
- Higher than 500 mg/L indicates problems and taste/odor concerns

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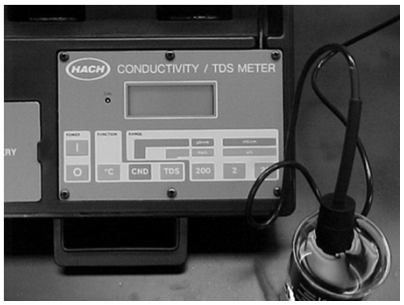
CONDUCTIVITY/TDS METER



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Meters

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TDS/Conductivity Sampling

- Collect samples in clean plastic or glass bottles
- Analyze as soon as possible after collection
- Samples may be stored at least 24 hours by cooling to 4°C (39°F)
- Meter will normally compensate for any variation of temperature from 20 to 25°C
- Samples coated with oils, grease, or fats will coat the electrode and effect accuracy
- Rinse probe with DI water after each sample tested

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Conductivity Measurement

- Electrolytic conductivity is the ability of a solution to pass an electric current and is the reciprocal of the solution resistivity
- Current carried by inorganic dissolved solids
- Organic materials like oils, alcohol's, phenols, and sugars do not carry electric current well
- Basic unit of measure is the siemens (mho)
- Microsiemens/cm are used more frequently as expression of measurement of meters

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TDS Measurement w/ Probe

- TDS expresses the concentration of a sample in grams/liter and milligrams/liter of the various ions
- The conductivity probe is not ion-selective but measures the total sum of the concentrations of the inorganic components of the solution
- The HACH Model 44600 Conductivity/TDS Meter the TDS value is half the conductivity value

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TDS Measurement Gravimetric

- TDS are referred to the weight per unit volume of solids remaining after a sample has been filtered to remove suspended and colloidal solids
- The solids passing through the filter are evaporated to dryness
- The residue left over after filtration and evaporation represents the total dissolved solids

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TDS Measurement Gravimetric

- The preferred temperature for evaporation is 180°C for at least an hour
- Cool in a dessicator to balance room temperature and weigh
- Repeat the drying cycle of drying, cooling, desiccating and weighing until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less

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Calculation

- $mg/L = \frac{(A-B)(1000)}{\text{sample vol, mL}}$
- A = weight of dried residue & dish, mg
- B = weight of dish, mg

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USE BENCH SHEETS PROVIDED FOR EACH TEST!

2320 ALKALINITY*

2320 A. Introduction

1. Discussion

Alkalinity of a water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the endpoint pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents. The measured values also may include contributions from borates, phosphates, silicates, or other bases if these are present. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of a water for irrigation. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes. Raw domestic wastewater has an alkalinity less than, or only slightly greater than, that of the water supply. Properly operating anaerobic digesters typically have supernatant alkalinities in the range of 2000 to 4000 mg calcium carbonate ($CaCO_3$)/L.[1]

2. Reference

1. Pohland, F.G. & D.E. Bloodgood. 1963. Laboratory studies on mesophilic and thermophilic anaerobic sludge digestion. *J. Water Pollut. Control Fed.* 35:11.

* Approved by Standard Methods Committee, 1997. Editorial revisions, 2011.

2320 B. Titration Method

1. General Discussion

a. Principle: Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the endpoint pH used. For methods of determining inflection points from titration curves and the rationale for titrating to fixed pH endpoints, see Section 2310B.1*a*.

For samples of low alkalinity (less than 20 mg $CaCO_3$/L) use an extrapolation technique based on the near proportionality of concentration of hydrogen ions to excess of titrant beyond the equivalence point. The amount of standard acid required to reduce pH exactly 0.30 pH unit is measured carefully. Because this change in pH corresponds to an exact doubling of the hydrogen ion concentration, a simple extrapolation can be made to the equivalence point.[1,2]

b. Endpoints: When alkalinity is due entirely to carbonate or bicarbonate content, the pH at the equivalence point of the titration is determined by the concentration of carbon dioxide (CO_2) at that stage. CO_2 concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration. The pH values in Table 2320:I are suggested as the equivalence points for the corresponding alkalinity concentrations as milligrams $CaCO_3$ per liter. "Phenolphthalein alkalinity" is the term traditionally used for the quantity measured by titration to pH 8.3 irrespective of the colored indicator, if any, used in the determination. Phenolphthalein or metacresol purple may be used for alkalinity titration to pH 8.3. Bromcresol green or a mixed bromcresol green-methyl red indicator may be used for pH 4.5.

T1

Table 2320:I Endpoint pH Values

Test Condition	Endpoint pH	
	Total Alkalinity	Phenolphthalein Alkalinity
Alkalinity, mg $CaCO_3$/L:		
30	4.9	8.3
150	4.6	8.3
500	4.3	8.3
Silicates, phosphates known or suspected	4.5	8.3
Routine or automated analyses	4.5	8.3
Industrial waste or complex system	4.5	8.3

c. Interferences: Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally. Do not filter, dilute, concentrate, or alter sample.

d. Selection of procedure: Determine sample alkalinity from volume of standard acid required to titrate a portion to a designated pH taken from ¶ *b* above. Titrate at room temperature with a properly calibrated pH meter or electrically operated titrator, or use color indicators. If using color indicators, prepare and titrate an indicator blank.

Report alkalinity less than 20 mg $CaCO_3$/L only if it has been determined by the low-alkalinity method of 2320B.4*d*.

https://doi.org/10.2105/SMWW.2882.023

Construct a titration curve for standardization of reagents.

Color indicators may be used for routine and control titrations in the absence of interfering color and turbidity and for preliminary titrations to select sample size and strength of titrant (see ¶ *e* below).

e. Sample size: See Section 2310B.1*e* for selection of size sample to be titrated and normality of titrant, substituting 0.02*N* or 0.1*N* sulfuric (H_2SO_4) or hydrochloric (HCl) acid for the standard alkali of that method. For the low-alkalinity method, titrate a 200-mL sample with 0.02*N* H_2SO_4 from a 10-mL buret.

f. Sampling and storage: See Section 2310B.1*f*.

g. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Tables 2020:I and II.

2. Apparatus

See Section 2310B.2.

3. Reagents

a. Sodium carbonate solution, approximately 0.05*N:* Dry 3 to 5 g primary standard Na_2CO_3 at 250°C for 4 h and cool in a desiccator. Weigh 2.5 ± 0.2 g (to the nearest mg), transfer to a 1-L volumetric flask, fill flask to the mark with distilled water, and dissolve and mix reagent. Do not keep longer than 1 week.

b. Standard sulfuric acid or hydrochloric acid, 0.1*N:* Prepare acid solution of approximately 0.1*N* and determine exact normality as follows. Standardize against 40.00 mL 0.05*N* Na_2CO_3 solution, with about 60 mL water, in a beaker by titrating potentiometrically to pH of about 5. Lift out electrodes, rinse into the same beaker, and boil gently for 3 to 5 min under a watch glass cover. Cool to room temperature, rinse cover glass into beaker, and finish titrating to the pH inflection point. Calculate normality:

$$\text{Normality, } N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1-L flask,
B = mL Na_2CO_3 solution taken for titration, and
C = mL acid used.

Use measured normality in calculations or adjust to 0.1000*N*; 1 mL 0.1000*N* solution = 5.00 mg $CaCO_3$.

c. Standard sulfuric acid or hydrochloric acid, 0.02*N:* Dilute 200.00 mL 0.1000*N* standard acid to 1000 mL with distilled or deionized water. Standardize by potentiometric titration of 15.00 mL 0.05*N* Na_2CO_3 according to the procedure of ¶ *b* above; 1 mL = 1.00 mg $CaCO_3$.

d. Bromcresol green indicator solution, pH 4.5 indicator: Dissolve 100 mg bromcresol green, sodium salt, in 100 mL distilled water.

e. Mixed bromcresol green-methyl red indicator solution:[3] Use either the aqueous or the alcoholic solution:

1) Dissolve 100 mg bromcresol green sodium salt and 20 mg methyl red sodium salt in 100 mL distilled water.
2) Dissolve 100 mg bromcresol green and 20 mg methyl red in 100 mL 95% ethyl alcohol or isopropyl alcohol.

f. Metacresol purple indicator solution, pH 8.3 indicator: Dissolve 100 mg metacresol purple in 100 mL water.

g. Phenolphthalein solution, alcoholic, pH 8.3 indicator.

4. Procedure

a. Color change: See Section 2310B.4*b*.

b. Potentiometric titration curve: Follow the procedure for determining acidity (Section 2310B.4*c*), substituting the appropriate normality of standard acid solution for standard NaOH, and continue titration to pH 4.5 or lower. Do not filter, dilute, concentrate, or alter the sample.

c. Potentiometric titration to preselected pH: Determine the appropriate endpoint pH according to 2320B.1*b*. Prepare sample and titration assembly (Section 2310B.4*c*). Titrate to the endpoint pH without recording intermediate pH values and without undue delay. As the endpoint is approached make smaller additions of acid and be sure that pH equilibrium is reached before adding more titrant.

d. Potentiometric titration of low alkalinity: For alkalinities less than 20 mg/L titrate 100 to 200 mL according to the procedure of ¶ *c* above, using a 10-mL microburet and 0.02*N* standard acid solution. Stop the titration at a pH in the range 4.3 to 4.7 and record volume and exact pH. Carefully add additional titrant to reduce the pH exactly 0.30 pH unit and again record volume.

5. Calculations

a. Potentiometric titration to endpoint pH:

$$\text{Alkalinity, mg } CaCO_3\text{/L} = \frac{A \times N \times 50\,000}{\text{mL sample}}$$

where:

A = mL standard acid used, and
N = normality of standard acid.

or

$$\text{Alkalinity, mg } CaCO_3\text{/L} = \frac{A \times t \times 1000}{\text{mL sample}}$$

where:

t = titer of standard acid, mg $CaCO_3$/mL.

Report pH of endpoint used as follows: "The alkalinity to pH _____ = _____ mg $CaCO_3$/L" and indicate clearly if this pH corresponds to an inflection point of the titration curve.

b. Potentiometric titration of low alkalinity:

$$\text{Total alkalinity, mg } CaCO_3\text{/L} = \frac{(2\,B - C) \times N \times 50\,000}{\text{mL sample}}$$

where:

B = mL titrant to first recorded pH,

https://doi.org/10.2105/SMWW.2882.023

TABLE 2320:II. ALKALINITY RELATIONSHIPS*

Result of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Concentration as $CaCO_3$
$P = 0$	0	0	T
$P < ½T$	0	$2P$	$T - 2P$
$P = ½T$	0	$2P$	0
$P > ½T$	$2P - T$	$2(T - P)$	0
$P = T$	T	0	0

* Key: P—phenolphthalein alkalinity; T—total alkalinity.

C = total mL titrant to reach pH 0.3 unit lower, and
N = normality of acid.

c. Calculation of alkalinity relationships: The results obtained from the phenolphthalein and total alkalinity determinations offer a means for stoichiometric classification of the three principal forms of alkalinity present in many waters. The classification ascribes the entire alkalinity to bicarbonate, carbonate, and hydroxide, and assumes the absence of other (weak) inorganic or organic acids, such as silicic, phosphoric, and boric acids. It further presupposes the incompatibility of hydroxide and bicarbonate alkalinities. Because the calculations are made on a stoichiometric basis, ion concentrations in the strictest sense are not represented in the results, which may differ significantly from actual concentrations especially at pH >10. According to this scheme:

1) Carbonate (CO_3^{2-}) alkalinity is present when phenolphthalein alkalinity is not zero but is less than total alkalinity.
2) Hydroxide (OH^-) alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity.
3) Bicarbonate (HCO_3^-) alkalinity is present if phenolphthalein alkalinity is less than half the total alkalinity. These relationships may be calculated by the following scheme, where P is phenolphthalein alkalinity and T is total alkalinity (2330B.1*b*).

Select the smaller value of P or ($T-P$). Then, carbonate alkalinity equals twice the smaller value. When the smaller value is P, the balance ($T-2P$) is bicarbonate. When the smaller value is ($T-P$), the balance ($2P-T$) is hydroxide. All results are expressed as $CaCO_3$. The mathematical conversion of the results is shown in Table 2320:II. (A modification of Table 2320:II that is more accurate when $P \simeq {}^1/_2T$ has been proposed.[4])

Alkalinity relationships also may be computed nomographically (see Carbon Dioxide, Section 4500-CO_2). Accurately measure pH, calculate OH^- concentration as milligrams $CaCO_3$ per liter, and calculate concentrations of CO_3^{2-} and HCO_3^- as milligrams $CaCO_3$ per liter from the OH^- concentration, and the phenolphthalein and total alkalinities by the following equations:

$$CO_3^{2-} = 2P - 2[OH^-]$$

$$HCO_3^- = T - 2P + [OH^-]$$

Similarly, if difficulty is experienced with the phenolphthalein endpoint, or if a check on the phenolphthalein titration is desired, calculate phenolphthalein alkalinity as $CaCO_3$ from the results of the nomographic determinations of carbonate and hydroxide ion concentrations:

$$P = 1/2\,[CO_3^{2-}] + [OH^-]$$

6. Precision and Bias

No general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and sample handling before the analysis.

In the range of 10 to 500 mg/L, when the alkalinity is due entirely to carbonates or bicarbonates, a standard deviation of 1 mg $CaCO_3$/L can be achieved. Forty analysts in 17 laboratories analyzed synthetic samples containing increments of bicarbonate equivalent to 120 mg $CaCO_3$/L. The titration procedure of 2320B.4*b* was used, with an endpoint pH of 4.5. The standard deviation was 5 mg/L and the average bias (lower than the true value) was 9 mg/L.[5]

Sodium carbonate solutions equivalent to 80 and 65 mg $CaCO_3$/L were analyzed by 12 laboratories according to the procedure of 2320B.4*c*.[6] The standard deviations were 8 and 5 mg/L, respectively, with negligible bias.[6] Four laboratories analyzed six samples having total alkalinities of about 1000 mg $CaCO_3$/L and containing various ratios of carbonate/bicarbonate by the procedures of both 2320B.4*a* and *c*. The pooled standard deviation was 40 mg/L, with negligible difference between the procedures.

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2340 HARDNESS*

2340 A. Introduction

1. Terminology

Originally, water hardness was understood to be a measure of the capacity of water to precipitate soap. Soap is precipitated chiefly by the calcium and magnesium ions present. Other polyvalent cations also may precipitate soap, but they often are in complex forms, frequently with organic constituents, and their role in water hardness may be minimal and difficult to define. In conformity with current practice, total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per liter.

When hardness numerically is greater than the sum of carbonate and bicarbonate alkalinity, that amount of hardness equivalent to the total alkalinity is called "carbonate hardness"; the amount of hardness in excess of this is called "noncarbonate hardness." When the hardness numerically is equal to or less than the sum of carbonate and bicarbonate alkalinity, all hardness is carbonate hardness and noncarbonate hardness is absent. The hardness may range from zero to hundreds of milligrams per liter, depending on the source and treatment to which the water has been subjected.

2. Selection of Method

Two methods are presented. Method B, hardness by calculation, is applicable to all waters and yields the higher accuracy. If a mineral analysis is performed, hardness by calculation can be reported. Method C, the EDTA titration method, measures the calcium and magnesium ions and may be applied with appropriate modification to any kind of water. The procedure described affords a means of rapid analysis.

3. Reporting Results

When reporting hardness, state the method used, for example, "hardness (calc.)" or "hardness (EDTA)."

* Approved by Standard Methods Committee, 1997. Editorial revisions, 2011.

2340 B. Hardness by Calculation

1. Discussion

The preferred method for determining hardness is to compute it from the results of separate determinations of calcium and magnesium.

2. Calculation

$$\text{Hardness, mg equivalent } CaCO_3/L = 2.497\,[\text{Ca, mg/L}] + 4.118\,[\text{Mg, mg/L}]$$

2340 C. EDTA Titrimetric Method

1. General Discussion

a. Principle: Ethylenediaminetetraacetic acid and its sodium salts (abbreviated EDTA) form a chelated soluble complex when added to a solution of certain metal cations. If a small amount of a dye such as Eriochrome Black T or Calmagite is added to an aqueous solution containing calcium and magnesium ions at a pH of 10.0 ± 0.1, the solution becomes wine red. If EDTA is added as a titrant, the calcium and magnesium will be complexed, and when all of the magnesium and calcium has been complexed the solution turns from wine red to blue, marking the endpoint of the titration. Magnesium ion must be present to yield a satisfactory endpoint. To ensure this, a small amount of complexometrically neutral magnesium salt of EDTA is added to the buffer; this automatically introduces sufficient magnesium and obviates the need for a blank correction.

The sharpness of the endpoint increases with increasing pH. However, the pH cannot be increased indefinitely because of the danger of precipitating calcium carbonate, $CaCO_3$, or magnesium hydroxide, $Mg(OH)_2$, and because the dye changes color at high pH values. The specified pH of 10.0 ± 0.1 is a satisfactory compromise. A limit of 5 min is set for the duration of the titration to minimize the tendency toward $CaCO_3$ precipitation.

b. Interference: Some metal ions interfere by causing fading or indistinct endpoints or by stoichiometric consumption of EDTA. Reduce this interference by adding certain inhibitors before titration. MgCDTA [see 2340C.2*b*3)], selectively complexes heavy metals, releases magnesium into the sample, and may be used as a substitute for toxic or malodorous inhibitors. It is useful only when the magnesium substituted for heavy metals does not contribute significantly to the total hardness. With heavy metal or polyphosphate concentrations below those indicated in Table 2340:I, use Inhibitor I or II. When higher concentrations of heavy metals are present, determine calcium and magnesium by a non-EDTA method (see Sections 3500-Ca and 3500-Mg) and obtain hardness by calculation. The values in Table 2340:I are T1

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TABLE 2340:I. MAXIMUM CONCENTRATIONS OF INTERFERENCES PERMISSIBLE WITH VARIOUS INHIBITORS*

Interfering Substance	Max. Interference Concentration *mg/L* Inhibitor I	Inhibitor II
Aluminum	20	20
Barium	†	†
Cadmium	†	20
Cobalt	over 20	0.3
Copper	over 30	20
Iron	over 30	5
Lead	†	20
Manganese (Mn^{2+})	†	1
Nickel	over 20	0.3
Strontium	†	†
Zinc	†	200
Polyphosphate		10

* Based on 25-mL sample diluted to 50 mL.
† Titrates as hardness.

intended as a rough guide only and are based on using a 25-mL sample diluted to 50 mL.

Suspended or colloidal organic matter also may interfere with the endpoint. Eliminate this interference by evaporating the sample to dryness on a steam bath and heating in a muffle furnace at 550°C until the organic matter is completely oxidized. Dissolve the residue in 20 mL 1*N* hydrochloric acid (HCl), neutralize to pH 7 with 1*N* sodium hydroxide (NaOH), and make up to 50 mL with distilled water; cool to room temperature and continue according to the general procedure.

c. Titration precautions: Conduct titrations at or near normal room temperature. The color change becomes impractically slow as the sample approaches freezing temperature. Indicator decomposition becomes a problem in hot water.

The specified pH may produce an environment conducive to $CaCO_3$ precipitation. Although the titrant slowly redissolves such precipitates, a drifting endpoint often yields low results. Completion of the titration within 5 min minimizes the tendency for $CaCO_3$ to precipitate. The following three methods also reduce precipitation loss:

1) Dilute sample with distilled water to reduce $CaCO_3$ concentration. This simple expedient has been incorporated in the procedure. If precipitation occurs at this dilution of 1 + 1 use modification 2) or 3). Using too small a sample contributes a systematic error due to the buret-reading error.

2) If the approximate hardness is known or is determined by a preliminary titration, add 90% or more of titrant to sample *before* adjusting pH with buffer.

3) Acidify sample and stir for 2 min to expel CO_2 *before* pH adjustment. Determine alkalinity to indicate amount of acid to be added.

d. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Tables 2020:I and II.

2. Reagents

a. Buffer solution:

1) Dissolve 16.9 g ammonium chloride (NH_4Cl) in 143 mL conc ammonium hydroxide (NH_4OH). Add 1.25 g magnesium salt of EDTA (available commercially) and dilute to 250 mL with distilled water.

2) If the magnesium salt of EDTA is unavailable, dissolve 1.179 g disodium salt of ethylenediaminetetraacetic acid dihydrate (analytical reagent grade) and 780 mg magnesium sulfate ($MgSO_4 \cdot 7H_2O$) or 644 mg magnesium chloride ($MgCl_2 \cdot 6H_2O$) in 50 mL distilled water. Add this solution to 16.9 g NH_4Cl and 143 mL conc NH_4OH with mixing and dilute to 250 mL with distilled water. To attain the highest accuracy, adjust to exact equivalence through appropriate addition of a small amount of EDTA or $MgSO_4$ or $MgCl_2$.

Store Solution 1) or 2) in a plastic or borosilicate glass container for no longer than 1 month. Stopper tightly to prevent loss of ammonia (NH_3) or pickup of carbon dioxide (CO_2). Dispense buffer solution by means of a bulb-operated pipet. Discard buffer when 1 or 2 mL added to the sample fails to produce a pH of 10.0 ± 0.1 at the titration endpoint.

3) Satisfactory alternate "odorless buffers" also are available commercially. They contain the magnesium salt of EDTA and have the advantage of being relatively odorless and more stable than the NH_4Cl-NH_4OH buffer. They usually do not provide as good an endpoint as NH_4Cl-NH_4OH because of slower reactions and they may be unsuitable when this method is automated. Prepare one of these buffers by mixing 55 mL conc HCl with 400 mL distilled water and then, slowly and with stirring, adding 300 mL 2-aminoethanol (free of aluminum and heavier metals). Add 5.0 g magnesium salt of EDTA and dilute to 1 L with distilled water.

b. Complexing agents: For most waters no complexing agent is needed. Occasionally water containing interfering ions requires adding an appropriate complexing agent to give a clear, sharp change in color at the endpoint. The following are satisfactory:

1) *Inhibitor I*—Adjust acid samples to pH 6 or higher with buffer or 0.1*N* NaOH. Add 250 mg sodium cyanide (NaCN) in powder form. Add sufficient buffer to adjust to pH 10.0 ± 0.1. [**CAUTION: NaCN is extremely poisonous. Take extra precautions in its use (see Section 1090)**]. Dispose of solutions containing this inhibitor in accordance with all applicable governmental regulations (see Section 1100C), taking special precautions to prevent its contact with acids, which can liberate volatile poisonous hydrogen cyanide.)

2) *Inhibitor II*—Dissolve 5.0 g sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$) or 3.7 g $Na_2S \cdot 5H_2O$ in 100 mL distilled water. Exclude air with a tightly fitting rubber stopper. This inhibitor deteriorates through air oxidation. It produces a sulfide precipitate that obscures the endpoint when appreciable concentrations of heavy metals are present. Use 1 mL in 2340C.3*b* below.

3) *MgCDTA*—Magnesium salt of 1, 2-cyclohexanediaminetetraacetic acid. Add 250 mg per 100 mL sample and dissolve completely before adding buffer solution. Use this complexing agent to avoid using toxic or odorous inhibitors when interfering substances are present in concentrations that affect the endpoint but will not contribute significantly to the hardness value.

Commercial preparations incorporating a buffer and a complexing agent are available. Such mixtures must maintain pH 10.0 ± 0.1 during titration and give a clear, sharp endpoint when the sample is titrated.

c. Indicators: Many types of indicator solutions have been advocated and may be used if the analyst demonstrates that they yield accurate values. The prime difficulty with indicator solutions is deterioration with aging, giving indistinct endpoints. For example,

alkaline solutions of Eriochrome Black T are sensitive to oxidants and aqueous or alcoholic solutions are unstable. In general, use the least amount of indicator providing a sharp endpoint. It is the analyst's responsibility to determine individually the optimal indicator concentration.

1) *Eriochrome Black T*—Sodium salt of 1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sulfonic acid; No. 203 in the Color Index. Dissolve 0.5 g dye in 100 g 2,2′,2″-nitrilotriethanol (also called triethanolamine) or 2-methoxymethanol (also called ethylene glycol monomethyl ether). Add 2 drops per 50 mL solution to be titrated. Adjust volume if necessary.

2) *Calmagite*—1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid. This is stable in aqueous solution and produces the same color change as Eriochrome Black T, with a sharper endpoint. Dissolve 0.10 g Calmagite in 100 mL distilled water. Use 1 mL per 50 mL solution to be titrated. Adjust volume if necessary.

3) Indicators 1 and 2 can be used in dry powder form if care is taken to avoid excess indicator. Prepared dry mixtures of these indicators and an inert salt are available commercially.

If the endpoint color change of these indicators is not clear and sharp, it usually means that an appropriate complexing agent is required. If NaCN inhibitor does not sharpen the endpoint, the indicator probably is at fault.

d. Standard EDTA titrant, 0.01*M:* Weigh 3.723 g analytical reagent-grade disodium ethylenediaminetetraacetate dihydrate, also called (ethylenedinitrilo)tetraacetic acid disodium salt (EDTA), dissolve in distilled water, and dilute to 1000 mL. Standardize against standard calcium solution (¶ *e* below) as described in 2340C.3*b* below.

Because the titrant extracts hardness-producing cations from soft-glass containers, store in polyethylene (preferable) or borosilicate glass bottles. Compensate for gradual deterioration by periodic restandardization and by using a suitable correction factor.

e. Standard calcium solution: Weigh 1.000 g anhydrous $CaCO_3$ powder (primary standard or special reagent low in heavy metals, alkalis, and magnesium) into a 500-mL Erlenmeyer flask. Place a funnel in the flask neck and add, a little at a time, 1 + 1 HCl until all $CaCO_3$ has dissolved. Add 200 mL distilled water and boil for a few minutes to expel CO_2. Cool, add a few drops of methyl red indicator, and adjust to the intermediate orange color by adding 3*N* NH_4OH or 1 + 1 HCl, as required. Transfer quantitatively and dilute to 1000 mL with distilled water; 1 mL = 1.00 mg $CaCO_3$.

f. Sodium hydroxide (NaOH), 0.1*N*.

3. Procedure

a. Pretreatment of polluted water and wastewater samples: Use nitric acid-sulfuric acid or nitric acid-perchloric acid digestion (Section 3030).

b. Titration of sample: Select a sample volume that requires less than 15 mL EDTA titrant and complete titration within 5 min, measured from time of buffer addition.

Dilute 25.0 mL sample to about 50 mL with distilled water in a porcelain casserole or other suitable vessel. Add 1 to 2 mL buffer solution. Usually 1 mL will be sufficient to give a pH of 10.0 to 10.1. The absence of a sharp endpoint color change in the titration usually means that an inhibitor must be added at this point (2340C.2*b et seq.*) or that the indicator has deteriorated.

Add 1 to 2 drops indicator solution or an appropriate amount of dry-powder indicator formulation [2340C.2*c*3)]. Add standard EDTA titrant slowly, with continuous stirring, until the last reddish tinge disappears. Add the last few drops at 3- to 5-s intervals. At the endpoint the solution normally is blue. Daylight or a daylight fluorescent lamp is recommended highly because ordinary incandescent lights tend to produce a reddish tinge in the blue at the endpoint.

If sufficient sample is available and interference is absent, improve accuracy by increasing sample size, as described in ¶ *c* below.

c. Low-hardness sample: For ion-exchanger effluent or other softened water and for natural waters of low hardness (less than 5 mg/L), take a larger sample, 100 to 1000 mL, for titration and add proportionately larger amounts of buffer, inhibitor, and indicator. Add standard EDTA titrant slowly from a microburet and run a blank, using redistilled, distilled, or deionized water of the same volume as the sample, to which identical amounts of buffer, inhibitor, and indicator have been added. Subtract volume of EDTA used for blank from volume of EDTA used for sample.

4. Calculation

$$\text{Hardness (EDTA) as mg } CaCO_3\text{/L} = \frac{A \times B \times 1000}{\text{mL sample}}$$

where:

A = mL titration for sample, and
B = mg $CaCO_3$ equivalent to 1.00 mL EDTA titrant.

5. Precision and Bias

A synthetic sample containing 610 mg/L total hardness as $CaCO_3$ contributed by 108 mg Ca/L and 82 mg Mg/L, and the following supplementary substances: 3.1 mg K/L, 19.9 mg Na/L, 241 mg Cl^-/L, 0.25 mg NO_2^--N/L, 1.1 mg NO_3^--N/L, 259 mg SO_4^{2-}/L, and 42.5 mg total alkalinity/L (contributed by $NaHCO_3$) in distilled water was analyzed in 56 laboratories by the EDTA titrimetric method with a relative standard deviation of 2.9% and a relative error of 0.8%.

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Solids, Total Filterable (Total Dissolved)

USEPA[1] Gravimetric Method[2] — Method 8163

Scope and application: For water and wastewater.

[1] USEPA accepted
[2] Adapted from *Standard Methods for the Examination of Water and Wastewater, Part 2540C*.

Test preparation

Before starting

Total Filterable Solids = Total Dissolved Solids (TDS)
Dry samples with high bicarbonate concentrations at 180 °C (356 °F) to make sure that the conversion of bicarbonate to carbonate is complete.
Limit the sample size to lessthan 200 mg residue.
When measuring volatile dissolved solids, heat the evaporating dish for 1 hour at 550 °C (1022 °F) before use.
If applicable, use sample residue from this procedure directly in Method 8277, Solids, Total Volatile and Fixed.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Description	Quantity
Evaporating dish	1
Filter flask	1
Filter holder	1
Filter, 47 mm	1
Graduated cylinder, 100 mL	1
Hot plate	1
Steam bath, 8" diameter	1
Analytical balance	1
Desiccator	1
Tongs	1
Tweezers	1
Drying oven	1
Deionized water	varies

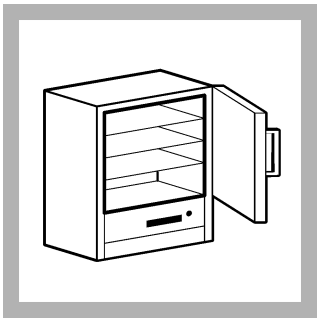
Refer to Consumables and replacement items on page 4 for order information.

Sample collection preservation and storage

- Collect samples in clean glass or plastic bottles.
- Analyze the samples as soon as possible for best results.

- If prompt analysis is not possible, keep the samples at or below 4 °C (39 °F) for up to 7 days.
- Let the sample temperature increase to room temperature before analysis.

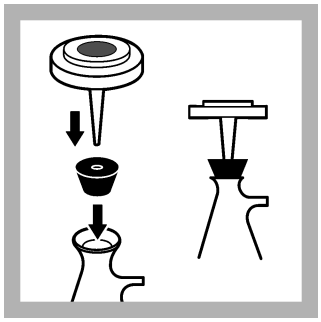
Test procedure



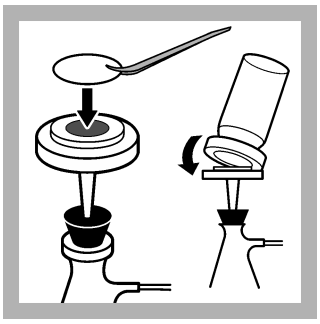
1. Put a clean evaporating dish in a drying oven at 180 °C (356 °F) for 1 hour.

2. Remove the dish from the oven. Let the dish temperature decrease to room temperature in a desiccator.

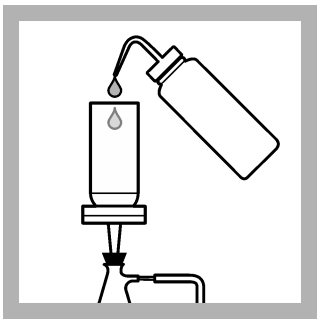
3. Remove all of the residue from the flask with a dilute solution of ammonium hydroxide. Rinse with deionized water.



4. Assemble the filter holder/flask assembly using a clean filter flask.



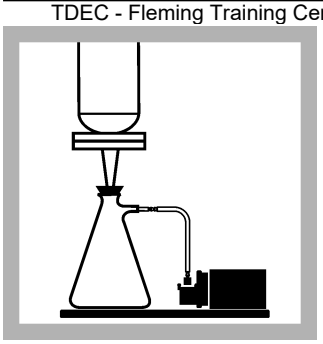
5. Use tweezers to put a 47-mm filter disc in the filter holder. Put the filter holder assembly in the filtering flask.



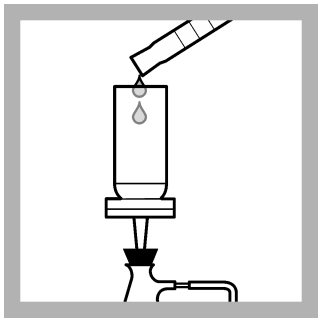
6. Connect vacuum to the filter holder/flask assembly and wash the filter with three separate 20-mL volumes of deionized water.

7. Apply vacuum for 2 to 3 minutes after the water has passed through the filter.

8. Disconnect the vacuum. Discard the washings from the flask.



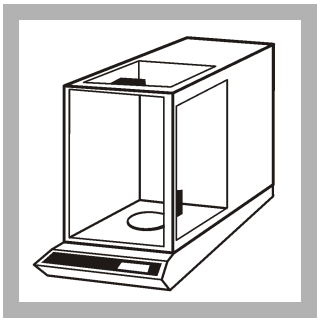
9. Connect vacuum to the filter holder/flask assembly again.



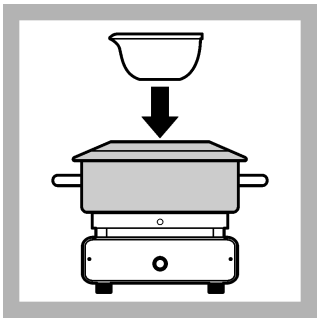
10. Use a clean 100-mL graduated cylinder to pour 100 mL (or more) of a well-mixed, representative water sample into the filter holder.

Note: *For best accuracy, filter as much sample as possible. A sample that contains more than 15 mg of solids can clog the filter. Adjust the volume of the water sample to get the optimum condition. 5-10 completed tests will show if an adjustment is necessary.*

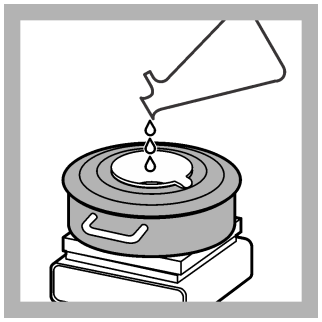
11. Apply vacuum for 2 to 3 minutes after the sample has passed through the filter. Disconnect the vacuum.



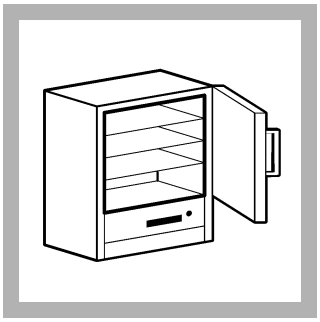
12. Use an analytical balance to weigh the dish to the nearest 0.1 mg (0.0001 g). Record this mg value as B.



13. Put the steam bath on the hot plate. Add water to the steam bath. Put the evaporating dish in the steam bath.

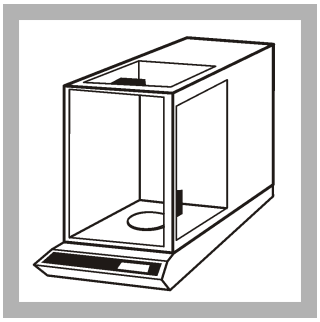


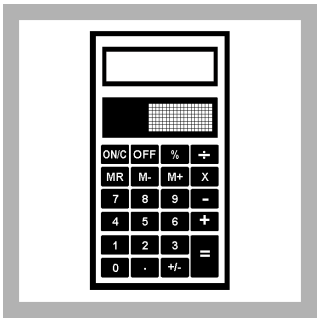
14. Pour the 100-mL filtrate sample from the filter flask into the evaporating dish. Dry for 4 hours. Examine the reservoir of the water bath at regular intervals. Add more water if necessary.



15. Put the evaporating dish in a drying oven at 180 °C (356 °F) for 1 hour.

16. Remove the dish from the oven. Let the dish temperature decrease to room temperature in a desiccator.





17. Use an analytical balance to weigh the dish to the nearest 0.1 mg (0.0001 g). Record this mg value as A. Do steps 15-16 again, until the difference between two successive sample weighings is less than 4% or 0.5 mg, whichever is less. If applicable, use the solid residue directly in method 8277 to determine Volatile Dissolved Solids.

18. Calculate the Total Filterable Residue (TFR).

A – B ÷ Sample volume in liters = mg/L TFR

Summary of method

A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated in a weighed dish and dried to a constant weight at 180 °C (356°F). The increase in the weight of the dish after drying is the total filterable solids (total dissolved solids).

Consumables and replacement items

Description	Quantity/test	Unit	Item no.
Aspirator, vacuum pump	1	each	213100
Balance, Analytical, 115 VAC, 60 Hz	1	each	2936701
Bottle, wash, 500 mL	1	each	62011
Cylinder, graduated, 100 mL	1	each	50842
Desiccant, indicating Drierite	1	each	2088701
Desiccator, without stopcock	1	each	1428500
Desiccator plate, ceramic	1	each	1428400
Evaporating dish, porcelain, w/lip, 120-mL, 90-mm	1	each	52561
Filter disc, 47 mm, glass fiber	1	100/pkg	253000
Filter holder, 47-mm, magnetic base	1	each	1352900
Flask, filtering, 1000 mL	1	each	54653
Hot plate/stirrer, 7 x 7 inch, 115 VAC	1	each	2881600
Hot plate, stirrer, 220–240 VAC	1	each	2881602
Oven, drying, 240 VAC	1	each	1428902
Oven, drying, 120 VAC	1	each	1428900
Steam bath, 8-inch diameter	1	each	2347900
Stopper, rubber, one-hole, No. 8	1	each	211908

Consumables and replacement items (continued)

Description	Quantity/test	Unit	Item no.
Tongs, crucible, 9 inch	1	each	56900
Tubing, rubber, 7.9 mm x 2.4 mm	varies	12 ft	56019
Tweezers, plastic	1	each	1428200
Water, deionized	varies	4 L	27256

Optional reagents and apparatus

Description	Unit	Item no.
Ammonium Hydroxide, 58%	500 mL	10649
Sampling bottle with cap, low density polyethylene, 500-mL	12/pkg	2087079
Brush	each	68700
Pump, vacuum, hand-operated	each	1428300
Pump, vacuum, 1.2 CFM, 220 VAC, European plug	each	2824802
Vacuum Pump, 1.2 CFM 115 V	each	2824800
Stirring rod, glass	3/pkg	177001

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Environmental Express
2345 A Charleston Regional Parkway Charleston, SC 29492
(800) 343-5319 www.envexp.com

Universal Solids Standard Data Sheet

The balance calibration is traceable to NIST through NIST Test Number 822/260017-98.
The calibration check weights are traceable to NIST through Test Number SC020813-1M.

Certified By: Amanda Wilmington Expiration Date: 12/28/2024

A. Basic Use

1. Add 1 to 2 mL of methanol or acetone (to cut static charge) to the vial and shake.
2. Add 5 to 10 mL of DI water to the vial. Recap and shake four or five times.
3. Pour the solution into the appropriate vessel. 1 Liter Vol. flask
4. Repeat steps 2 and 3 until the vial has been rinsed three separate times. This will ensure a quantitative transfer.
5. Bring the standard solution to volume. Use a final volume similar to common sample size.
6. Perform appropriate solids analyses following laboratory SOP.
7. Acceptable result = Nominal Wt. +/- Range Wt.

Note: The Nominal will result in mg/L when sample size is one liter. Dilutions > or < one liter will result in calculably appropriate results.

Catalog Number: F95010

B. Nominal Weight

Nominal Weight = Actual Weight X Average Recovery of statistical data.

C. Range

Range = 3 X Standard Deviation

D. ID#

Each bottle of standard has a unique ID# and corresponding unique solids values. This discreet ID# and solids values are retained on file.

Standard Set # 289770

ID Number	TDS, mg Nominal	Range
58663	152.2	13.6
58664	145.5	13.0
58665	155.6	13.9
58666	150.1	13.4
58667	142.9	12.8
58668	155.0	13.9
58669	155.4	13.9
58670	151.1	13.5
58671	145.5	13.0
58672	152.6	13.6

Conductivity

USEPA Direct Measurement Method[1, 2]

Method 8160

0.01 µS/cm to 200.0 mS/cm

Conductivity Probe

Scope and application: For water and wastewater.

[1] USEPA accepted for reporting for Standard Method 2510-B
[2] Procedure is equivalent to Standard Method 2510-B for wastewater.

Test preparation

Instrument-specific information

This procedure is applicable to the meters and probes that are shown in Table 1. Procedures for other meters and probes can be different.

Table 1 Instrument-specific information

Meter	Probe
HQ14d portable single input, conductivity HQ30d portable single input, multi-parameter HQ40d portable dual input, multi-parameter HQ430d benchtop single input, multi-parameter HQ440d benchtop dual input, multi-parameter	IntelliCAL CDC401 Conductivity
sensION™+ MM156 portable pH/EC/DO	sensION+ 5049 multi-parameter
sensION™+ EC5 portable conductivity sensION™+ MM150 portable pH/ORP/EC	sensION+ 5048, 5059, 5060 or 5062 Conductivity
sensION™+ EC7 lab conductivity sensION™+ EC71 GLP lab conductivity sensION™+ MM374 lab dual input, pH/mV/EC/ISE sensION™+ MM378 lab dual input, pH/ISE/EC/DO	sensION+ 5070 Conductivity

Before starting

Refer to the meter documentation for meter settings and operation. Refer to probe documentation for probe preparation, maintenance and storage information.
Prepare the probe before initial use. Refer to probe documentation.
When an IntelliCAL™ probe is connected to an HQd meter, the meter automatically identifies the measurement parameter and is prepared for use.
Small differences in concentration between samples can increase the stabilization time. Make sure to condition the probe correctly. Try different stir rates to see if the stabilization time decreases.
If solutions are not at the reference temperature, the meter automatically adjusts the conductivity value to the value at the reference temperature.
Measurement errors can occur if the correct temperature correction value is not selected. Refer to Table 2 on page 3 for typical temperature correction values.
Do not touch the tip of the probe.
The cell constant is derived from the calibration standard.
Do not dilute conductivity standards and samples.
For the most accurate results with high conductivity samples, calibrate the cell constant or check the accuracy of the meter with a 111.3 mS/cm (1 Demal) certified conductivity standard.

Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

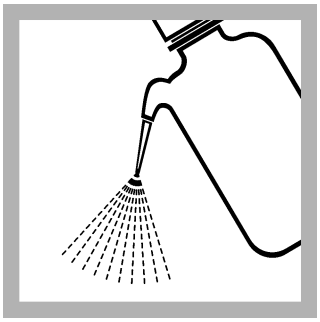
Description	Quantity
Beaker, 100 mL, polypropylene	1
Wash bottle with deionized water	1
Conductivity standard solution (refer to Recommended standards on page 5)	1

Refer to Consumables and replacement items on page 4 for order information.

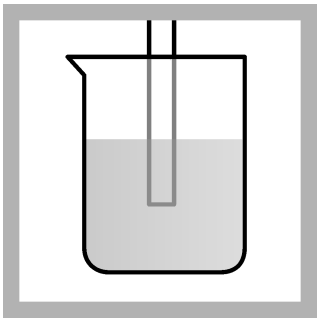
Sample collection and storage

- Collect samples in clean glass or plastic bottles.
- To preserve samples for later analysis, keep the samples at or below 6 °C (43 °F) for a minimum of 24 hours.
- Let the sample temperature increase to room temperature before analysis.

Test procedure

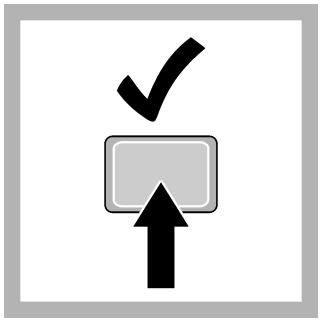


1. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

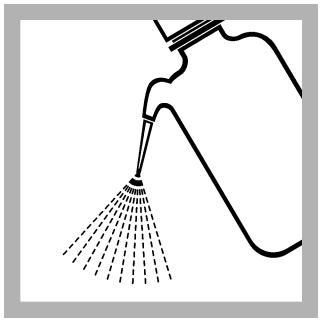


2. Laboratory test: Put the probe in a beaker that contains the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip. Stir the sample at a slow to moderate rate.
Field test: Put the probe in the sample. Move the probe up and down to remove bubbles from the electrode.

Make sure to put the temperature sensor fully in the sample.



3. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.



4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

Conversions

Table 2 shows the conversions to change the readings on the display to other conductivity units.

Table 2 Unit conversion

From	To	Use this equation
mS/cm	µS/cm	mS/cm × 1000
µS/cm	mS/cm	µS/cm × 0.001
µS/cm	µmhos/cm	µS/cm × 1
mS/cm	mmhos/cm	mS/cm × 1
µS/cm	mg/L TDS	µS/cm × 0.64[1]
g/L TDS	mg/L TDS	g/L TDS × 1000
mS/cm	g/L TDS	mS/cm × 0.64
mg/L TDS	g/L TDS	mg/L TDS × 0.001
mg/L TDS	gpg TDS	mg/L TDS × 0.05842
g/L TDS	gpg TDS	g/L TDS × 58.42
µS/cm	ohms cm	1,000,000 ÷ µS/cm
mS/cm	ohms cm	1,000 ÷ mS/cm

Temperature correction

Table 3 shows typical temperature correction values for selected solutions from the linear temperature correction option.

Table 3 Temperature correction

Solution	Percent per °C
Ultrapure water	4.55
Salt (NaCl)	2.125
NaOH	1.72
Dilute ammonia	1.8810
10% HCl	1.325
5% sulfuric acid	0.9698

Interferences

To remove the conductivity that occurs from hydroxide ions, adjust the sample pH as follows:

1. Add 4 drops of phenolphthalein indicator solution to 50 mL of sample. The sample becomes pink.
2. Add 1 drop of gallic acid solution at a time until the pink color is gone.
3. Measure the conductivity.

Accuracy check

Standard solution method

Use the standard solution method to validate the test procedure, the reagents (if applicable) and the instrument.

Items to collect:

- Sodium chloride standard solution with a conductivity value that is near the value of typical samples

[1] TDS is an empirically-derived value from the conductivity measurement. Select a value of 0.5 for simplicity and suitability to a wide variety of waters.

1. Use the test procedure to measure the concentration of the standard solution.
2. Compare the expected result to the actual result.

Clean the probe

Clean the probe when:

- Drifting/inaccurate readings occur as a result of contamination on the sensing element or incorrect storage conditions.
- Slow response time occurs as a result of contamination on the sensing element.
- The slope is out of range as a result of contamination on the sensing element.

For general contamination, complete the steps that follow.

1. Rinse the probe with deionized water. Blot dry with a lint-free cloth.
2. If harsh contaminants are attached to the probe, polish the probe tip with a soft cloth or cotton swab to remove the contaminants.
3. Soak the probe in deionized water for 1 minute.

Method performance

The accuracy of the measurements is dependent on many factors that are related with the overall system, which includes the meter, the probe and calibration solutions. Refer to the meter or probe documentation for more information.

Summary of method

Electrolytic conductivity is the movement of ions in a solution, which makes an electrical current and is the reciprocal of the solution resistivity. The ions come from inorganic dissolved solids (e.g., chloride, nitrate, sulfate and phosphate anions and sodium, calcium, magnesium, iron and aluminum cations). Organic material such as oils, phenols, alcohols and sugars do not have sufficient conductivity for a good estimate of the concentration.

Conductivity meters measure the resistance that occurs in an area of the solution that is defined by the physical design of the probe. A voltage is applied between the electrodes, and the voltage decrease caused by the resistance of the solution is used to calculate the conductivity for each centimeter. The basic unit of measure for conductivity is the Siemen (or mho), which is the reciprocal of the ohm. Other common units for aqueous solutions are milliSiemens/cm (10^{-3} S or mS/cm) and microSiemens/cm (10^{-6} S or µS/cm).

Consumables and replacement items

HQd meters and probes

Description	Unit	Item no.
HQ14d portable single input, conductivity meter	each	HQ14D53201000
HQ30d portable single input, multi-parameter meter	each	HQ30D53000000
HQ40d portable dual input, multi-parameter meter	each	HQ40D53000000
HQ430d benchtop single input, multi-parameter meter	each	HQ430D
HQ440d benchtop dual input, multi-parameter meter	each	HQ440D
IntelliCAL™ standard conductivity probe, 1 m cable	each	CDC40101
IntelliCAL™ standard conductivity probe, 3 m cable	each	CDC40103
IntelliCAL™ rugged conductivity probe, 5 m cable	each	CDC40105
IntelliCAL™ rugged conductivity probe, 10 m cable	each	CDC40110
IntelliCAL™ rugged conductivity probe, 15 m cable	each	CDC40115
IntelliCAL™ rugged conductivity probe, 30 m cable	each	CDC40130

sensION+ meters and probes

Description	Unit	Item no.
sensION™+ EC7 lab conductivity meter	each	LPV3010.97.0002
sensION™+ EC71 GLP lab conductivity meter	each	LPV3110.97.0002
sensION™+ MM374 lab dual input, pH/mV/EC/ISE meter	each	LPV4110.97.0002
sensION™+ MM378 lab dual input, pH/ISE/EC/DO meter	each	LPV4130.97.0002
sensION™+ 5048 portable multi-parameter (pH, conductivity, ORP and temperature) probe	each	LZW5048.97.0002
sensION™+ 5049 portable multi-parameter (pH, conductivity, dissolved oxygen and temperature) probe	each	LZW5049.97.0002
sensION™+ 5059 portable multi-parameter (pH, conductivity and temperature) probe	each	LZW5059.97.0002
sensION™+ 5060 portable platinum conductivity cell probe	each	LZW5060.97.0002
sensION™+ 5062 portable titanium conductivity cell probe	each	LZW5062.97.0002
sensION™+ 5070 laboratory platinum conductivity cell probe	each	LZW5070.97.0002

Recommended standards

Description	Unit	Item no.
NaCl conductivity standards:		
Sodium chloride standard solution, 180 ± 10 mS/cm, 90 ± 1 mg/L TDS	100 mL	2307542
Sodium chloride standard solution, 1000 ± 10 mS per cm, 500 ± 5 mg/L TDS	100 mL	1440042
Sodium chloride standard solution, 1990 ± 20 mS/cm, 995 ± 10 mg/L TDS	100 mL	210542
Sodium chloride standard solution, 18,000 ± 50 mS/cm, 9000 ± 25 mg/L TDS	100 mL	2307442
KCl conductivity standards:		
KCl, 0.1 M, 12.88 mS/cm at 25 °C (77 °F)	500 mL	C20C250
KCl, 0.01 M, 1413 µS/cm at 25 °C (77 °F)	500 mL	C20C270
KCl, 0.001 M, 148 µS/cm at 25 °C (77 °F)	500 mL	C20C280
Certified conductivity standards:		
KCl, 1 Demal, 111.3 mS/cm ± 0.5% at 25 °C (77 °F)	500 mL	S51M001
KCl, 0.1 Demal, 12.85 mS/cm ± 0.35% at 25 °C (77 °F)	500 mL	S51M002
KCl, 0.01 Demal, 1408 mS/cm ± 0.5% at 25 °C (77 °F)	500 mL	S51M003
NaCl, 0.05%, 1015 µS/cm ± 0.5% at 25 °C (77 °F)	500 mL	S51M004

Optional reagents and accessories

Description	Unit	Item no.
Beaker, polypropylene, 100-mL	each	108042
Gallic acid solution	50 mL SCDB	1442326
Hydrochloric Acid Solution, 6 N, 1:1	500 mL	88449
Phenolphthalein indicator solution	15 mL SCDB	16236
Wash bottle, 125-mL	each	62014
Water, deionized	4 L	27256

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03/2015, Edition 8

Water Treatment Laboratory
Conductivity/TDS Meter

Tap Water	Conductivity Standard	Distilled Reagent Water
mg/L	µS/cm	mg/L
mg/L	µS/cm	mg/L
mg/L	µS/cm	mg/L
mg/L	µS/cm	mg/L
mg/L	µS/cm	mg/L
mg/L	µS/cm	mg/L

According to EPA *Manual for the Certification of Laboratories Analyzing Drinking Water*, 5th edition, Reagent water should be less than 2 uS/cm at 25 degrees C

TDS Determination by Gravimetrics

	Dish #	Initial Dish Weight (B)	Volume Sample	Final Dish Weight (A)	Calculated TDS
Tap water		milligrams	mL	milligrams	
Distilled water		milligrams	mL	milligrams	
Standard		milligrams	mL	milligrams	
Sample 1		milligrams	mL	milligrams	
Sample 2		milligrams	mL	milligrams	
		milligrams	mL	milligrams	

$$\text{TDS, mg/L} = \frac{(A - B)(100{,}000)}{\text{sample vol, mL}}$$

Alkalinity

DOC316.53.01151

Phenolphthalein and Total Alkalinity[1]

Method 8221

0 to 5000 mg/L as $CaCO_3$

Buret Titration

Scope and application: For water, wastewater and seawater.

[1] This procedure can be used for *Standard Methods for the Examination of Water and Wastewater* 2320 B for USEPA NPDES reporting.

Test preparation

Before starting

A pH meter must be used for NPDES reporting and is recommended for best results.
As an alternative to the Bromcresol Green-Methyl Red Indicator Powder Pillow, use 4 drops of Bromcresol Green-Methyl Red Indicator Solution.
As an alternative to the Phenolphthalein Indicator Powder Pillow, use 4 drops of Phenolphthalein Indicator Solution.
Color or turbidity in the sample can make it difficult to see the color change at the endpoint. For these samples, use a pH meter to determine the titration endpoint. Refer to Alkalinity pH endpoints on page 3.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Description	Quantity
Bromcresol Green-Methyl Red Indicator Powder Pillow	1
Phenolphthalein Indicator Powder Pillow	1
Sulfuric Acid Standard Solution, 0.020 N	varies
pH meter and probe (for samples that have a lot of color or turbidity)	1
Buret, Class A, 25 mL	1
Graduated cylinder (use a size that is applicable to the selected sample volume), or TenSette pipet with tips	1
Erlenmeyer flask, 250 mL	1
Funnel, micro	1
Support stand with buret clamp	1
Water, deionized	varies

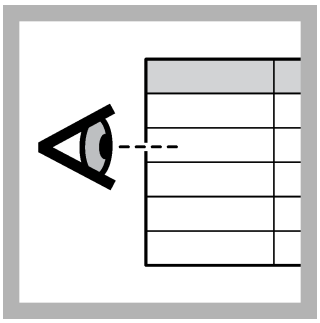
Refer to Consumables and replacement items on page 5 for order information.

Sample collection

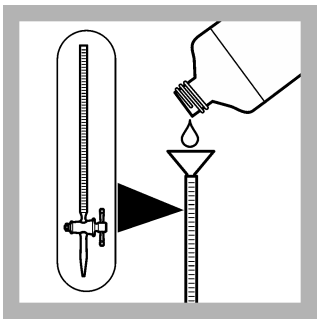
- Collect samples in clean glass or plastic bottles with tight-fitting caps. Completely fill the bottle and immediately tighten the cap.
- Prevent agitation of the sample and exposure to air.
- Analyze the samples as soon as possible for best results.
- If immediate analysis is not possible, keep the samples at or below 6 °C (43 °F) for a maximum of 24 hours. If there is biological activity in the sample, analyze the sample within 6 hours.

- Let the sample temperature increase to room temperature before analysis.

Test procedure

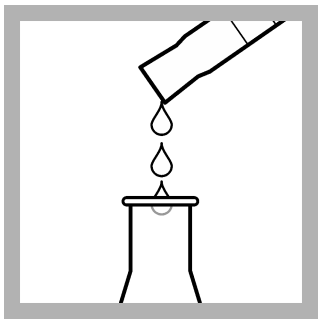


1. Select a sample volume and titrant from Table 1 on page 3.

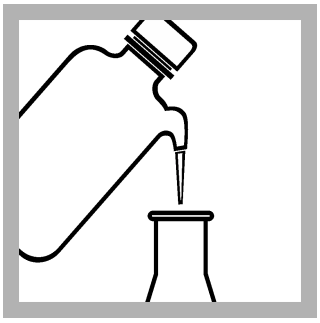


2. Fill a 25-mL buret to the zero mark with the titrant.

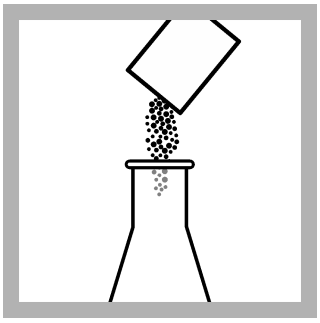
3. Use a graduated cylinder or pipet[1] to measure the sample volume from Table 1 on page 3.



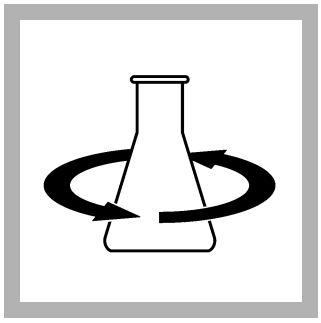
4. Pour the sample into a clean, 250-mL Erlenmeyer flask.



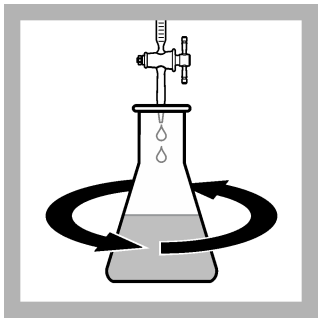
5. If the sample volume is less than 50 mL, dilute to approximately 50 mL with deionized water.



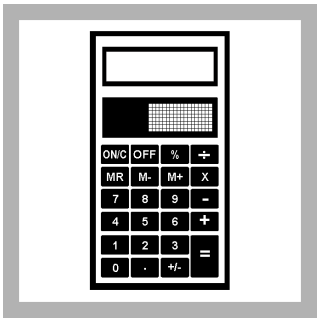
6. Add the contents of one Phenolphthalein Indicator Powder Pillow.
The indicator is not necessary if a pH meter is used.



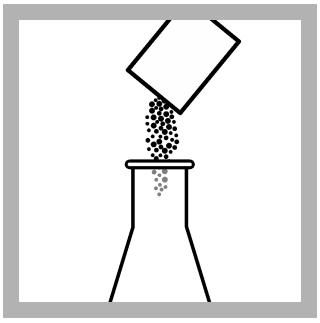
7. Swirl to mix.
If the solution is colorless or the pH is less than 8.3, the Phenolphthalein alkalinity is zero. Go to step 10.



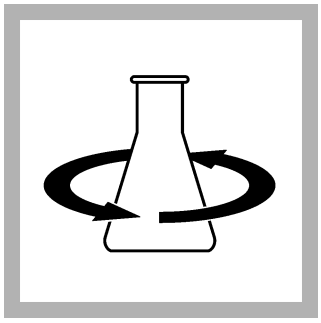
8. Put the flask under the buret. Swirl the flask. Add titrant until the color changes from pink to colorless, or until the pH is 8.3. Do not fill the buret again..



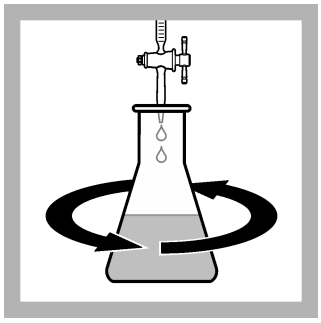
9. Use the multiplier in Table 1 on page 3 to calculate the concentration.
mL of titrant × multiplier = mg/L as $CaCO_3$ Phenolphthalein alkalinity.



10. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow.
The indicator is not necessary if a pH meter is used.

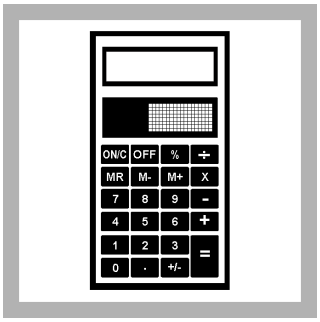


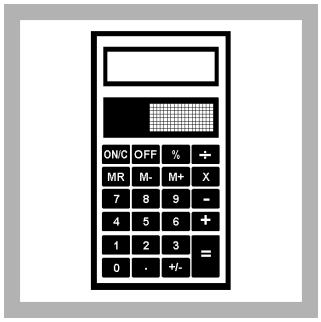
11. Swirl to mix.



12. Put the flask under the buret. Swirl the flask. Add titrant until the color changes to a light pink color, or the pH is 4.5 (refer to Table 2 on page 3 for additional pH endpoints).

[1] Titration accuracy has a direct relation to the accuracy of the sample volume measurement. For smaller volumes, it is recommended to use a pipet to increase accuracy.





13. Use the multiplier in Table 1 on page 3 to calculate the concentration. mL of titrant × multiplier = mg/L as $CaCO_3$ Total alkalinity.

14. Calculate the bicarbonate, carbonate and hydroxide alkalinities as shown in Determine the alkalinity relationships on page 3.

Sample volumes and multipliers

Select a range in Table 1, then read across the table row to find the applicable information for this test. Use the multiplier to calculate the concentration in the test procedure.

Example: A 50-mL sample was titrated with 0.020 N titrant and 12 mL of titrant was used at the endpoint. The concentration is 12 mL × 20 = 240 mg/L as $CaCO_3$ alkalinity.

Table 1 Sample volumes and multipliers

Range (mg/L)	Sample volume (mL)	Titrant—sulfuric acid	Multiplier
1–500	50	0.020 N	20
400–1000	25	0.020 N	40
1000–2000	10	0.020 N	100
2000–5000	5	0.020 N	200

Alkalinity pH endpoints

The titration pH endpoints in Table 2 are recommended for alkalinity determinations in water samples of various compositions and alkalinity concentrations.

Table 2 Alkalinity pH endpoints

Sample composition	Phenolphthalein alkalinity	Total alkalinity
Alkalinity approximately 30 mg/L	pH 8.3	pH 4.9
Alkalinity approximately 150 mg/L	pH 8.3	pH 4.6
Alkalinity approximately 500 mg/L	pH 8.3	pH 4.3
Contains silicates or phosphates	pH 8.3	pH 4.5
Industrial wastes or complex system	pH 8.3	pH 4.5
Routine or automated analyses	pH 8.3	pH 4.5

Determine the alkalinity relationships

The primary forms of alkalinity in water are hydroxide, carbonate and bicarbonate ions. The concentration of these ions in a sample can be determined from the phenolphthalein alkalinity and total alkalinity values. Refer to Table 3 and the steps that follow to determine the hydroxide, carbonate and bicarbonate alkalinities.

1. If the phenolphthalein (P) alkalinity is 0 mg/L, use Row 1.
2. If the phenolphthalein (P) alkalinity is equal to the total alkalinity, use Row 2.

3. Divide the total alkalinity by 2 to calculate one-half of the total alkalinity.
   a. Compare the phenolphthalein (P) alkalinity to one-half of the total alkalinity. Then, use Row 3, 4 or 5.
   b. Do the calculations in the row (if applicable).
4. Make sure that the sum of the three alkalinity types is equal to the total alkalinity.
   Example:

   A sample has 170 mg/L as $CaCO_3$ phenolphthalein alkalinity and 250 mg/L as $CaCO_3$ total alkalinity.

   The phenolphthalein alkalinity of 170 mg/L is more than one-half of the total alkalinity, so use Row 5.

   - Hydroxide alkalinity: 2 x 170 = 340; 340 – 250 = 90 mg/L hydroxide alkalinity
   - Carbonate alkalinity: 250 – 170 = 80; 80 x 2 = 160 mg/L carbonate alkalinity
   - Bicarbonate alkalinity: 0 mg/L

   Sum of the alkalinity types: 90 mg/L hydroxide alkalinity + 160 mg/L carbonate alkalinity + 0 mg/L bicarbonate alkalinity = 250 mg/L total alkalinity.

Table 3 Alkalinity relationships

Row	Titration result	Hydroxide alkalinity	Carbonate alkalinity	Bicarbonate alkalinity
1	P alkalinity = 0	0	0	= Total alkalinity
2	P alkalinity = Total alkalinity	= Total alkalinity	0	0
3	P alkalinity is less than ½ of Total alkalinity	0	= P alkalinity × 2	= Total alkalinity – (P alkalinity × 2)
4	P alkalinity = ½ Total alkalinity	0	= Total alkalinity	0
5	P alkalinity is more than ½ Total alkalinity	= (P alkalinity × 2) – Total alkalinity	= (Total alkalinity – P alkalinity) × 2	0

Conversions

To change the units or chemical form of the test result, multiply the test result by the factor in Table 4.

Table 4 Conversions

mg/L as $CaCO_3$ to...	multiply by...	Example
meq/L as $CaCO_3$	0.02	1000 mg/L alkalinity as $CaCO_3$ x 0.02 = 20 meq/L alkalinity as $CaCO_3$
Grains per gallon (gpg)	0.0584	500 mg/L alkalinity as $CaCO_3$ x 0.0584 = 29.20 gpg alkalinity as $CaCO_3$

Interferences

Interfering substance	Interference level
Chlorine	Chlorine at levels more than 3.5 mg/L can cause a yellow-brown color when the Bromcresol Green-Methyl Red Powder Pillow is added. Add 1 drop of 0.1 N Sodium Thiosulfate to the sample to remove chlorine before the test is started.
Color or turbidity	Color or turbidity can make it difficult to see the color change at the endpoint. Do not filter or dilute samples with color or turbidity. Use a pH meter and titrate the samples to a pH of 8.3 for phenolphthalein alkalinity. For total alkalinity, refer to Table 2 on page 3 for the correct endpoint pH.
Soaps, oily matter, suspended solids and precipitates	Oils or solids can collect on the pH probe and cause a slow response. Clean the probe immediately after use (refer to Clean the pH probes on page 5).

Clean the pH probes

Make sure to clean the pH probes regularly when a pH meter is used to determine the endpoint. Refer to the probe documentation for maintenance instructions. Use the cleaning solution that is specified for the type of contamination that is in the sample. Clean the probe when one or more of the conditions that follow occur:

- Drifting/inaccurate readings
- Slow stabilization times
- Calibration errors

Accuracy check

Standard additions method (sample spike)

Use the standard additions method to validate the test procedure, reagents, apparatus, technique and to find if there is an interference in the sample.

Items to collect:

- Alkalinity Standard Solution, 0.500 N (25-g/L as $CaCO_3$)
- Ampule Breaker
- Pipet, TenSette, 0.1–1.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the sample.
2. Use a TenSette pipet to add 0.1 mL of the standard solution to the titrated sample.
3. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
4. Add one more 0.1-mL addition of the standard solution to the titrated sample.
5. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
6. Add one more 0.1-mL addition of the standard solution to the titrated sample.
7. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
8. Compare the actual result to the correct result. The correct result for this titration is 2.5 mL of titrant for each 0.1-mL addition of the standard solution. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

Summary of method

A phenolphthalein indicator is added to the sample. Then, the sample is titrated with a sulfuric acid solution. The phenolphthalein indicator changes color at the endpoint pH of 8.3. This value indicates the phenolphthalein (P) alkalinity and is a measure of the total hydroxide and one-half of the carbonate in the sample.

A bromcresol green-methyl red indicator is added and the titration continues to the second endpoint at a pH between 4.3 and 4.9. This value indicates the total (T) alkalinity and is a measure of all carbonate, bicarbonate and hydroxide in the sample. The endpoint pH is determined with color indicators or with a pH meter.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Bromcresol Green-Methyl Red Indicator Powder Pillows	1 pillow	100/pkg	94399
Phenolphthalein Indicator Powder Pillows	1 pillow	100/pkg	94299
Sulfuric Acid Standard Solution, 0.020 N	varies	1 L	20353
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity/test	Unit	Item no.
Buret clamp, double	1	each	32800
Buret, Class A, 25 mL	1	each	2636540
Support stand	1	each	56300
Funnel, micro	1	each	2584335
Graduated cylinders—Select one or more for the sample volume:			
Cylinder, graduated, 5 mL	1	each	50837
Cylinder, graduated, 10 mL	1	each	50838
Cylinder, graduated, 25 mL	1	each	50840
Cylinder, graduated, 50 mL	1	each	50841
Cylinder, graduated, 100 mL	1	each	50842
Tensette® pipets and pipet tips—Select one or more for the sample volume:			
Pipet, TenSette®, 0.1–1.0 mL	1	each	1970001
Pipet tips, TenSette® Pipet, 0.1–1.0 mL	varies	50/pkg	2185696
Pipet, TenSette®, 1.0–10.0 mL	1	each	1970010
Pipet tips, TenSette® Pipet, 1.0–10.0 mL	varies	50/pkg	2199796
Flask, Erlenmeyer, 250 mL	1	each	50546

Recommended standards

Description	Unit	Item no.
Alkalinity Voluette® Ampule Standard Solution, 0.500 N (25 g/L as $CaCO_3$), 10-mL	16/pkg	1427810

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
Bromcresol Green-Methyl Red Indicator Solution	100 mL MDB	2329232
Buffer Powder Pillows, pH 8.3	25/pkg	89868
Clippers	each	96800
Phenolphthalein Indicator Solution, 5-g/L	100 mL MDB	16232
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL	32332
Stir bar, octagonal	each	2095352
TitraStir® Titration Stand, 115 VAC	each	1940000
TitraStir® Titration Stand, 230 VAC	each	1940010

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Water Treatment Laboratory
Alkalinity

	mL of titrant required to reach end point		**Calculated Alkalinity** (see equation below)	
	end point = 8.3	endpoint = 4.5	Phenolphthalein Alkalinity	Total Alkalinity
Tap Water (pH meter)				
Sample 1 (color change)				
Sample 2 (TNT)				
Sample 3 (Orion)				

Phenolphthalein Alkalinity = $\frac{\text{(mL titrant used to reach pH of 8.3)(0.02 N } H_2SO_4\text{)(50,000)}}{\text{mL sample}}$

Total Alkalinity = $\frac{\text{(mL titrant used to reach pH of 4.5)(0.02 N } H_2SO_4\text{)(50,000)}}{\text{mL sample}}$

QA/QC - Standard Additions
(perform with color change sample)

Standard Addition 1 : mL to reach color change = _____

Standard Addition 2 : mL to reach color change = _____

Standard Addition 3 : mL to reach color change = _____

Hardness, Calcium

DOC316.53.01157

Titration Method with EDTA[1, 2]

Method 8222

0–25,000 mg/L as $CaCO_3$

Buret Titration

Scope and application: For water, wastewater and seawater.

[1] USEPA accepted when 0.020 N titrant is used.
[2] Adapted from *Standard Methods for the Examination of Water and Wastewater*.

Test preparation

Before starting

Magnesium is not included in the results but must be in the sample for a sharp endpoint. If the sample does not contain magnesium, add 1 to 2 drops of Magnesium Standard Solution, 10-g/L as $CaCO_3$, to the sample before the test is started.
As an alternative to the CalVer 2 Calcium Indicator Powder Pillow, use a 0.1-g scoop of CalVer 2 Calcium Indicator Powder.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

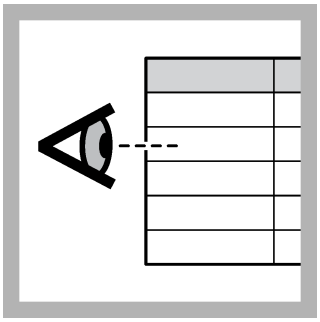
Description	Quantity
CalVer 2 Calcium Indicator Powder Pillow	1
Potassium Hydroxide Standard Solution, 8 N	1 mL
TitraVer Hardness Titrant (use a concentration that is applicable to the selected sample volume)	varies
Buret, Class A, 25 mL	1
Graduated cylinder (use a size that is applicable to the selected sample volume), or TenSette pipet with tips	1
Erlenmeyer flask, 250 mL	1
Funnel, micro	1
Support stand with buret clamp	1
Water, deionized	varies

Refer to Consumables and replacement items on page 6 for order information.

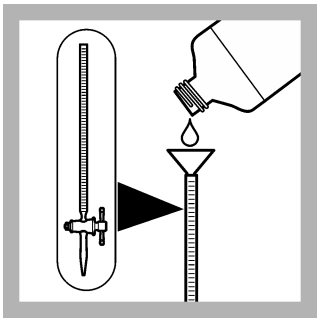
Sample collection

- Collect samples in clean glass or plastic bottles that have been cleaned with a detergent and rinsed with 1:1 nitric acid and deionized water.
- To preserve samples for later analysis, adjust the sample pH to 2 or less with concentrated nitric acid (about 2 mL per liter). No acid addition is necessary if the sample is tested immediately.
- Keep the preserved samples at room temperature for a maximum of 6 months.
- Before analysis, adjust the pH to 7 with Potassium Hydroxide Standard Solution.
- Correct the test result for the dilution caused by the volume additions.

Test procedure

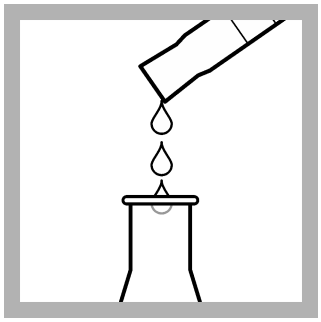


1. Select a sample volume and titrant from Table 1 on page 3.

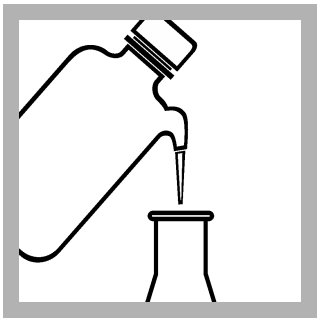


2. Fill a 25-mL buret to the zero mark with the titrant.

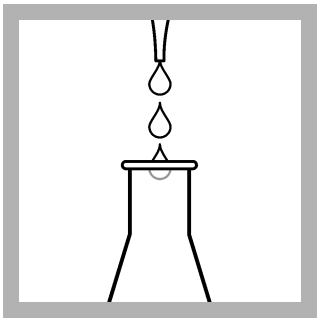
3. Use a graduated cylinder or a pipet[1] to measure the sample volume from Table 1 on page 3.



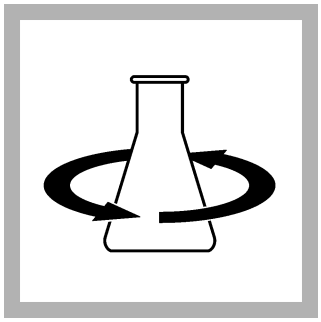
4. Pour the sample into a clean, 250-mL Erlenmeyer flask.



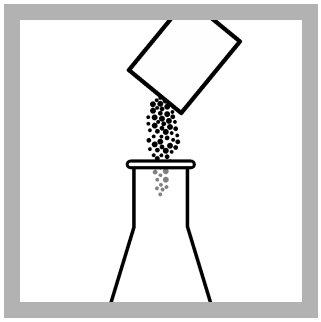
5. If the sample volume is less than 50 mL, dilute to approximately 50 mL with deionized water.



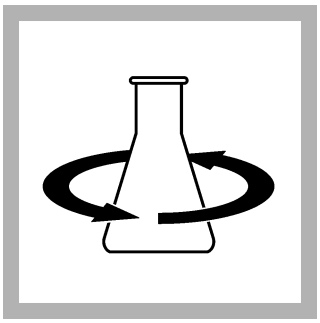
6. Add 1 mL of 8 N Potassium Hydroxide Standard Solution.



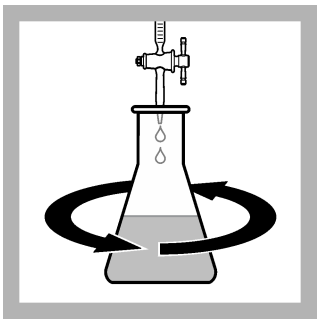
7. Swirl to mix.



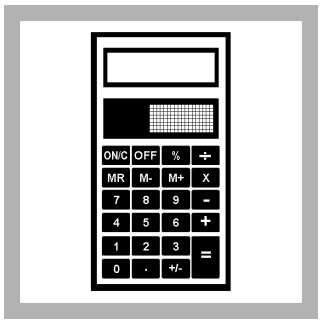
8. Add the contents of one CalVer 2 Calcium Indicator Powder Pillow.



9. Swirl to mix.



10. Put the flask under the buret. Swirl the flask. Add titrant until the color changes from red to pure blue.



11. Use the multiplier in Table 1 on page 3 to calculate the concentration. mL of titrant × multiplier = mg/L Ca as $CaCO_3$.

Sample volumes and multipliers

Select a range in Table 1, then read across the table row to find the applicable information for this test. Use the multiplier to calculate the concentration in the test procedure.

[1] Titration accuracy has a direct relation to the accuracy of the sample volume measurement. For smaller volumes, it is recommended to use a pipet to increase accuracy.

Example: A 50-mL sample was titrated with 0.020 N titrant and 12 mL of titrant was used at the endpoint. The concentration is 12 mL × 20 = 240 mg/L Ca as $CaCO_3$.

Table 1 Sample volumes and multipliers

Range (mg/L)	Sample volume (mL)	Titrant—TitraVer hardness	Multiplier
0–500	50	0.020 N	20
400–1000	25	0.020 N	40
1000–2500	10	0.020 N	100
2000–5000	5	0.020 N	200
1000–5000	50	0.200 N	200
4000–10,000	25	0.200 N	400
10,000–25,000	10	0.200 N	1000

Conversions units

To change the units or chemical form of the test result, multiply the test result by the factor in Table 2.

Table 2 Conversions

mg/L Ca as $CaCO_3$ to...	multiply by...	Example
mg/L as Ca	0.40	1000 mg/L as $CaCO_3$ x 0.40 = 400 mg/L Ca
German degrees hardness (Gdh)	0.056	1000 mg/L as $CaCO_3$ × 0.056 = 56 Gdh
Grains per gallon (gpg)	0.058	1000 mg/L as $CaCO_3$ x 0.058 = 58 gpg

Interferences

⚠ WARNING

Chemical hazard. Potassium cyanide is toxic. Make sure to add potassium cyanide to the sample after the 8 N Potassium Hydroxide Standard Solution has been added. Keep cyanide solutions at more than pH 11 to prevent exposure to hydrogen cyanide gas. Dispose of reacted solutions according to local, state and federal regulations.

An interfering substance can prevent the color change at the titration endpoint. A smaller sample volume can often dilute the interfering substance to a level at which the substance does not interfere. Table 3 shows the substances that can interfere with this test.

Table 3 Interferences

Interfering substance	Interference level
Acidity	10,000 mg/L acidity as $CaCO_3$ does not interfere.
Alkalinity	10,000 mg/L alkalinity as $CaCO_3$ does not interfere.
Aluminum	Causes a slow endpoint. The sample can contain a maximum of 200 mg/L aluminum if sufficient time is given for the color change.
Barium	Barium is titrated at the same time with calcium and interferes with this test, but it is unusual to find high levels of Barium in natural waters.
Chloride	The chloride level in seawater does not interfere. Solutions that are saturated with chloride do not show a sharp endpoint.
Cobalt	Interferes directly. Add 0.5 grams of potassium cyanide after the 8 N Potassium Hydroxide Standard Solution during the test procedure to remove the interference from a maximum of 20 mg/L cobalt.

Table 3 Interferences (continued)

Interfering substance	Interference level
Copper	Interferes at 0.1 mg/L copper. Add 0.5 grams of potassium cyanide after the 8 N Potassium Hydroxide Standard Solution during the test procedure to remove the interference from a maximum of 100 mg/L copper.
Iron	More than 8 mg/L iron causes an orange-red to green endpoint. Results are accurate to 20 mg/L iron with this endpoint.
Magnesium	The formation of magnesium hydroxide at the high test pH prevents interference from 200 mg/L magnesium. Samples with more than 200 mg/L magnesium do not give a distinct endpoint.
Manganese	Interferes at more than 5 mg/L manganese.
Nickel	Interferes at 0.5 mg/L nickel. Add 0.5 grams of potassium cyanide after the 8 N Potassium Hydroxide Standard Solution during the test procedure to remove the interference from a maximum of 200 mg/L nickel.
Orthophosphate	Forms calcium phosphate and causes a slow endpoint. If sufficient time is given to let the calcium phosphate dissolve during the titration, the orthophosphate will not interfere with the test.
Polyphosphates	Interfere directly and are included in the test result.
Strontium	Strontium is titrated at the same time with calcium and interferes with this test, but it is unusual to find high levels of Strontium in natural waters.
Temperature	Samples at 20 °C (68 °F) or colder should be titrated slowly near the endpoint to give sufficient time for the color change.
Zinc	Interferes at 5 mg/L zinc. Add 0.5 grams of potassium cyanide after the 8 N Potassium Hydroxide Standard Solution during the test procedure to remove the interference from a maximum of 100 mg/L zinc.
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary.

Accuracy check

Standard additions method (sample spike)—0.020 N titrant

Use the standard additions method to validate the test procedure, reagents, apparatus, technique and to find if there is an interference in the sample.

Items to collect:

- Calcium Hardness Standard Solution, 10,000 mg/L as $CaCO_3$, 10-mL Voluette ampule
- Ampule Breaker
- Pipet, TenSette, 0.1–1.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the standard solution. Use the 0.020 N titrant.
2. Use a TenSette pipet to add 0.1 mL of the standard solution to the titrated sample.
3. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
4. Add one more 0.1-mL addition of the standard solution to the titrated sample.
5. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
6. Add one more 0.1-mL addition of the standard solution to the titrated sample.
7. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
8. Compare the actual result to the correct result. The correct result for this titration is 1.0 mL of titrant for each 0.1-mL addition of the standard solution. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

Standard additions method (sample spike)—0.200 N titrant

Use the standard additions method to validate the test procedure, reagents, apparatus, technique and to find if there is an interference in the sample.

Items to collect:

- Calcium Hardness Standard Solution, 10,000 mg/L as $CaCO_3$, 10-mL Voluette ampule
- Ampule Breaker
- Pipet, TenSette, 0.1–1.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the standard solution. Use the 0.200 N titrant.
2. Use a TenSette pipet to add 1.0 mL of the standard solution to the titrated sample.
3. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
4. Add one more 1.0-mL addition of the standard solution to the titrated sample.
5. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
6. Add one more 1.0-mL addition of the standard solution to the titrated sample.
7. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
8. Compare the actual result to the correct result. The correct result for this titration is 1.0 mL of titrant for each 1.0-mL addition of the standard solution. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

Standard solution method—0.020 N titrant

Use the standard solution method to validate the test procedure, reagents, apparatus and technique.

Items to collect:

- Calcium Chloride Standard Solution, 1000 mg/L as $CaCO_3$
- Pipet, TenSette, 1.0–10.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the standard solution. Use 25.0 mL of the standard solution and the 0.020 N titrant.
2. Compare the actual result to the correct result. The correct result for this titration is 25 mL of titrant.

Standard solution method—0.200 N titrant

Use the standard solution method to validate the test procedure, reagents, apparatus and technique.

Items to collect:

- Calcium Hardness Standard Solution, 10,000 mg/L as $CaCO_3$, 10-mL Voluette ampule
- Ampule Breaker
- Pipet, TenSette, 1.0–10.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the standard solution. Use 10.0 mL of the standard solution and the 0.200 N titrant.
2. Compare the actual result to the correct result. The correct result for this titration is 10 mL of titrant.

Summary of method

Potassium hydroxide is added to the sample to adjust the pH to 12 to 13, which causes a magnesium hydroxide precipitate to form. CalVer 2 Calcium Indicator is then added, which reacts with calcium to give a red color. The EDTA titrant is added, which reacts with all the free calcium. After the EDTA has reacted with all of the free calcium ions, the

EDTA removes the calcium from the indicator. The indicator color then changes from red to blue.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Hardness (Calcium) Reagent Set (approximately 100 tests):	—	each	2447000
CalVer 2 Calcium Indicator Powder Pillows	1 pillow	100/pkg	85299
Potassium Hydroxide Standard Solution, 8 N	1 mL	100 mL MDB	28232H
TitraVer® Hardness Titrant, 0.020 N	varies	1 L	20553
TitraVer® Hardness Titrant, 0.200 N	varies	500 mL	102149

Required apparatus

Description	Quantity/test	Unit	Item no.
Buret clamp, double	1	each	32800
Buret, Class A, 25 mL	1	each	2636540
Support stand	1	each	56300
Funnel, micro	1	each	2584335
Graduated cylinders—Select one or more for the sample volume:			
Cylinder, graduated, 5 mL	1	each	50837
Cylinder, graduated, 10 mL	1	each	50838
Cylinder, graduated, 25 mL	1	each	50840
Cylinder, graduated, 50 mL	1	each	50841
Cylinder, graduated, 100 mL	1	each	50842
Tensette® pipets and pipet tips—Select one or more for the sample volume:			
Pipet, TenSette®, 0.1–1.0 mL	1	each	1970001
Pipet tips, TenSette® Pipet, 0.1–1.0 mL	varies	50/pkg	2185696
Pipet, TenSette®, 1.0–10.0 mL	1	each	1970010
Pipet tips, TenSette® Pipet, 1.0–10.0 mL	varies	50/pkg	2199796
Flask, Erlenmeyer, 250 mL	1	each	50546

Recommended standards

Description	Unit	Item no.
Calcium Chloride Standard Solution, 1000 mg/L as $CaCO_3$	1 L	12153
Calcium Hardness Standard Solution, 10,000 mg/L as $CaCO_3$, 10-mL Voluette ampule	16/pkg	218710

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
Bottle, sampling, with cap, low density polyethylene, 250 mL	12/pkg	2087076
CalVer® 2 Calcium Indicator Powder	113 g	28114H
Magnesium Standard Solution, 10-g/L as $CaCO_3$	29 mL	102233

Optional reagents and apparatus (continued)

Description	Unit	Item no.
Nitric Acid, concentrated	500 mL	15249
Nitric Acid Solution, 1:1	500 mL	254049
Potassium Cyanide, ACS	100 g	76714
Potassium Hydroxide Standard Solution, 8 N	500 mL	28249
Spoon, measuring, 0.1 g	each	51100
Stir bar, octagonal	each	2095352
TitraStir® Titration Stand, 115 VAC	each	1940000
TitraStir® Titration Stand, 230 VAC	each	1940010

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03/2016, Edition 9

Hardness, Total

DOC316.53.01158

Titration Method with EDTA[1,2]

0–25,000 mg/L as $CaCO_3$

Method 8226

Buret Titration

Scope and application: For water, wastewater and seawater.

[1] USEPA accepted when 0.020 N titrant is used.
[2] Adapted from *Standard Methods for the Examination of Water and Wastewater*.

Test preparation

Before starting

As an alternative to the ManVer 2 Hardness Indicator Powder Pillow, use 4 drops of Hardness 2 Indicator Solution or a 0.1-g scoop of ManVer 2 Hardness Indicator Powder.
The optional TitraStir Titration Stand can hold the buret and stir the sample.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

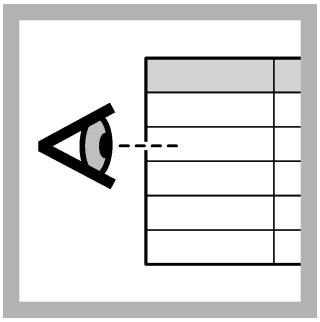
Description	Quantity
ManVer 2 Hardness Indicator Powder Pillow	1
Hardness 1 Buffer Solution	1 mL
TitraVer Hardness Titrant (use a concentration that is applicable to the selected sample volume)	varies
Buret, Class A, 25 mL	1
Graduated cylinder (use a size that is applicable to the selected sample volume), or TenSette pipet with tips	1
Erlenmeyer flask, 250 mL	1
Funnel, micro	1
Support stand with buret clamp	1
Water, deionized	varies

Refer to Consumables and replacement items on page 7 for order information.

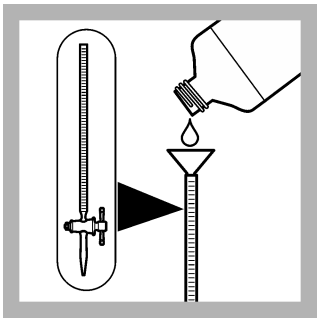
Sample collection and storage

- Collect samples in clean glass or plastic bottles that have been cleaned with a detergent and rinsed with 1:1 nitric acid and deionized water.
- To preserve samples for later analysis, adjust the sample pH to 2 or less with concentrated nitric acid (about 2 mL per liter). No acid addition is necessary if the sample is tested immediately.
- Keep the preserved samples at or below 6 °C (43 °F) for a maximum of 7 days.
- Before analysis, adjust the pH to 7 with sodium hydroxide solution.
- Correct the test result for the dilution caused by the volume additions.

Test procedure

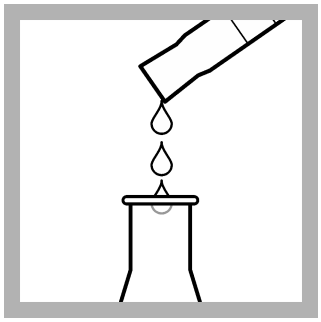


1. Select a sample volume and titrant from Table 1 on page 3.

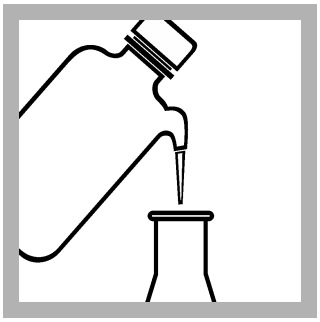


2. Fill a 25-mL buret to the zero mark with the titrant.

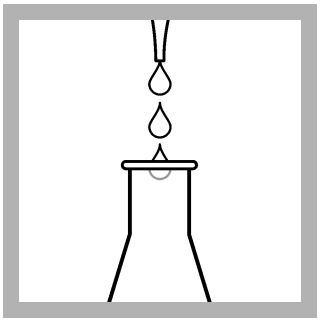
3. Use a graduated cylinder or pipet[1] to measure the sample volume from Table 1 on page 3.



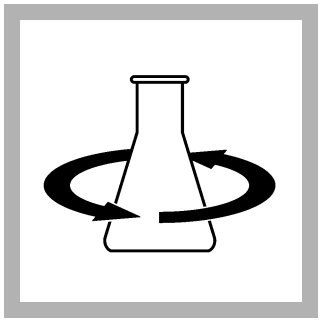
4. Pour the sample into a clean, 250-mL Erlenmeyer flask.



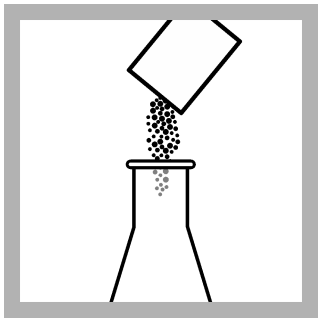
5. If the sample volume is less than 50 mL, dilute to approximately 50 mL with deionized water.



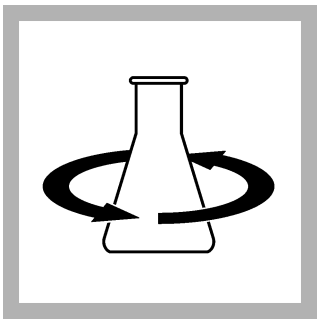
6. Add 1 mL of Hardness 1 Buffer Solution.



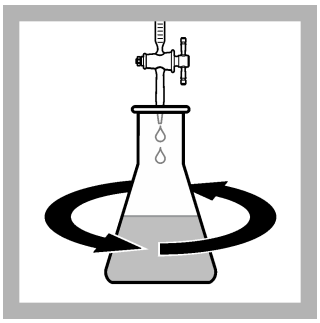
7. Swirl to mix.



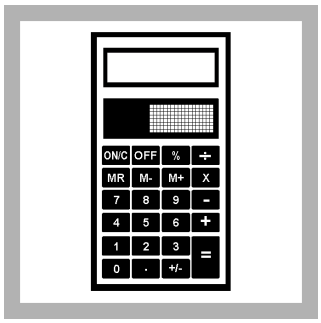
8. Add the contents of one ManVer 2 Hardness Indicator Powder Pillow.



9. Swirl to mix.



10. Put the flask under the buret. Swirl the flask. Add titrant until the color changes from red to pure blue.



11. Use the multiplier in Table 1 on page 3 to calculate the concentration. mL of titrant × multiplier = mg/L total hardness as $CaCO_3$.

Sample volumes and multipliers

Select a range in Table 1, then read across the table row to find the applicable information for this test. Use the multiplier to calculate the concentration in the test procedure.

[1] Titration accuracy has a direct relation to the accuracy of the sample volume measurement. For smaller volumes, it is recommended to use a pipet to increase accuracy.

Example: A 50-mL sample was titrated with 0.020 N titrant and 12 mL of titrant was used at the endpoint. The concentration is 12 mL × 20 = 240 mg/L total hardness as $CaCO_3$.

Table 1 Sample volumes and multipliers

Range (mg/L)	Sample volume (mL)	Titrant—TitraVer hardness	Multiplier
0–500	50	0.020 N	20
400–1000	25	0.020 N	40
1000–2500	10	0.020 N	100
2000–5000	5	0.020 N	200
1000–5000	50	0.200 N	200
4000–10,000	25	0.200 N	400
10,000–25,000	10	0.200 N	1000

Conversions

To change the units or chemical form of the test result, multiply the test result by the factor in Table 2.

Table 2 Conversions

mg/L as $CaCO_3$ to...	multiply by...	Example
mg/L as Ca	0.40	1000 mg/L as $CaCO_3$ x 0.40 = 400 mg/L Ca
mg/L as Mg	0.243	1000 mg/L as $CaCO_3$ x 0.243 = 243 mg/L Mg
Grains per gallon (gpg)	0.058	1000 mg/L as $CaCO_3$ x 0.058 = 58 gpg
German degrees hardness (Gdh)	0.056	1000 mg/L as $CaCO_3$ × 0.056 = 56 Gdh

Interferences

⚠ WARNING

Chemical hazard. Potassium cyanide is toxic. Make sure to add potassium cyanide to the sample after the Hardness 1 Buffer Solution has been added. Keep cyanide solutions at more than pH 11 to prevent exposure to hydrogen cyanide gas. Dispose of reacted solutions according to local, state and federal regulations.

An interfering substance can prevent the color change at the titration endpoint. A smaller sample volume can often dilute the interfering substance to a level at which the substance does not interfere. Table 3 shows the substances that can interfere with this test.

Table 3 Interferences

Interfering substance	Interference level
Acidity	10,000 mg/L acidity as $CaCO_3$ does not interfere.
Alkalinity	10,000 mg/L alkalinity as $CaCO_3$ does not interfere.
Aluminum	Interferes when the sample contains more than 0.20 mg/L aluminum. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 1 mg/L aluminum. As an alternative, add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 4.
Barium	Barium is titrated at the same time with calcium and interferes with this test, but it is unusual to find high levels of Barium in natural waters.
Chloride	The chloride level in seawater does not interfere. Solutions that are saturated with chloride do not show a sharp endpoint.

Table 3 Interferences (continued)

Interfering substance	Interference level
Cobalt	Interferes directly at all levels. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 20 mg/L cobalt. As an alternative, add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 4.
Copper	Interferes when the sample contains 0.1 mg/L copper. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 100 mg/L copper. As an alternative, add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 4.
Iron	More than 8 mg/L iron causes an orange-red to green endpoint. Results are accurate to 20 mg/L iron with this endpoint. For more accurate endpoints in solutions that have higher levels of iron, use HexaVer Hardness Titrant (CDTA) and not TitraVer Hardness Titrant (EDTA).
Manganese	Interferes when the sample contains more than 5 mg/L manganese. Add a 0.10-gram scoop of Hydroxylamine Hydrochloride Monohydrate to increase the interference level to 200 mg/L manganese.
Nickel	Interferes directly at all levels. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 200 mg/L nickel. As an alternative, add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 4.
Orthophosphate	Forms calcium phosphate and causes a slow endpoint. If sufficient time is given to let the calcium phosphate dissolve during the titration, the orthophosphate will not interfere with the test.
Polyphosphates	Interferes at all levels.
Polyvalent metal ions	Although less common than calcium and magnesium, other polyvalent metal ions are titrated with the calcium and magnesium and are included in the results.
Strontium	Strontium is titrated at the same time with calcium and magnesium and interferes with this test, but it is unusual to find high levels of Strontium in natural waters.
Zinc	Interferes directly and is included in the test result. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 100 mg/L zinc. As an alternative, add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 4.
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary. Before analysis, adjust the pH to 7.

Use CDTA to remove metal interferences

Add one CDTA Magnesium Salt Powder Pillow to remove the interference from metals at or below the levels shown in Table 4. If more than one metal is in the sample at or more than the concentration in Table 4, add an additional CDTA Magnesium Salt Powder Pillow.

The results given with CDTA Magnesium Salt include the hardness from these metals. If the concentration of each metal is known, a correction can be made to get the hardness from calcium and magnesium only. The hardness value from different metal ions is shown in Table 5.

Metal hardness = (mg/L of metal in the sample) x (hardness equivalence factor)

Calcium and magnesium hardness = (total hardness) – (metal hardness)

Table 4 Interference level with one CDTA pillow

Interfering substance	Interference level
Aluminum	50 mg/L
Cobalt	200 mg/L
Copper	100 mg/L
Iron	100 mg/L
Manganese	200 mg/L
Nickel	400 mg/L
Zinc	300 mg/L

Table 5 Hardness equivalence factors (mg/L as $CaCO_3$)

Interfering substance	Hardness equivalence factor
Aluminum	3.710
Barium	0.729
Cobalt	1.698
Copper	1.575
Iron	1.792
Manganese	1.822
Nickel	1.705
Strontium	1.142
Zinc	1.531

Accuracy check

Standard additions method (sample spike)—0.020 N titrant

Use the standard additions method to validate the test procedure, reagents, apparatus, technique and to find if there is an interference in the sample.

Items to collect:

- Calcium Hardness Standard Solution, 10,000 mg/L as $CaCO_3$, 10-mL Voluette ampule
- Ampule Breaker
- Pipet, TenSette, 0.1–1.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the standard solution. Use the 0.020 N titrant.
2. Use a TenSette pipet to add 0.1 mL of the standard solution to the titrated sample.
3. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
4. Add one more 0.1-mL addition of the standard solution to the titrated sample.
5. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
6. Add one more 0.1-mL addition of the standard solution to the titrated sample.
7. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
8. Compare the actual result to the correct result. The correct result for this titration is 1.0 mL of titrant for each 0.1-mL addition of the standard solution. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

Standard additions method (sample spike)—0.200 N titrant

Use the standard additions method to validate the test procedure, reagents, apparatus, technique and to find if there is an interference in the sample.

Items to collect:

- Calcium Hardness Standard Solution, 10,000 mg/L as $CaCO_3$, 10-mL Voluette ampule
- Ampule Breaker
- Pipet, TenSette, 0.1–1.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the standard solution. Use the 0.200 N titrant.
2. Use a TenSette pipet to add 1.0 mL of the standard solution to the titrated sample.
3. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
4. Add one more 1.0-mL addition of the standard solution to the titrated sample.
5. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
6. Add one more 1.0-mL addition of the standard solution to the titrated sample.
7. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
8. Compare the actual result to the correct result. The correct result for this titration is 1.0 mL of titrant for each 1.0-mL addition of the standard solution. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

Standard solution method—0.020 N titrant

Use the standard solution method to validate the test procedure, reagents, apparatus and technique.

Items to collect:

- Calcium Chloride Standard Solution, 1000 mg/L as $CaCO_3$
- Pipet, TenSette, 1.0–10.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the standard solution. Use 25.0 mL of the standard solution and the 0.020 N titrant.
2. Compare the actual result to the correct result. The correct result for this titration is 25 mL of titrant.

Standard solution method—0.200 N titrant

Use the standard solution method to validate the test procedure, reagents, apparatus and technique.

Items to collect:

- Calcium Hardness Standard Solution, 10,000 mg/L as $CaCO_3$, 10-mL Voluette ampule
- Ampule Breaker
- Pipet, TenSette, 1.0–10.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the standard solution. Use 10.0 mL of the standard solution and the 0.200 N titrant.
2. Compare the actual result to the correct result. The correct result for this titration is 10 mL of titrant.

Summary of method

A buffer solution (an organic amine and one of its salts) is added to the sample to adjust the pH to 10.1. An organic dye, calmagite, is then added as the indicator for the test. The organic dye reacts with calcium and magnesium ions to give a red-colored complex. The EDTA (ethylenediaminetetraacetic acid) titrant is added, which reacts with all of the free calcium and magnesium ions in the sample. After the EDTA has reacted with all of the

free magnesium ions, the EDTA removes the magnesium ions from the indicator. The indicator color then changes from red to blue.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Hardness (Total) Reagent Set (approximately 100 tests):	—	each	2447600
ManVer 2 Hardness Indicator Powder Pillows	1 pillow	100/pkg	85199
Buffer Solution, Hardness 1	1 mL	1 L	42432
TitraVer® Hardness Titrant, 0.020 N	varies	1 L	20553
Hardness (Total) Reagent Set (approximately 100 tests):	—	each	2447700
ManVer 2 Hardness Indicator Powder Pillows	1 pillow	100/pkg	85199
Buffer Solution, Hardness 1	1 mL	1 L	42432
TitraVer® Hardness Titrant, 0.200 N	varies	500 mL	102149

Required apparatus

Description	Quantity/test	Unit	Item no.
Buret clamp, double	1	each	32800
Buret, Class A, 25 mL	1	each	2636540
Support stand	1	each	56300
Funnel, micro	1	each	2584335
Graduated cylinders—Select one or more for the sample volume:			
Cylinder, graduated, 5 mL	1	each	50837
Cylinder, graduated, 10 mL	1	each	50838
Cylinder, graduated, 25 mL	1	each	50840
Cylinder, graduated, 50 mL	1	each	50841
Cylinder, graduated, 100 mL	1	each	50842
Tensette® pipets and pipet tips—Select one or more for the sample volume:			
Pipet, TenSette®, 0.1–1.0 mL	1	each	1970001
Pipet tips, TenSette® Pipet, 0.1–1.0 mL	varies	50/pkg	2185696
Pipet, TenSette®, 1.0–10.0 mL	1	each	1970010
Pipet tips, TenSette® Pipet, 1.0–10.0 mL	varies	50/pkg	2199796
Flask, Erlenmeyer, 250 mL	1	each	50546

Recommended standards

Description	Unit	Item no.
Calcium Chloride Standard Solution, 1000 mg/L as $CaCO_3$	1 L	12153
Calcium Hardness Standard Solution, 10,000 mg/L as $CaCO_3$, 10-mL Voluette ampule	16/pkg	218710

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
CDTA Magnesium Salt Powder Pillow	100/pkg	1408099
Delivery tube for Digital Titrator, 90-degree bend for use with TitraStir Titration Stand	5/pkg	4157800
ManVer Hardness Indicator Solution	100 mL	42532
ManVer 2 Hardness Indicator Powder	113 g	28014
Nitric Acid, concentrated	500 mL	15249
Nitric Acid Solution, 1:1	500 mL	254049
Potassium Cyanide, ACS	100 g	76714
Bottle, sampling, with cap, low density polyethylene, 250 mL	12/pkg	2087076
Sodium Hydroxide Solution, 5 N	50 mL	245026
Spoon, measuring, 0.1 g	each	51100
Spoon, measuring, 0.5 g	each	90700
Stir bar, octagonal	each	2095352
TitraStir® Titration Stand, 115 VAC	each	1940000
TitraStir® Titration Stand, 230 VAC	each	1940010

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Water Treatment Laboratory

Hardness

	Ca Hardness	Total Hardness	Calculated Hardness	
	mL titrant used to reach endpoint		Ca Hardness (mg/L)	Total Hardness (mg/L)
Tap Water				
Sample 1				
Sample 2				
Sample 3				

Hardness = $\frac{\text{(mL titrant used to reach endpoint)(multiplier from chart)}}{\text{mL sample used}}$

QA/QC - Standard Additions

(perform with color change sample)

Standard Addition 1 : mL to reach color change = _____

Standard Addition 2 : mL to reach color change = _____

Standard Addition 3 : mL to reach color change = _____

USE THIS SHEET FOR TAP WATER ONLY!!

Langlier Saturation Index Bench Sheet

Sample #	pH	Temperature (°C) A	TDS (mg/L) B	Calcium Hardness (mg/L)	Total Alkalinity (mg/L)
1					
2					
3					
4					
5					
6					

$$LSI = pH - pH_s$$

$$pH_s = A + B - \log(\text{Ca hardness}) - \log(\text{alkalinity})$$

Values of "A" for various Temperatures, °C	
Temperature, °C	A
0	2.34
5	2.27
10	2.20
15	2.12
20	2.04
25	1.98
30	1.91
40	1.76
50	1.62
60	1.47

Values for "B" for various levels of TDS, mg/L	
TDS, mg/L	B
0	9.63
50	9.72
100	9.75
200	9.80
400	9.86
800	9.94
1,600	10.04

Corrosivity Characteristics as Addressed by Indices		
Corrosive Characteristics	Langelier Index (LSI)	Aggressive Index (AI)
Highly Aggressive	< -2.0	< 10.0
Moderately Aggressive	-2.0 to < 0.0	10.0 to < 12.0
Non-aggressive	> 0.0	> 12.0

Section 6
Heterotrophic Plate Count

Heterotrophic Plate Count (HPC)

2

Water Quality

- The presence or absence of total or fecal coliforms is a good indication of overall water quality
- However, there are other bacteria that are less sensitive to disinfection and environmental changes

TDEC - Fleming Training Center

3

Microbial Growth

- High levels can affect the taste and odor of drinking water
- High levels may indicate the presence of nutrients and biofilms that could harbor pathogens

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4

Heterotrophs

- Heterotrophs are organisms that require an external source of organic carbon for growth

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Heterotrophic Bacteria

- The heterotrophic bacteria are more likely to persist in the water throughout the treatment process and into the distribution system
- The presence and enumeration of heterotrophic bacteria can be an indication of treatment efficiency and distribution conditions

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Heterotrophic Plate Count

- HPC can be used to determine the water quality in the distribution system
- Samples that have an increased number of heterotrophic bacteria are an indication that the chlorine residual is decreased and there is an overall water quality degradation
  - This can help determine when to flush to maintain water quality

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Heterotrophic Plate Count

- Heterotrophic bacteria do not pose a health risk to the public, and are not currently regulated by the SDWA
- The SDWA does recognize the fact that excessive numbers of Heterotrophs (> 500 cfu/mL) may interfere with membrane filtration for total coliforms
  - If too many non-coliform colonies are present, the development of the metallic sheen on coliform colonies may be inhibited

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Heterotrophs

- There is no firm evidence that non-pathogenic bacterial growth as measured by HPC is accompanied by increased risk of illness among customers

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SimPlate for HPC

- IDEXX
  - SimPlate: Video Demonstration

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# Positive Wells	MPN	95% confidence limits lower	upper
0	<0.2	<0.03	<1.4
1	0.2	0.0	1.4
2	0.4	0.1	1.6
3	0.6	0.2	1.9
4	0.8	0.3	2.2
5	1.0	0.4	2.5
6	1.2	0.6	2.7
7	1.5	0.7	3.0
8	1.7	0.8	3.3
9	1.9	1.0	3.6
10	2.1	1.1	3.9
11	2.3	1.3	4.2
12	2.6	1.5	4.5
13	2.8	1.6	4.8
14	3.0	1.8	5.1

HPC for Quanti-Tray* Test Kit

Introduction

The HPC for Quanti-Tray* Test is used for the quantification of heterotrophic organisms in 100 mL of water. The HPC for Quanti-Tray Test is based on IDEXX-patented Multiple Enzyme Technology*, which detects viable heterotrophic organisms by testing for the presence of key enzymes known to be present in these organisms. The test uses multiple enzyme substrates that produce blue fluorescence when metabolized by waterborne bacteria. The sample/reagent mixture is added to a Quanti-Tray*, incubated, and then examined for fluorescing wells. The number of fluorescing wells corresponds to a most probable number (MPN) of total heterotrophic organisms in the original sample. The HPC for Quanti-Tray Test detects organisms at 1 cfu/100 mL after 44–72 hours of incubation.

Storage

Store at 2–25°C away from light.

Quanti-Tray Enumeration Procedure

1. Add contents of one pack to a 100 mL water sample in a sterile vessel.
2. Cap vessel and shake until powder is dissolved.
3. Pour sample/reagent mixture into a Quanti-Tray or Quanti-Tray*/2000 and seal using a Quanti-Tray* Sealer.
4. Place the sealed tray in a 36°±2°C incubator for 44 hours. Results are valid for up to 72 hours.
5. Interpret results according to the Result Interpretation table below. Refer to the MPN table provided with the trays to obtain a most probable number.

Result Interpretation

Appearance	Result
Blue fluorescence†	Positive for heterotrophic organisms
No blue fluorescence	Negative for heterotrophic organisms

†Presence of blue fluorescent color greater than the amount present in a negative control sample.

- Look for fluorescence with a 6-watt, 365-nm UV light within 5 inches of the sample in a dark environment. Face light away from your eyes and towards the sample.
- HPC for Quanti-Tray results are definitive at 44–72 hours.

Procedural Notes

- This insert may not reflect your local regulations. For compliance testing, be sure to follow appropriate regulatory procedures.
- HPC for Quanti-Tray sample/reagent mixture will appear pale pink in color after the reagent is added to the sample. This color helps to differentiate the HPC for Quanti-Tray samples from other IDEXX water test samples in the laboratory.
- If the sample has been diluted, multiply the MPN value by the dilution factor to obtain the correct quantitative result.
- Use only sterile, nonbuffered, oxidant-free water for dilutions.
- The HPC for Quanti-Tray Test is a primary water test. HPC for Quanti-Tray performance characteristics do not apply to samples altered by preenrichment or concentration.
- Chlorinated samples should be treated with sodium thiosulfate prior to testing. If the chlorine is not neutralized, consider the sample invalid and discontinue testing.
- For comparison, an incubated sterile water blank containing HPC for Quanti-Tray reagent (negative control) can be used when interpreting results.
- Aseptic technique should always be followed when using the HPC for Quanti-Tray Test. Dispose of in accordance with Good Laboratory Practices.

Quality Control Procedure

The following quality control procedures is recommended for each lot of the HPC for Quanti-Tray Test:

1. Positive Control: IDEXX-QC HPC/TVC[1]: *Enterococcus faecalis*.
   A. Review the range for the control - if greater than 200, a dilution may be necessary for the Quanti-Tray prior to proceeding to step 2.A.
2. Negative/blank control:
   A. Add the contents of one snap pack to 100 mL of sterile, deionized water.
   B. Cap the vessel and shake until powder is dissolved.
   C. Pour sterile water/reagent mixture into a Quanti-Tray or Quanti-Tray/2000, and seal using a Quanti-Tray Sealer.
   D. Incubate the sealed tray at 36°±2°C for 44–72 hours.
   E. Note appearance of wells under UV light. Negative Control/Blank wells should not fluoresce up to 72 hours of incubation.

1. IDEXX-QC HPC/TVC, IDEXX Catalog #UN3373-WQC-HPC

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Section 7
Metals and Organic Analysis

Metals and Organic Analysis

Water Treatment Laboratory

1

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Metals Analysis

- Aluminum
- Arsenic
- Cadmium
- Chromium
- Iron
- Manganese
- Nickel
- Sodium
- Antimony
- Barium
- Calcium
- Copper
- Lead
- Mercury
- Silver
- Zinc

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Metals Analysis

- Most metals need to be collected in a plastic or glass container and preserved with HNO_3 (nitric acid) to pH less than 2
- Holding time is 6 months
- Mercury is preserved with HNO_3, but holding time is 28 days
- Samples for silver need to be stored in light-absorbing containers
- Use only containers that have been acid rinsed

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Metals Analysis

- Plastic pipet tips are often contaminated with copper, iron, zinc and cadmium
- Avoid using colored plastics, which can contain metals
- Use certified metal-free plastic containers and pipet tips when possible
- Avoid using glass if analyzing for aluminum or silica
- Use metal-free water and acids

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Metals Analysis

- Samples have to go through an acid digestion before they are analyzed for about 2 hours
- Instrument does complete scan for all metals at one time
- Instrument has mirrors inside that reflect light
- Light rays given off are seen as different metals that the sample has in it

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Total Organic Carbon

- High-temperature combustion at 950°C
- Sample is injected into a heated reaction chamber packed with oxidative catalyst such as cobalt oxide
- Water is vaporized and the organic carbon is oxidized to CO_2 and H_2O
- CO_2 is transported in the carrier-gas streams and is measured by means of a nondispersive infrared analyzer (NDIR)
- Samples are preserved with sulfuric or phophoric acid and cooled to 4°C

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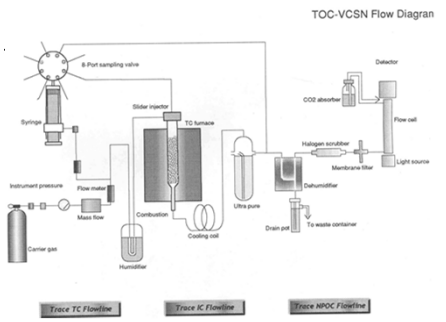

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Organic Analysis

- TPH – total petroleum hydrocarbons extracted by hexane
  - Silica gel is used to adsorb polar materials (fatty acids)
- Other organics analyzed on GC-MS
  - THM's – extraction and analysis time is about 30 minutes per sample
  - HAA5 – extracted then analyzed

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UV-254

- UV-254 is a test you could run in your lab if your spec has UV capabilities
- May correlate to TOC
  - Need to run UV-254 when you collect TOC samples
  - Track over time
- Cheaper and quicker to run than TOC for process control determinations

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UV-254

- Filtered sample is measured at 254 nm
- Blank sample is organic-free water
- Samples are read in absorbance/cm or cm^{-1}
- Estimation of how much organics are in water

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SUVA

- Specific UV Absorbance
- Compares UV-254 to Dissolved Organic Carbon (DOC)
  - There is a relationship between SUVA levels and humic substances

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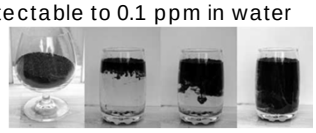
Humic Substances

- Humic substances are the organic portion of soil that remains after prolonged microbial decomposition, and that is formed by the decay of leaves, wood, and other vegetable matter.
- They can impart a yellowish-brown to brownish-black color to water; detectable to 0.1 ppm in water



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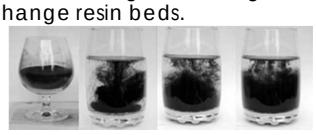
Fulvic Acid

- A water-soluble, natural organic substance of low molecular weight which is derived from humus, often found in surface water.
- Fulvic acid contributes to the formation of trihalomethanes in chlorinated water supplies, and can contribute to organic fouling of ion exchange resin beds.



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Color

- sMCL for color is 15 color units

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Color

- Color in water can be caused by a number of contaminants such iron, tannins and humics.
- Color from iron is referred to as "apparent color" rather than "true color".
  - True color is distinguished from apparent color by filtering the sample.

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Color

- The most common source of true color is decaying organic matter such as the yellowish "tea color" of water.
- True color is mostly found in surface water, although ground water may contain some color if the aquifer flows through a layer of buried vegetation, such as from a long buried slough of a river.

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Color

- Color is not a toxic characteristic, but is listed by the EPA as a secondary (aesthetic) parameter affecting the appearance and palatability of the water.
- Color can be removed by activated carbon, coagulation and/or sedimentation.

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Color

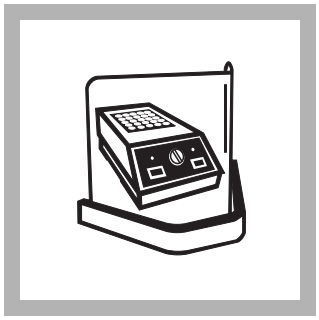
- True color
  - Color of water from which turbidity has been removed
- Apparent color
  - Includes true color and color caused by suspended matter

Method 10140 **THM Reactor Method***

Powder Pillows **(0–200 ppb as Chloroform)**

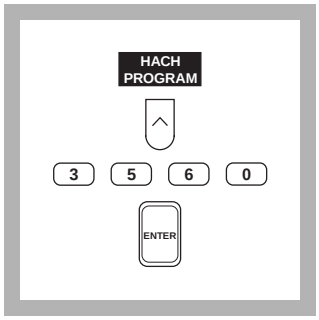
Scope and Application: *For drinking water.*

* Patent Pending



1. Place the reactor in a fume hood and place a plastic shield in front of the reactor.

Turn on the COD Reactor. Preheat to 100 °C.



2. Press the soft key under ***HACH PROGRAM***. Select the stored program number for Trihalomethane (THM) Plus by pressing **3560** on the numeric keys.

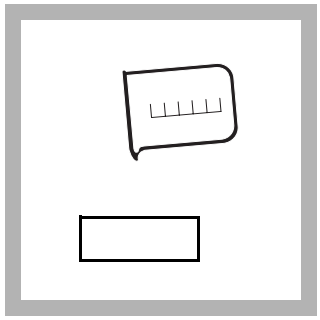
Press **ENTER**.

Note: *For the most precise results, use matched cells. See Sample Cell Matching on page 5.*

3. The display will show:

HACH PROGRAM: 3560 THM Plus

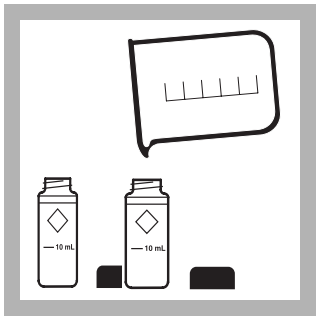
The wavelength (λ), 515 nm, is automatically selected.



4. Prepare a cooling bath by adding 500 mL of cold (18–25 °C) tap water to an evaporating dish.

Note: *Maintain the water temperature between 18 and 25 °C.*

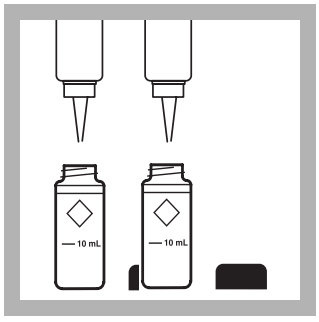
Note: *If analyzing more than four samples, use 450 mL of water.*



5. Fill two sample cells to the 10 mL mark with sample. Label one **sample** and the other **blank**.

Note: *Perform steps 5 through 9* ***rapidly*** *so as not to lose volatile THMs from the sample. If you are testing more than one sample, complete steps 5 through 9 for one sample before going on to the next.*

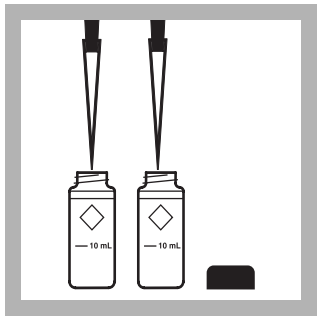
Note: *If dispensing sample with a pipette, the pipette must dispense quickly without causing aeration or back pressure.*



6. Add three drops of THM Plus Reagent 1 to each cell.

7. Cap tightly and mix gently by swirling each cell three times.

Note: *Vigorous shaking can cause loss of THMs.*

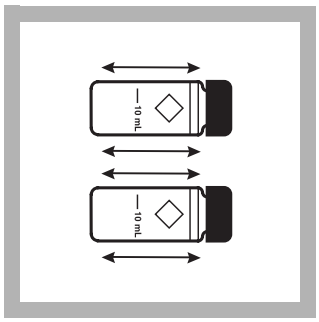


8. Use a TenSette® pipette to add 3 mL of THM Plus Reagent 2 to each cell.

Note: *The liquid is viscous and a small amount may remain in the tip after dispensing. This will not affect the results.*

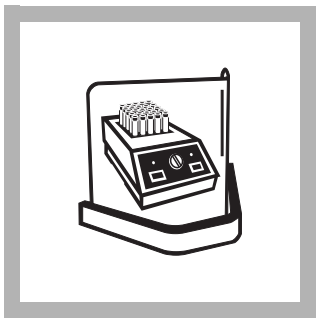
Note: *The THM Plus Reagent 2 must be at room temperature before use.*

THM Plus™ TRIHALOMETHANES, continued

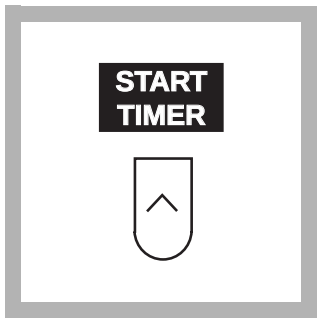


9. Cap tightly and mix by shaking ten times.

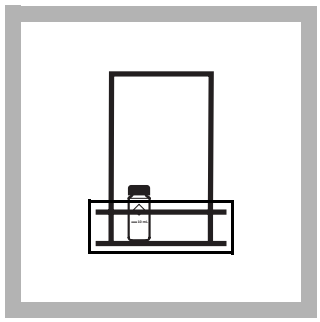
Note: *Thorough mixing ensures that all of the THM goes into the liquid and does not accumulate in the head space.*



10. Place the sample cell in the THM reactor at 100 °C. Set the blank aside.



11. Press ***800 START TIMER*** to begin an eight-minute reaction period.

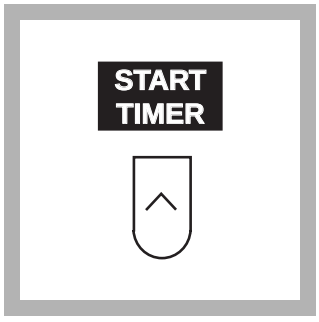


12. At the end of the reaction period, remove the cell from the reactor and place in the cell holder assembly.

Place the assembly in a cooling bath.

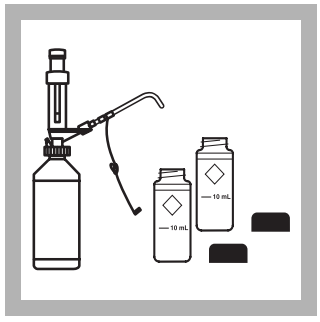
13. Press: ***NEXT TIMER*** twice.

Note: *Pressing* ***NEXT TIMER*** *twice skips Timer 1, which is used for a water bath digestion.*



14. Press: ***START TIMER 2***. Cool for three minutes.

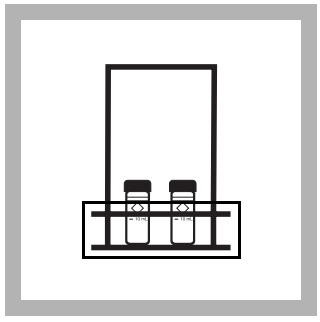
At the end of the cooling period, remove the cell from the cooling bath.



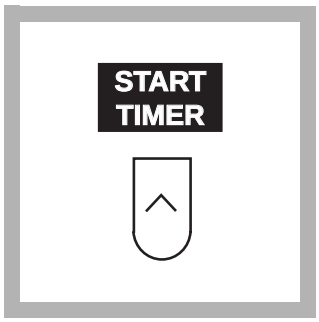
15. Use the Repipet Jr. to add 1 mL of THM Plus Reagent 3 to the sample cell and to the blank. Swirl to mix.

Note: *The sample will become warm*

Note: *The liquid is viscous and may not be entirely dispensed if measured using any other pipetting method.*



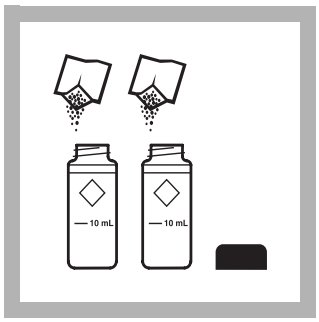
16. Replace the cooling water with fresh, cold tap water. Place the assembly containing the sample and blank cells into the cooling bath.



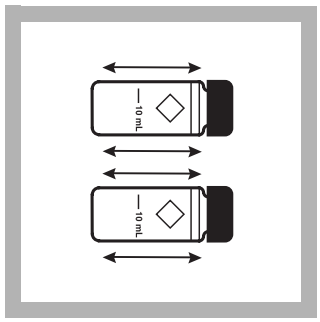
17. Press: ***START TIMER 3*** to begin a three-minute cooling time.

At the end of the cooling period, remove the cells from the cooling bath.

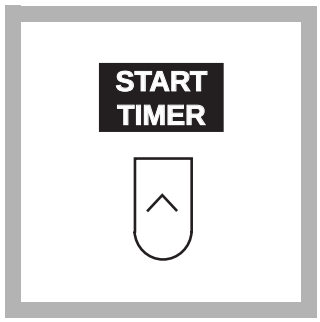
Note: *At the end of the cooling time, the sample temperature should be between 15 and 25 °C.*



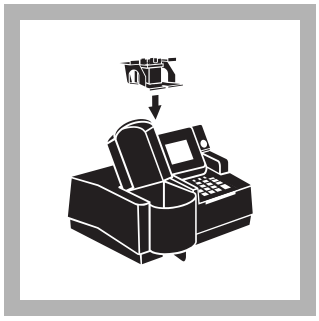
18. Add one THM Plus Reagent 4 Powder Pillow each to the sample cell and to the blank.



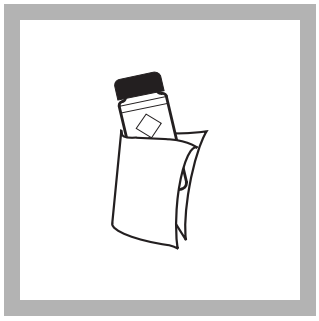
19. Cap each cell tightly and shake to dissolve.



20. Press ***START TIMER 4*** to begin a 15-minute color development time.

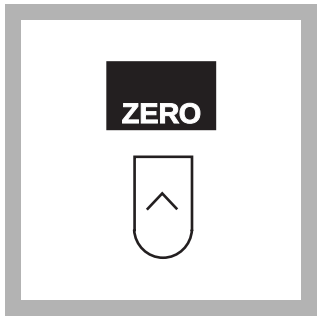


21. While the color is developing, insert the AccuVac® Ampul Adapter into instrument.



22. Wipe the reagent blank with a damp towel, followed by a dry one, to remove fingerprints or other marks.

23. At the end of the 15 minutes, place the blank into the cell holder and close the light shield.

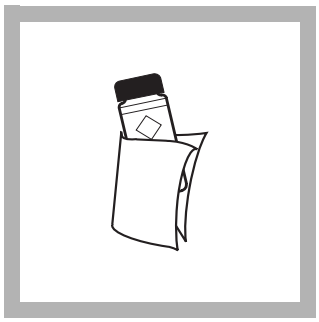


24. Press the soft key under ***ZERO***.

The display will show:

0 ppb $CHCl_3$

Note: *For alternate concentration units, press the soft key under* ***OPTIONS****, and then the soft key under* ***UNITS****. Scroll through the available options. Press* **ENTER** *to return to the Read screen.*



25. Wipe the sample cell with a damp towel, followed by a dry one, to remove fingerprints or other marks.

26. Place the prepared sample into the cell holder. Close the lid. Results will be displayed in ppb chloroform.

Sampling and Storage

Collect samples in 40-mL glass bottles sealed with Teflon®-lined septa caps. Use Cat. No. 27940-05 or equivalent for best results. Fill the bottles slowly to overflowing so that no air is included with the sample. Seal the bottles tightly and invert to check that no air has been trapped.

Because trihalomethane compounds (THMs) are extremely volatile, immediate analysis yields the greatest accuracy. If the samples cannot be analyzed immediately, cool samples to 4 °C. This will slow the formation of any additional THM compounds in chlorinated samples. Store the preserved samples at 4 °C in an atmosphere free of organic vapors. Samples should not be held more than 48 hours. Allow the samples to equilibrate to room temperature before analyzing.

Ascorbic acid cannot be used as a preservative with the THM Plus method. Sodium Thiosulfate may be used as a preservative in samples containing hardness of 100 mg/L or less as $CaCO_3$.

Accuracy Check

Standard Additions Method

Prepare the standard additions sample at the same time as the unspiked water sample. Snap the neck off a THM Standard Ampule, 10 ppm as chloroform. Using a Wiretrol™ Pipet (Cat. No. 25689-05), add 0.050 mL of the standard to 10 mL of water sample. Immerse the tip of the pipet below the surface of the water sample and dispense the aliquot of chloroform standard. Cap the sample cell immediately and swirl three times to mix. Prepare the sample and the spiked sample according to the procedure steps 6–26.

a. Leave the unspiked sample in the sample compartment after completing step 26. Verify that the units displayed are in ppb. Select standard additions mode by pressing the soft keys under ***OPTIONS, (MORE)*** and the ***STD ADD***.

b. Press **ENTER** to accept the default sample volume (mL), 10.0.

c. Use the keypad to enter **10000**. Press **ENTER**.

d. Press the soft key under ***ENTRY DONE***.

e. Read the standard additions sample prepared above. Accept the standard additions reading by pressing the soft key under ***READ***. The addition should reflect
80–120% recovery. To view % Recovery, press the soft key under ***EDIT TABLE***.

See the *Procedures Manual* for more information.

Standard Solutions Method

Chloroform is extremely volatile! Do not shake it when mixing.

Prepare a 99 ppb chloroform standard by pipetting 10.0 mL of organic-free water into a sample cell. Snap the neck off a THM Standard Ampule, 10 ppm as chloroform. Using a Wiretrol Pipette (Cat. No. 25689-05), transfer 0.100 mL of the chloroform standard into the organic-free water. Immerse the end of the pipet tip under the water to dispense the chloroform. Cap the sample cell immediately and swirl three times to mix. Immediately perform steps 6–25 of the procedure. Do not make up the standard in advance. Use the standard immediately upon preparation.

Method Performance

Precision
Standard: 60 ppb $CHCl_3$

Program	95% Confidence Limits
3560	56–64 ppm $CHCl_3$

For more information on determining precision data and method detection limits, refer to the *Procedures Manual*.

Estimated Detection Limit

Program	EDL
3560	6 ppb $CHCl_3$

For more information on the derivation and use of Hach's estimated detection limit, see the *Procedures Manual*. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, appendix B, see the *Procedures Manual*.

Sensitivity

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	21 ppb as $CHCl_3$

See the *Procedures Manual* for more information.

Sample Cell Matching

The THM Plus method requires that the 1" sample cells be optically matched for best performance. Although sample cells supplied by Hach Company are distortion-free, nicks and scratches from handling, fingerprints, and other foreign material on the glass surfaces may cause an optical mismatch between two sample cells and introduce error into the test results. This type of error may be avoided by optically matching the sample cells and following the cell precaution statements listed in the procedure.

Procedure:

1. Turn on your instrument and select the THM Plus method. Select the wavelength indicated in the procedure if your instrument has not automatically done so.
2. Change the instrument to the absorbance mode.
3. Pour at least 10 mL of deionized water into each of the samples cells to be matched.
4. Place one of the sample cells into the cell holder. Note and mark the orientation of the cell in the cell holder. Close the light shield. (Sample cells should be carefully wiped with a lint free cloth to remove any fingerprints or other foreign matter on the outside of the cell.)
5. Press: **ZERO**. The display will show: **0.000 Abs**
6. Place the next sample cell into the cell holder. Close the light shield.
7. Wait for the absorbance value to stabilize. Record the value.
8. Turn the cell 180 degrees and repeat *steps 6–7*. Try to achieve an absorbance value within ±0.001 Abs of the first cell. Note the orientation of the sample cell in the cell holder. This will allow the cells to be oriented consistently in the cell holder.

Reagent Storage

Refrigerate THM Plus Reagent 2 for maximum stability. Long-term exposure to temperatures above 35 °C may cause reagent degradation.

Interferences

The substances in the following table have been tested and found not to interfere up to the indicated levels (in ppm):

Interferences that have no effect up to the maximum level tested

Interference	Maximum Level tested
Chlorine	<10 ppm
Copper	<1000 ppm
Hardness, Ca	<1000 ppm as $CaCO_3$ May have some turbidity until Reagent 3 is added
Hardness, Mg	<4000 ppm as $CaCO_3$ May have some turbidity until Reagent 3 is added
Iron	<10 ppm
Lead	<2 ppm
Mercury	<10 ppm
Monochloramine	<20 ppm
Nickel	<10ppm
Sodium Bisulfite	<100 ppm
EDTA	Interferes negatively at all levels

Additional disinfection by-products that react

Compound	Effect
1,1,1-trichloro-2-propanone	Interferes positively
1,1,1-tricholoacetonitrile	Interferes positively
Chloral hydrate	Interferes positively
Dibromochloroacetic acid	Interferes positively
Dichlorobromoacetic acid	Interferes positively
Tribromoacetic acid	Interferes positively
Trichloroacetic acid	Interferes positively

Summary of Method

The THM Plus method reacts with the trihalogenated disinfection by-products formed as the result of the disinfection of drinking water with chlorine in the presence of naturally occurring organic materials. These disinfection by-products (DBPs) may be produced in the treatment plant or the distribution system as long as the water is in contact with free chlorine residual. The formation of the DBPs is influenced by chlorine contact time, chlorine dose and residual, temperature, pH, precursor concentration, and bromide concentration.

The predominant DBPs formed by the chlorination of drinking water are the trihalomethanes or THMs. The four trihalogenated compounds that form are chloroform, bromoform, dichlorobromomethane, and dibromochloromethane. These four compounds comprise the Total Trihalomethanes (TTHMs) group which is regulated under the Safe Drinking Water Act. The combined concentration of the TTHMs, reported as chloroform, is regulated to be 100 ppb or less in drinking water samples. Other DBPs that may be present and react under the conditions of the THM Plus method are listed in Interferences.

In the THM Plus method, THM compounds present in the sample react with N, N,-diethylnicotinamide under heated alkaline conditions to form a dialdehyde intermediate. The sample is then cooled and acidified to pH 2.5. The dialdehyde intermediate formed is then reacted with 7-napthylamine-1,3 disulfonic acid to form a colored Schiff base which absorbs at 515 nm. The color formed is directly proportional to the total amount of THM compounds present in the sample. The results are reported as ppb chloroform.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet for information specific to the reagents used.

REQUIRED REAGENTS

Reagent Set (50 tests) 27908-00
Includes: (1) 27539-29, (1) 27540-48, (1) 27541-42, (1) 27566-99

Description	Quantity Required Per Test	Unit	Cat. No.
THM Plus Reagent 1	6 drops	30 mL/bottle	27539-29
THM Plus Reagent 2	6 mL	330 mL/bottle	27540-48
THM Plus Reagent 3	2 mL	100 mL/bottle	27541-42
THM Plus Reagent 4	2 pillows	100 pillows	27566-99

REQUIRED APPARATUS

Beaker, 600-mL		each	500-52
Cell Holder Assembly, TTHM	1	each	47880-00
Evaporating Dish, 125 mm x 65 mm	1	each	27647-00
Repipet Jr., 1-mL	1	each	21113-02
Pipet, Tensette, 1–10 mL	1	each	19700-10
Pipet tips, 1–10 mL (for 19700-10)		50/pkg	25589-96
Sample cells, 10 mL, w/caps	2	6/box	24276-06
THM Reactor, Model 49100, 115 VAC		each	49100-00
THM Reactor, Model 49100, 230 VAC		each	49100-02
Wipers, Disposable, KimWipes		280/pkg	20970-00

OPTIONAL REAGENTS

THM Standard Ampules, 10-ppm as Chloroform	7/pkg	27567-07
Water, Reagent, Organic-free	500 mL	26415-49

OPTIONAL APPARATUS

Flask, volumetric, 100-mL, class A	each	14574-42
Pipet, filler, safety bulb	each	14651-00
Pipet, volumetric, class A, 10-mL	each	14515-38
Pipettes, Wiretrol™, 50–100 µL	250/pkg	25689-05
Vials, glass, 40-mL, with Septa cap	5/pkg	27940-05

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Organic Constituents, UV-Absorbing (UV-254)

Direct Reading Method[1] — Method 10054

Scope and application: For the determination of UV-absorbing organic compounds in drinking water and surface water.

[1] Adapted from *Standard Methods for the Examination of Water and Wastewater*, Method 5910.

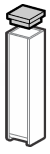
Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows requirements that can change between instruments, such as adapter and sample cell requirements.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information

Instrument	Adapter	Sample cell orientation	Sample cell
DR 6000	LZV902.99.00020 (universal) LZV902.99.00002 (1-cm carousel)	The clear side is to the right.	2624410 
DR 5000	A23618	The clear side is toward the user.	

Before starting

The sample pH must be 4 to 10 for accurate results. For SUVA calculations, do not adjust the sample pH.
Use a non-plastic filter assembly. Use a glass fiber filter of nominal pore size (1 to 1.5 µm) with no organic binder. For SUVA calculations, use a 0.45-µm filter and vacuum filtration apparatus.
Use only quartz sample cells for this test.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

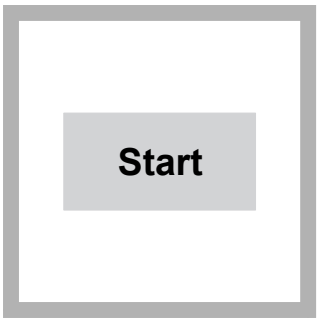
Description	Quantity
Organic-free reagent water	varies
Filter assembly	1
Buret stand	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	1

Refer to Consumables and replacement items on page 4 for order information.

Sample collection

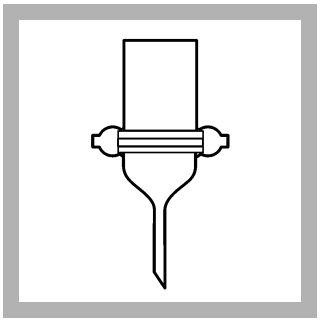
- Collect samples in clean glass bottles.
- Analyze the samples as soon as possible for best results.

Test procedure

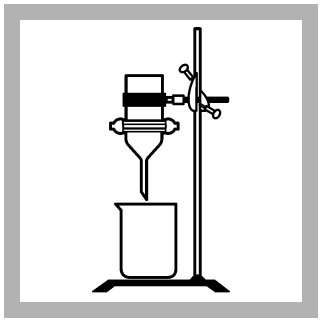


1. Start program **410 Organics, UV - 254**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

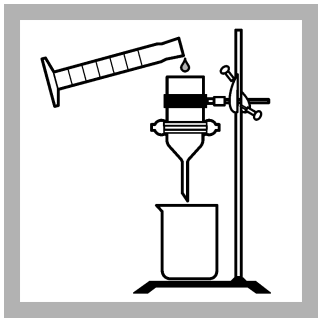
Note: *Although the program name can be different between instruments, the program number does not change.*



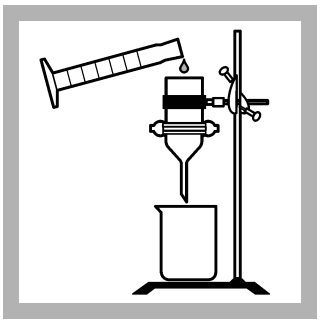
2. Assemble the filter apparatus. Make sure to use the white PTFE support plate. Insert the filter with the wrinkled surface pointed up.



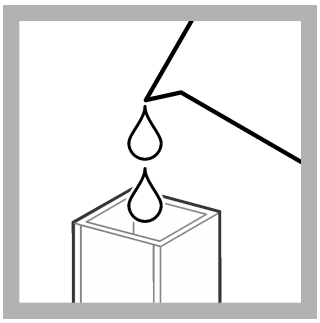
3. Install the apparatus in a support stand. Put a clean glass beaker below the filter.



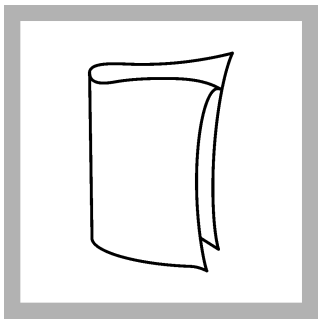
4. Prewash the filter assembly: Pour 50 mL of organic-free reagent water through the filter to remove soluble matter from the filter. Discard the filtered water.



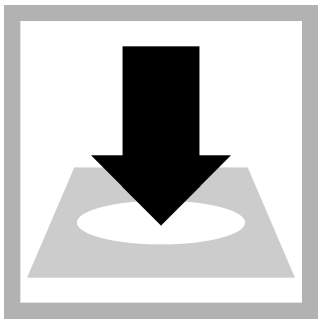
5. Prepare the sample: Pour 50 mL of sample through the filter.



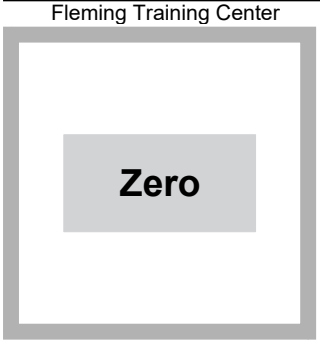
6. Prepare the blank: Rinse the sample cell several times with organic-free reagent water.
Fill the sample cell with organic-free reagent water.



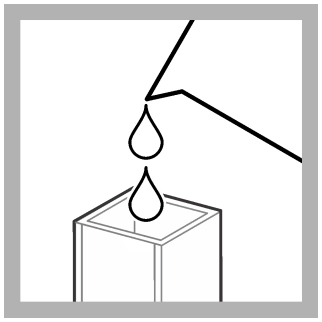
7. Clean the blank sample cell.



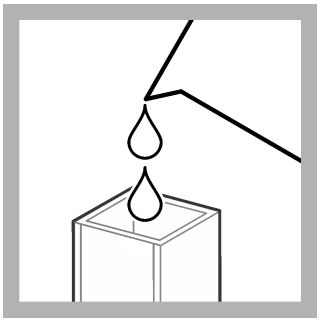
8. Insert the blank into the cell holder.



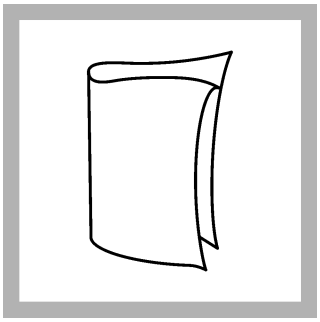
9. Push **ZERO**. The display shows 0.000 cm^{-1} and 1-cm cell. If necessary, wait 2 to 3 minutes for the Lamp Warm Up to complete.



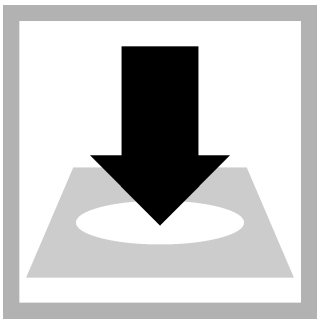
10. Discard the contents of the blank sample cell. Rinse the sample cell several times with the filtered sample.



11. Fill the sample cell with the filtered sample.



12. Clean the sample cell.



13. Insert the sample cell into the cell holder.

14. Push **READ**. Results show in absorbance per centimeter (cm^{-1}).

Interferences

Interfering substance	Interference level
Extreme sample pH	Add 1 N Sodium Hydroxide or 1 N Sulfuric Acid to the sample to adjust the sample pH to 4 to 10.
UV-absorbing inorganics (bromide, ferrous iron, nitrate, nitrites)	Refer to Identify interferences in the sample on page 3.
UV-absorbing oxidants and reductants (chloramines, chlorates, chlorites, ozone, thiosulfates)	

Identify interferences in the sample

Do a baseline scan from 200 to 400 nm on the sample and the blank to identify if there are interferences in the sample.

1. From the main menu, push **WAVELENGTH SCAN>OPTIONS>λ**.
2. Push **200>OK**.
3. Push **400>OK**.
4. Push **1 NM>OK**.
5. Do steps 5 to 14 of the test procedure.
   If the sample scan shows sharp peaks, interferences may be in the sample.

Typically, natural organic material shows a featureless curve in the UV region with increased absorption as the wavelength decreases. If sharp peaks show, select and report a different wavelength.

Clean the sample cells

⚠ WARNING

Chemical exposure hazard. Obey laboratory safety procedures and wear all of the personal protective equipment appropriate to the chemicals that are handled. Refer to the current safety data sheets (MSDS/SDS) for safety protocols.

Clean new and dirty sample cells before use to remove all organic contamination. When the sample cells are rinsed every time with organic-free reagent water after use, it is only necessary to clean the sample cells occasionally.

1. Put the sample cells in Chromic Acid Cleaning Solution for a maximum of 12 hours.
2. Rinse the sample cells 10 times or more with organic-free reagent water.

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
410	—	0.431 to 0.433 cm^{-1}	—

Summary of method

The filtered sample is measured at 254 nm to show organic constituents in the sample water. Organic-free reagent water is used for the blank sample cell. Results are given in absorbance per centimeter (cm^{-1}). The results are used to calculate Specific Ultraviolet Absorbance (SUVA).

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Organic-Free Reagent Water	varies	500 mL	2641549

Required apparatus

Description	Quantity/test	Unit	Item no.
Beaker, 100-mL	1	each	50042H
Buret stand	1	each	32900
Clamp holder	1	each	32600
Clamp, 3-prong	1	each	42200
Filter funnel assembly, 7-cm	1	each	2164100
Filter plate, PTFE, for filter funnel assembly	1	each	2164200
Filter, glass fiber, 70-mm	1	100/pkg	253053
Sample cell, 1-cm quartz	1	each	2624410

Optional reagents and apparatus

Description	Unit	Item no.
Cell holder for 10-cm sample cells (DR 5000 only)	each	LZY421
Chromic Acid Cleaning Solution	500 mL	123349
Sodium Hydroxide Standard Solution, 1.00 N	100 mL MDB	104532
Sulfuric Acid Standard Solution, 1 N	100 mL MDB	127032
Filter pump, aspirator (SUVA)	each	213100
Filter, membrane, hydrophilic, polyethersulfone SUVA, 0.45-micron, 47-mm	100/pkg	2894700
Filter holder, glass for vacuum filtration (SUVA)	each	234000
Flask, filtering, glass, 1000-mL (SUVA)	each	54653
Graduated cylinder, 50-mL	each	50841
Paper, pH, 1.0–11.0	5 rolls/pkg	39133
Potassium Acid Phthalate (KHP), ACS	500 g	31534
Sample cells, 1-cm quartz matched pair	each	4822800
Sample cell, 5-cm rectangular quartz	each	2624450
Sample cell, 10-cm rectangular quartz	each	2624401
Standard Methods Book, most current edition	each	2270800
Tubing, latex rubber (SUVA), 5/16-in. inside diameter	3.66 m (12 ft)	56019

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Section 8
Iron

Iron

Water Treatment Lab

TDEC - Fleming Training Center 1

Iron

- Iron is the fourth most abundant element in the earth's crust
- In streams, the average concentration is about 0.7 mg/L
- In groundwater, the iron concentration can range from 0.1 – 10.0 mg/L

TDEC - Fleming Training Center 2

Iron

- Symbol for Iron is Fe
- The soluble (dissolved) form is ferrous iron
  - Fe^{+2} (divalent)
- The insoluble (precipiated) form is ferric iron
  - Fe^{+3} (oxidized)
- The soluble form is converted to insoluble form by a chemical process called oxidation

TDEC - Fleming Training Center 3

Iron Bacteria

- Gallionella
- Only one cell of iron bacteria needed to start an infestation
- Obtains energy from reaction between iron and dissolved oxygen
- Forms thick slime on pipe walls
  - Rust colored
  - Variation in flow will result in slimes coming loose creating dirty water and taste & odor complaints
- Controlled by chlorination
  - Iron converted into rust particles

4

Iron

- Elevated levels of iron may cause staining of plumbing fixtures and laundry and may give an objectionable taste or color
- sMCL = 0.3 mg/L

TDEC - Fleming Training Center 5

Red Water

- Iron concentrations above 0.3 mg/L can cause "red water" complaints
- Iron can provide a nutrient source for bacteria that grown in distribution pipes

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Sample Collection

- Samples are difficult to collect leading to many incorrect readings
- Forms loosely attached scales on pipe walls
- When tap is opened, scale particles may be dislodged and enter the sample bottle leading to large errors
- If not acidified, iron can form scale on sample bottle walls if sample is left for days before testing
  - When sample is poured out of bottle, most of the iron will be left behind

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Sample Collection

- Samples should be taken from plastic sample line
- Open tap slowly
- Allow water to flow 1 minute for each 10 feet of sample line
- Samples should be tested within 48 hours unless acidified
  - Acidify – lower sample pH to 2 with nitric acid
  - Sample pH must be raised prior to running test

TDEC - Fleming Training Center 8

Sample Preparation

- Analyze samples as soon as possible to prevent air oxidation of ferrous iron to ferric iron
- Hach's method has a detection range of 0.02 – 3.0 mg/L
- Three minute reaction period needs to take place before reading

TDEC - Fleming Training Center 9

3500-Fe IRON*

3500-Fe A. Introduction

1. Occurrence and Significance

Iron (Fe) is the first element in Group VIII of the periodic table; it has an atomic number of 26, an atomic weight of 55.85, and common valences of 2 and 3 (and occasionally valences of 1, 4, and 6). The average abundance of Fe in the earth's crust is 6.22%; in soils Fe ranges from 0.5 to 4.3%; in streams it averages about 0.7 mg/L; and in groundwater it is 0.1 to 10 mg/L. Iron occurs in the minerals hematite, magnetite, taconite, and pyrite. It is widely used in steel and in other alloys.

The solubility of ferrous ion (Fe^{2+}) is controlled by the carbonate concentration. Because groundwater is often anoxic, any soluble iron in groundwater is usually in the ferrous state. On exposure to air or addition of oxidants, ferrous iron is oxidized to the ferric state (Fe^{3+}) and may hydrolyze to form red, insoluble hydrated ferric oxide. In the absence of complex-forming ions, ferric iron is not significantly soluble unless the pH is very low.

Elevated iron levels in water can cause stains in plumbing, laundry, and cooking utensils, and can impart objectionable tastes and colors to foods. The United Nations Food and Agriculture Organization recommended level for irrigation waters is 5 mg/L. The U.S. EPA secondary drinking water standard MCL is 0.3 mg/L.

2. Selection of Method

Sensitivity and detection levels for the atomic absorption spectrometric methods (Sections 3111B and C), the inductively coupled plasma method (Section 3120), and the phenanthroline colorimetric procedure described here (3500-Fe.B) are similar and generally adequate for analysis of natural or treated waters. Lower detection levels can be achieved with electrothermal atomic absorption spectrometry (Section 3113B) when an appropriate matrix modifier is used. The complexing reagents used in the colorimetric procedures are specific for ferrous iron but the atomic absorption procedures are not. However, because of the instability of ferrous iron, which is changed easily to the ferric form in solutions in contact with air, determination of ferrous iron requires special precautions and may need to be done in the field at the time of sample collection.

The procedure for determining ferrous iron using 1,10-phenanthroline (3500-Fe.B.4*c*) has a somewhat limited applicability; avoid long storage time or exposure of samples to light. A rigorous quantitative distinction between ferrous and ferric iron can be obtained with a special procedure using bathophenanthroline. Spectrophotometric methods using bathophenanthroline[1–6] and other organic complexing reagents such as ferrozine[7] or TPTZ[8] are capable of determining iron concentrations as low as 1 μg/L. A chemiluminescence procedure[9] is stated to have a detection limit of 5 ng/L. Additional procedures are described elsewhere.[10–13]

3. Sampling and Storage

Plan in advance the methods of collecting, storing, and pretreating samples. Clean sample container with acid and rinse with reagent water. Equipment for membrane filtration of samples in the field may be required to determine iron in solution (dissolved iron). Dissolved iron, considered to be that passing through a 0.45-μm membrane filter, may include colloidal iron. The value of the determination depends greatly on the care taken to obtain a representative sample. Iron in well or tap water samples may vary in concentration and form with duration and degree of flushing before and during sampling. When taking a sample portion for determining iron in suspension, shake the sample bottle often and vigorously to obtain a uniform suspension of precipitated iron. Use particular care when colloidal iron adheres to the sample bottle. This problem can be acute with plastic bottles.

For a precise determination of total iron, use a separate container for sample collection. Treat with acid at the time of collection to place the iron in solution and prevent adsorption or deposition on the walls of the sample container. Take account of the added acid in measuring portions for analysis. The addition of acid to the sample may eliminate the need for adding acid before digestion (3500-Fe.B.4*a*).

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* Approved by Standard Methods Committee, 1997. Editorial revisions, 2011. Joint Task Group: 20th Edition—See Section 3500-Al.

https://doi.org/10.2105/SMWW.2882.055

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3500-Fe B. Phenanthroline Method

1. General Discussion

a. Principle: Iron is brought into solution, reduced to the ferrous state by boiling with acid and hydroxylamine, and treated with 1,10-phenanthroline at pH 3.2 to 3.3. Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange-red complex. The colored solution obeys Beer's law; its intensity is independent of pH from 3 to 9. A pH between 2.9 and 3.5 ensures rapid color development in the presence of an excess of phenanthroline. Color standards are stable for at least 6 months.

b. Interference: Among the interfering substances are strong oxidizing agents, cyanide, nitrite, and phosphates (polyphosphates more so than orthophosphate), chromium, zinc in concentrations exceeding 10 times that of iron, cobalt and copper in excess of 5 mg/L, and nickel in excess of 2 mg/L. Bismuth, cadmium, mercury, molybdate, and silver precipitate phenanthroline. The initial boiling with acid converts polyphosphates to orthophosphate and removes cyanide and nitrite that otherwise would interfere. Adding excess hydroxylamine eliminates errors caused by excessive concentrations of strong oxidizing reagents. In the presence of interfering metal ions, use a larger excess of phenanthroline to replace that complexed by the interfering metals. Where excessive concentrations of interfering metal ions are present, the extraction method may be used.

If noticeable amounts of color or organic matter are present, it may be necessary to evaporate the sample, gently ash the residue, and redissolve in acid. The ashing may be carried out in silica, porcelain, or platinum crucibles that have been boiled for several hours in 6*N* HCl. The presence of excessive amounts of organic matter may necessitate digestion before use of the extraction procedure.

c. Minimum detectable concentration: Dissolved or total concentrations of iron as low as 10 μg/L can be determined with a spectrophotometer using cells with a 5 cm or longer light path. Carry a blank through the entire procedure to allow for correction.

d. Quality control (QC): The QC practices considered to be an integral part of each method can be found in Section 3020.

2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for use at 510 nm, providing a light path of 1 cm or longer.

2) *Filter photometer,* providing a light path of 1 cm or longer and equipped with a green filter having maximum transmittance near 510 nm.

3) *Nessler tubes,* matched, 100-mL, tall form.

b. Acid-washed glassware: Wash all glassware with conc hydrochloric acid (HCl) and rinse with reagent water before use to remove deposits of iron oxide.

c. Separatory funnels: 125-mL, Squibb form, with ground-glass or TFE stopcocks and stoppers.

3. Reagents

Use reagents low in iron. Use reagent water (see Sections 1080 and 3111B.3*c*) in preparing standards and reagent solutions and in procedure. Store reagents in glass-stoppered bottles. The HCl and ammonium acetate solutions are stable indefinitely if tightly stoppered. The hydroxylamine, phenanthroline, and stock iron solutions are stable for several months. The standard iron solutions are not stable; prepare daily as needed by diluting the stock solution. Visual standards in nessler tubes are stable for several months if sealed and protected from light.

a. Hydrochloric acid (HCl), conc, containing less than 0.5 ppm iron.

b. Hydroxylamine solution: Dissolve 10 g $NH_2OH{\cdot}HCl$ in 100 mL water.

c. Ammonium acetate buffer solution: Dissolve 250 g $NH_4C_2H_3O_2$ in 150 mL water. Add 700 mL conc (glacial) acetic acid. Because even a good grade of $NH_4C_2H_3O_2$ contains a significant amount of iron, prepare new reference standards with each buffer preparation.

d. Sodium acetate solution: Dissolve 200 g $NaC_2H_3O_2 \cdot 3H_2O$ in 800 mL water.

e. Phenanthroline solution: Dissolve 100 mg 1,10-phenanthroline monohydrate, $C_{12}H_8N_2 \cdot H_2O$, in 100 mL water by stirring and heating to 80°C. Do not boil. Discard the solution if it darkens. Heating is unnecessary if 2 drops conc HCl are added to the water. (Note: One milliliter of this reagent is sufficient for no more than 100 μg Fe.)

f. Potassium permanganate, 0.02*M:* Dissolve 0.316 g $KMnO_4$ in reagent water and dilute to 100 mL.

g. Stock iron solution: Use metal (1) or salt (2) for preparing the stock solution.

1) Use electrolytic iron wire, or "iron wire for standardizing," to prepare the solution. If necessary, clean wire with fine sandpaper to remove any oxide coating and to produce a bright surface. Weigh 200.0 mg wire and place in a 1000-mL volumetric flask. Dissolve in 20 mL 6*N* sulfuric acid (H_2SO_4) and dilute to mark with water; 1.00 mL = 200 μg Fe.

2) If ferrous ammonium sulfate is preferred, slowly add 20 mL conc H_2SO_4 to 50 mL water and dissolve 1.404 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Slowly add potassium permanganate (¶ *f* above) until a faint pink color persists. Add the last few milliliters of the solution dropwise. Approximately 50 mL of the

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potassium permanganate will be required. Dilute to 1000 mL with water and mix; 1.00 mL = 200 μg Fe.

h. Standard iron solutions: Prepare daily for use.

1) Pipet 50.00 mL stock solution into a 1000-mL volumetric flask and dilute to mark with water; 1.00 mL = 10.0 μg Fe.

2) Pipet 5.00 mL stock solution into a 1000-mL volumetric flask and dilute to mark with water; 1.00 mL = 1.00 μg Fe.

i. Diisopropyl or isopropyl ether. **CAUTION: Ethers may form explosive peroxides; test before using**.

4. Procedure

a. Total iron: Mix sample thoroughly and measure 50.0 mL into a 125-mL Erlenmeyer flask. If this sample volume contains more than 200 μg iron use a smaller accurately measured portion and dilute to 50.0 mL. Add 2 mL conc HCl and 1 mL $NH_2OH \cdot HCl$ solution. Add a few glass beads and heat to boiling. To ensure dissolution of all the iron, continue boiling until volume is reduced to 15 to 20 mL. (If the sample is ashed, take up residue in 2 mL conc HCl and 5 mL water.) Cool to room temperature and transfer to a 50- or 100-mL volumetric flask or nessler tube. Add 10 mL $NH_4C_2H_3O_2$ buffer solution and 4 mL phenanthroline solution, and dilute to mark with water. Mix thoroughly and allow a minimum of 10 min for maximum color development.

b. Dissolved iron: Immediately after collection filter sample through a 0.45-μm membrane filter into a vacuum flask containing 1 mL conc HCl/100 mL sample. Analyze filtrate for total dissolved iron (¶ *a* above) and/or dissolved ferrous iron (¶ *c* below). (This procedure also can be used in the laboratory if it is understood that normal sample exposure to air during shipment may result in precipitation of iron.)

Calculate suspended iron by subtracting dissolved from total iron.

c. Ferrous iron: Determine ferrous iron at sampling site because of the possibility of change in the ferrous-ferric ratio with time in acid solutions. To determine ferrous iron only, acidify a separate sample with 2 mL conc HCl/100 mL sample at time of collection. Fill bottle directly from sampling source and stopper. Immediately withdraw a 50-mL portion of acidified sample and add 20 mL phenanthroline solution and 10 mL $NH_4C_2H_3O_2$ solution with vigorous stirring. Dilute to 100 mL and measure color intensity within 5 to 10 min. Do not expose to sunlight. (Color development is rapid in the presence of excess phenanthroline. The phenanthroline volume given is suitable for less than 50 μg total iron; if larger amounts are present, use a correspondingly larger volume of phenanthroline or a more concentrated reagent.)

Calculate ferric iron by subtracting ferrous from total iron.

d. Color measurement: Prepare a series of standards by accurately pipetting calculated volumes of standard iron solutions [use solution described in 3500-Fe.B.3*h*2) to measure 1- to 10-μg portions] into 125-mL Erlenmeyer flasks and diluting to 50 mL by adding measured volumes of water. Add 2 mL conc HCl and 1 mL $NH_2OH \cdot HCl$ solution. Carry out the steps in ¶ *a* above beginning with transfer to a 100-mL volumetric flask or nessler tube.

For visual comparison, prepare a set of at least 10 standards, ranging from 1 to 100 μg Fe in the final 100-mL volume. Compare colors in 100-mL tall-form nessler tubes.

TABLE 3500-Fe:I. SELECTION OF LIGHT PATH LENGTH FOR VARIOUS IRON CONCENTRATIONS

Fe μg		
50-mL Final Volume	100-mL Final Volume	Light Path *cm*
50–200	100–400	1
25–100	50–200	2
10–40	20–80	5
5–20	10–40	10

For photometric measurement, use Table 3500-Fe:I as a rough guide for selecting proper light path at 510 nm. Read standards against water set at zero absorbance and plot a calibration curve, including a blank (see Sections 1080 and 3111B.3*c*).

If samples are colored or turbid, carry a second set of samples through all steps of the procedure without adding phenanthroline. Instead of water, use the prepared blanks to set photometer to zero absorbance and read each sample developed with phenanthroline against the corresponding blank without phenanthroline. Translate observed photometer readings into iron values by means of the calibration curve. This procedure does not compensate for interfering ions.

e. Samples containing organic interferences: Digest samples containing substantial amounts of organic substances according to the directions given in Section 3030G or H.

1) If a digested sample has been prepared according to the directions given in Section 3030G or H, pipet 10.0 mL or other suitable portion containing 20 to 500 μg Fe into a 125-mL separatory funnel. If the volume taken is less than 10 mL, add water to make up to 10 mL. To the separatory funnel add 15 mL conc HCl for a 10-mL aqueous volume; or, if the portion taken was greater than 10.0 mL, add 1.5 mL conc HCl/mL sample. Mix, cool, and proceed with ¶ *e*3) below.

2) To prepare a sample solely for determining iron, measure a suitable volume containing 20 to 500 μg Fe and carry it through the digestion procedure described in either Section 3030G or H. However, use only 5 mL H_2SO_4 or $HClO_4$ and omit H_2O_2. When digestion is complete, cool, dilute with 10 mL water, heat almost to boiling to dissolve slowly soluble salts, and, if the sample is still cloudy, filter through a glass-fiber, sintered-glass, or porcelain filter, washing with 2 to 3 mL water. Quantitatively transfer filtrate or clear solution to a 25-mL volumetric flask and make up to 25 mL with water. Empty flask into a 125-mL separatory funnel, rinse flask with 5 mL conc HCl and add to the funnel. Add 25 mL conc HCl measured with the same flask. Mix and cool to room temperature.

3) Extract the iron from the HCl solution in the separatory funnel by shaking for 30 s with 25 mL isopropyl ether (**CAUTION**). Draw off lower acid layer into a second separatory funnel. Extract acid solution again with 25 mL isopropyl ether, drain acid layer into a suitable clean vessel, and add ether layer to the ether in the first funnel. Pour acid layer back into second separatory funnel and re-extract with 25 mL isopropyl ether. Withdraw and discard acid layer and add ether layer to first funnel. Persistence of a yellow color in the HCl solution after three extractions does not signify incomplete separation of iron be-

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cause copper, which is not extracted, gives a similar yellow color.

Shake combined ether extracts with 25 mL water to return iron to aqueous phase and transfer lower aqueous layer to a 100-mL volumetric flask. Repeat extraction with a second 25-mL portion of water, adding this to the first aqueous extract. Discard ether layer.

4) Add 1 mL $NH_2OH \cdot HCl$ solution, 10 mL phenanthroline solution, and 10 mL $NaC_2H_3O_2$ solution. Dilute to 100 mL with water, mix thoroughly, and let stand for a minimum of 10 min. Measure absorbance at 510 nm using a 5-cm absorption cell for amounts of iron less than 100 μg or 1-cm cell for quantities from 100 to 500 μg. As reference, use either water or a sample blank prepared by carrying the specified quantities of acids through the entire analytical procedure. If water is used as reference, correct sample absorbance by subtracting absorbance of a sample blank.

Determine micrograms of iron in the sample from the absorbance (corrected, if necessary) by reference to the calibration curve prepared by using a suitable range of iron standards containing the same amounts of phenanthroline, hydroxylamine, and sodium acetate as the sample.

5. Calculation

When the sample has been treated according to 3500-Fe.B.4*a, b, c,* or 4*e*2):

$$\text{mg Fe/L} = \frac{\mu\text{g Fe (in 100 mL final volume)}}{\text{mL sample}}$$

When the sample has been treated according to 4*e*1):

$$\text{mg Fe/L} = \frac{\mu\text{g Fe (in 100 mL final volume)}}{\text{mL sample}} \times \frac{100}{\text{mL portion}}$$

Report details of sample collection, storage, and pretreatment if they are pertinent to interpretation of results.

6. Precision and Bias

Precision and bias depend on the method of sample collection and storage, the method of color measurement, the iron concentration, and the presence of interfering color, turbidity, and foreign ions. In general, optimum reliability of visual comparison in nessler tubes is not better than 5% and often only 10%, whereas, under optimum conditions, photometric measurement may be reliable to 3% or 3 μg, whichever is greater. The sensitivity limit for visual observation in nessler tubes is approximately 1 μg Fe. Sample variability and instability may affect precision and bias of this determination more than will the errors of analysis. Serious divergences have been found in reports of different laboratories because of variations in methods of collecting and treating samples.

A synthetic sample containing 300 μg Fe/L, 500 μg Al/L, 50 μg Cd/L, 110 μg Cr/L, 470 μg Cu/L, 70 μg Pb/L, 120 μg Mn/L, 150 μg Ag/L, and 650 μg Zn/L in distilled water was analyzed in 44 laboratories by the phenanthroline method, with a relative standard deviation of 25.5% and a relative error of 13.3%.

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SKOUGSTAD, M.W., M.J. FISHMAN, L.C. FRIEDMAN, D.E. ERDMANN & S.S. DUNCAN. 1979. Methods for determination of inorganic substances in water and fluvial sediment. Chapter A1 *in* Book 5, Techniques of Water Resources Investigations of the United States Geological Survey. U.S. Geological Surv., Washington, D.C.

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Iron, Total

USEPA[1] FerroVer® Method[2] **Method 8008**

0.02 to 3.00 mg/L Fe **Powder Pillows or AccuVac® Ampuls**

Scope and application: For water, wastewater and seawater; digestion is required for determining total iron.

[1] USEPA approved for reporting wastewater analysis, Federal Register, June 27, 1980; 45 (126:43459).
[2] Adapted from Standard Methods for the Examination of Water and Wastewater.

Test preparation

Instrument-specific information

Table 1 shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests. Table 2 shows sample cell and adapter requirements for AccuVac Ampul tests. The tables also show all of the instruments that have the program for this test.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information for reagent addition

Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700 DR 1900	The fill line is to the right.	2495402
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The orientation mark is toward the user.	2401906

Table 2 Instrument-specific information for AccuVac Ampuls

Instrument	Adapter	Sample cell
DR 6000 DR 5000 DR 900	—	2427606
DR 3900	LZV846 (A)	
DR 1900	9609900 or 9609800 (C)	
DR 3800 DR 2800 DR 2700	LZV584 (C)	2122800

Before starting

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
The reagent in this test procedure converts all soluble iron and most insoluble forms of iron in the sample to soluble ferrous iron for measurement. For regulatory reporting, however, the sample must be digested with heat and acid to make sure that all forms of the metal are measured.
For the best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to determine the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option.
For turbid samples, treat the blank with one 0.1-g scoop of RoVer Rust Remover. Swirl to dissolve.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Powder pillows

Description	Quantity
FerroVer® Iron Reagent Powder Pillows, 10-mL[1]	1
Sample cells. (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

[1] FerroVer is a registered trademark of Hach Company.

Refer to Consumables and replacement items on page 7 for order information.

AccuVac Ampuls

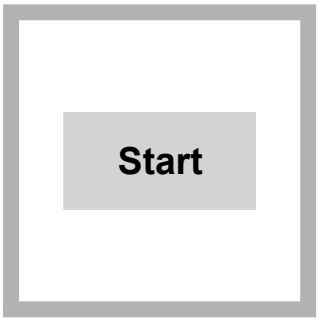
Description	Quantity
FerroVer® Iron Reagent AccuVac® Ampul	1
Beaker, 50-mL	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	1
Stopper for 18-mm tubes and AccuVac Ampuls	1

Refer to Consumables and replacement items on page 7 for order information.

Sample collection and storage

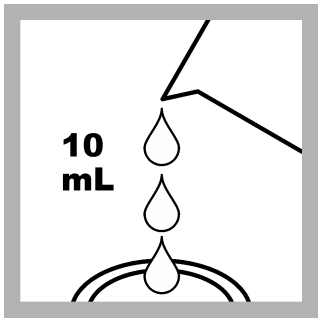
- Collect samples in clean glass or plastic bottles that have been cleaned with 6 N (1:1) hydrochloric acid and rinsed with deionized water.
- To measure only dissolved iron, filter the sample immediately after collection and before acidification.
- To preserve samples for later analysis, adjust the sample pH to less than 2 with concentrated nitric acid (approximately 2 mL per liter). No acid addition is necessary if the sample is tested immediately.
- Keep the preserved samples at room temperature for a maximum of 6 months.
- Before analysis, adjust the pH to 3–5 with 5 N sodium hydroxide solution.
- Correct the test result for the dilution caused by the volume additions.

Powder pillow procedure

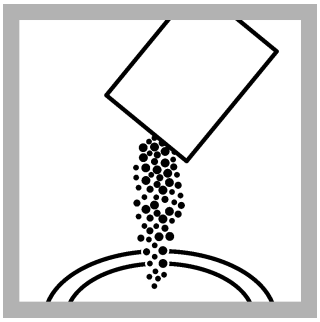


1. Start program **265 Iron, FerroVer**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

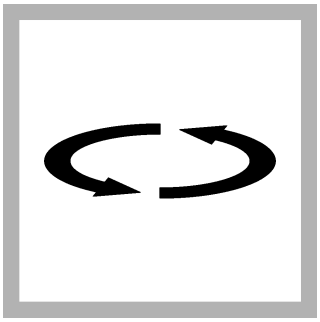
Note: *Although the program name can be different between instruments, the program number does not change.*



2. Prepare the sample: Fill a sample cell with 10 mL of sample.



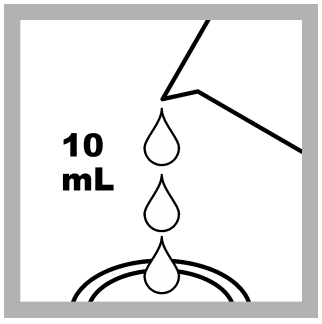
3. Add the contents of one FerroVer Iron Reagent Powder Pillow to the sample cell.



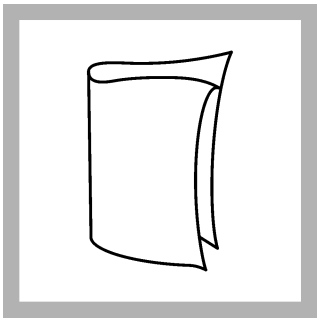
4. Swirl the sample cell to mix. Undissolved powder will not affect accuracy.

5. Start the instrument timer. A 3-minute reaction time starts.

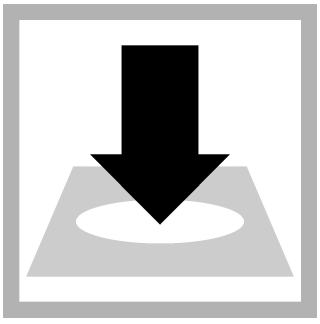
An orange color will show if iron is present. Let samples that contain rust react for 5 minutes or more.



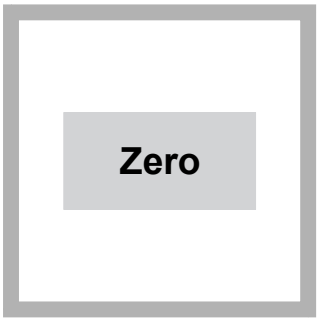
6. Prepare the blank: Fill a second sample cell with 10 mL of sample.



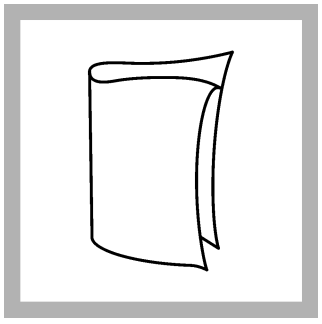
7. Clean the blank sample cell.



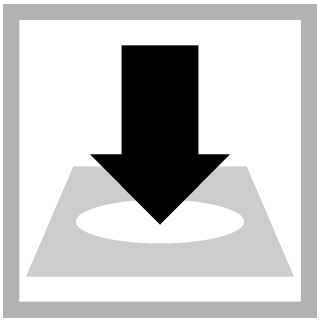
8. When the timer expires, insert the blank into the cell holder.



9. Push **ZERO**. The display shows 0.00 mg/L Fe.



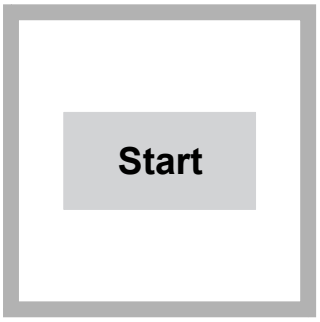
10. Clean the prepared sample cell.



11. Insert the prepared sample into the cell holder.

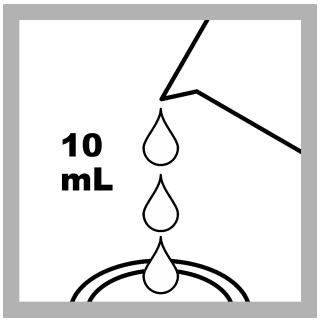
12. Push **READ**. Results show in mg/L Fe.

AccuVac procedure

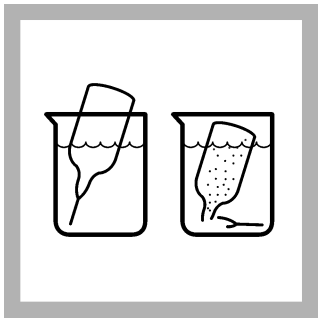


1. Start program **267 Iron, FerroVer AV**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

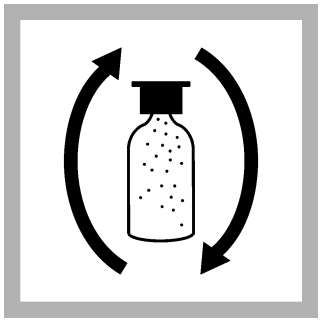
Note: *Although the program name can be different between instruments, the program number does not change.*



2. Prepare the blank: Fill the sample cell with 10 mL of sample.



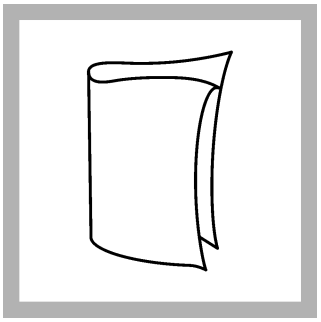
3. Prepare the sample: Collect at least 40 mL of sample in a 50-mL beaker. Fill the AccuVac Ampul with sample. Keep the tip immersed while the AccuVac Ampul fills completely.



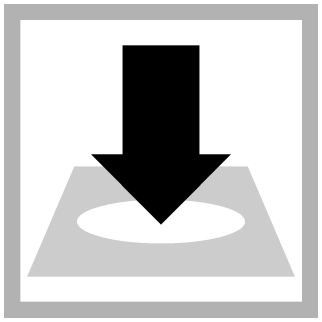
4. Quickly invert the AccuVac Ampul several times to mix. Undissolved powder will not affect accuracy.

5. Start the instrument timer. A 3-minute reaction time starts.

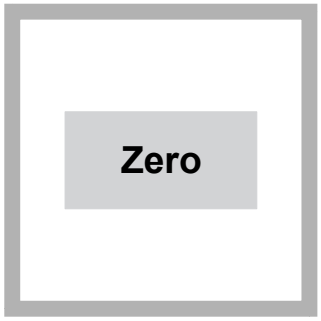
An orange color will show if iron is present. Let samples that contain rust react for 5 minutes or more.



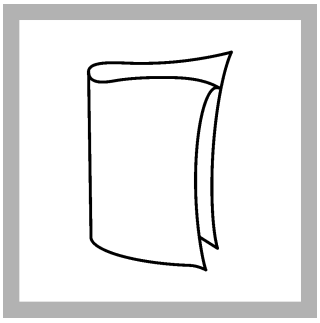
6. Clean the blank sample cell.



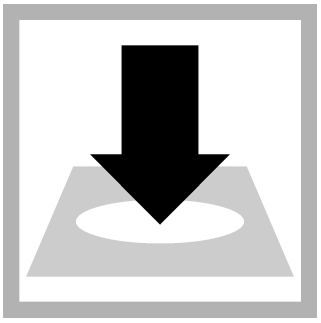
7. When the timer expires, insert the blank into the cell holder.



8. Push **ZERO**. The display shows 0.00 mg/L Fe.



9. Clean the AccuVac Ampul.



10. Insert the prepared sample AccuVac Ampul into the cell holder.

11. Push **READ**. Results show in mg/L Fe.

Interferences

Interfering substance	Interference level
Calcium, Ca^{2+}	No effect at less than 10,000 mg/L as $CaCO_3$.
Chloride, Cl^-	No effect at less than 185,000 mg/L.
Copper, Cu^{2+}	No effect. Masking agent is contained in FerroVer Reagent.
High iron levels	Inhibit color development. Dilute sample and re-test to verify results.
Iron oxide	A mild, vigorous or Digesdahl digestion is necessary. After digestion, adjust the sample pH to 3–5 with sodium hydroxide, then analyze.
Magnesium	No effect at 100,000 mg/L as $CaCO_3$.
Molybdate molybdenum	No effect at 50 mg/L as Mo.
High sulfide levels, S^{2-}	Pretreat the sample in a fume hood or in an area with sufficient airflow before analysis: **1.** Add 5 mL of 6.0 N (1:1) hydrochloric acid solution to 100 mL of sample in a 250-mL Erlenmeyer flask. **2.** Boil for 20 minutes. **3.** Let the solution cool to room temperature. **4.** Adjust the pH to 3–5 with 5 N sodium hydroxide solution. **5.** Add deionized water until the volume is 100 mL. **6.** Use the treated sample in the test procedure.
Turbidity	Pre-treat the sample before analysis: **1.** Add one 0.1-g scoop of RoVer® Rust Remover to the blank. Swirl to mix. **2.** If the sample remains turbid, add three 0.2-g scoops of RoVer Rust Remover to 75 mL of sample. Let stand 5 minutes. **3.** Filter through a 0.45-micron membrane filter and filter holder. **4.** Use the treated sample in the test procedure.
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment of the sample by the reagents. Sample pre-treatment may be necessary. Adjust the pH to 3–5.

Accuracy check

Standard additions method (sample spike)

Use the standard additions method (for applicable instruments) to validate the test procedure, reagents and instrument and to find if there is an interference in the sample.

Items to collect:

- Iron Voluette® Ampule Standard, 25 mg/L
- Ampule Breaker
- Pipet, TenSette®, 0.1–1.0 mL and tips

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 10-mL portions of fresh sample. Mix well.

   Note: *For AccuVac® Ampuls, add 0.2 mL, 0.4 mL and 0.6 mL of the standard solution to three 50-mL portions of fresh sample.*

6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

Items to collect:

- Iron standard solution, 100 mg/L
- 100-mL volumetric flask, Class A
- 2-mL volumetric pipet, Class A and pipet filler
- Deionized water

1. Prepare a 2.00-mg/L iron standard solution as follows:
   a. Use a pipet to add 2 mL of the 100-mg/L iron standard solution into the volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
2. Use the test procedure to measure the concentration of the prepared standard solution.
3. Compare the expected result to the actual result.

   Note: *The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are slight variations in the reagents or instruments.*

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% Confidence Interval)	Sensitivity Concentration change per 0.010 Abs change
265	2.00 mg/L Fe	1.99–2.01 mg/L Fe	0.021 mg/L Fe
267	2.00 mg/L Fe	1.98–2.02 mg/L Fe	0.023 mg/L Fe

Summary of method

FerroVer Iron Reagent converts all soluble iron and most insoluble forms of iron in the sample to soluble ferrous iron. The ferrous iron reacts with the 1-10 phenanthroline indicator in the reagent to form an orange color in proportion to the iron concentration. The measurement wavelength is 510 nm for spectrophotometers or 520 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
FerroVer® Iron Reagent Powder Pillow[1], 10-mL	1	100/pkg	2105769
OR			
FerroVer® Iron Reagent AccuVac® Ampul	1	25/pkg	2507025

[1] FerroVer is a registered trademark of Hach Company

Required apparatus

Description	Quantity/Test	Unit	Item no.
Beaker, 50-mL	1	each	50041H
Stoppers for 18-mm tubes and AccuVac Ampuls	2	6/pkg	173106

Recommended standards and apparatus

Description	Unit	Item no.
Flask, volumetric, Class A, 100-mL glass	each	1457442
Iron Standard Solution, 100-mg/L Fe	100 mL	1417542
Iron Standard Solution, 10-mL Voluette® Ampule, 25-mg/L Fe	16/pkg	1425310
Metals Drinking Water Standard, LR for Cu, Fe, Mn	500 mL	2833749
Metals Drinking Water Standard, HR for Cu, Fe, Mn	500 mL	2833649
Pipet filler, safety bulb	each	1465100
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	1000/pkg	2185628
Pipet, volumetric, Class A, 2-mL	each	1451536
Water, deionized	4 L	27256

Optional reagents and apparatus

Description	Unit	Item no.
AccuVac® Ampul Snapper	each	2405200
Mixing cylinder, graduated, 50-mL	each	189641
Filter, glass fiber membrane, 1.5-micron, 47-mm	100/pkg	253000
Filter membrane filter holder, 47-mm	each	234000
Hydrochloric Acid, concentrated	500 mL	13449
Nitric Acid, concentrated	500 mL	15249
RoVer Rust Remover	454 g	30001
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	245032
Spoon, measuring, 0.1-g	each	51100

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Iron Bench Sheet

	mg/L		
Sample			
Standard Addition (r^2)			
Duplicate			
Standard			

Section 9
Manganese

Manganese

Water Treatment Lab

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1

Manganese

- An essential trace element for plants and animals
- More abundant in soils than in water
- In streams, the average concentration is 0.7µg/L
- In groundwater, it is generally less than 0.1 mg/L
- Concentrations can be much higher in stratified lakes
  - Reducing conditions may occur in the hypolimnion causing manganese to be dissolved from the sediment

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2

Manganese

- The soluble (dissolved) state of manganese is Mn^{2+}
- Manganese can be oxidized to Mn^{3+}
  - This form is insoluble
  - The insoluble form creates a black precipitant that can color water – manganese dioxide

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3

MCL

- sMCL = 0.05 mg/L
- High levels of manganese in water can cause staining of plumbing fixtures and laundry
- If water contains more than 0.02 mg/L, operator should initiate a flushing program to avoid complaints
  - This will help to prevent buildup of manganese dioxide

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4

Sample Collection

- Samples are difficult to collect leading to many incorrect readings
- Forms loosely attached scales on pipe walls
- When tap is opened, scale particles may be dislodged and enter the sample bottle leading to large errors
- If not acidified, iron can form scale on sample bottle walls if sample is left for days before testing
  - When sample is poured out of bottle, most of the iron will be left behind
- Samples should be taken from plastic sample line
- Open tap slowly
- Allow water to flow 1 minute for each 10 feet of sample line
- Samples should be tested within 48 hours unless acidified
  - Acidify – lower sample pH to 2 with nitric acid

Manganese Analysis

- Hach has two methods
  - High range
    - 0.2 – 20.0 mg/L
  - Low range
    - PAN Method
    - 0.007 – 0.700 mg/L
- Iron can be an interference if it is in excess of 5 mg/L
  - If high levels of iron are present, allow 10 minute reaction period instead of 2 minutes with Hach method

Make sure to use low range, this sees down to sMCL

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6

Manganese, LR

1-(2-Pyridylazo)-2-Naphthol PAN Method[1] — Method 8149

0.006 to 0.700 mg/L Mn (LR) — Powder Pillows

Scope and application: For water and wastewater; digestion is necessary for total manganese determinations.

[1] Adapted from Goto, K., et al., Talanta, 24, 652-3 (1977).

Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700 DR 1900	The fill line is to the right.	2495402
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The orientation mark is toward the user.	2401906

Before starting

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
To make sure that all forms of the metal are measured, digest the sample with heat and acid. Use the mild or vigorous digestion. Refer to the *Water Analysis Guide* for more information.
Rinse all glassware with a 1:1 (50%) nitric acid solution. Rinse again with deionized water.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
The alkaline cyanide solution contains cyanide. Make sure to read the Safety Data Sheets and obey the safety precautions.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

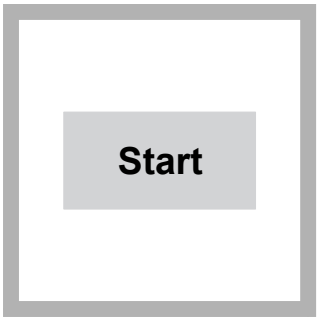
Description	Quantity
Alkaline Cyanide Reagent	12 drops
Water, deionized	10 mL
Ascorbic Acid Powder Pillow	2
PAN Indicator Solution, 0.1%	12 drops
Stoppers for 18-mm tubes and AccuVac Ampul	2
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

Refer to Consumables and replacement items on page 5 for order information.

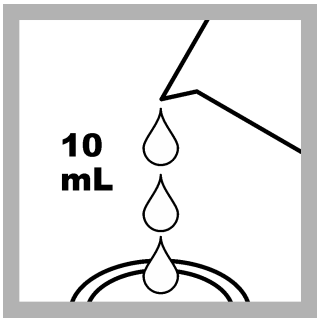
Sample collection and storage

- Collect samples in clean glass or plastic bottles that have been cleaned with 6 N (1:1) hydrochloric acid and rinsed with deionized water.
- To preserve samples for later analysis, adjust the sample pH to less than 2 with concentrated nitric acid (approximately 2 mL per liter). No acid addition is necessary if the sample is tested immediately.
- Keep the preserved samples at room temperature for a maximum of 6 months.
- Before analysis, adjust the pH to 4–5 with 5 N sodium hydroxide solution.
- Correct the test result for the dilution caused by the volume additions.

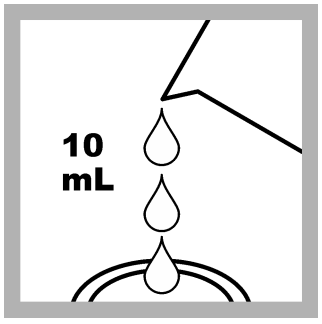
Powder pillow procedure



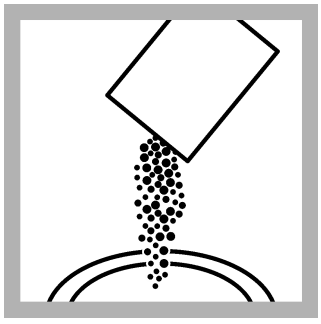
1. Start **Program 290 Manganese, LR PAN**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



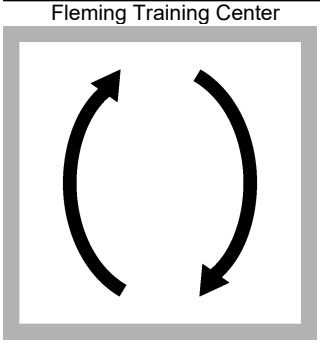
2. Prepare the blank: Fill the sample cell with 10 mL of deionized water. Digestion is necessary for total manganese determination.



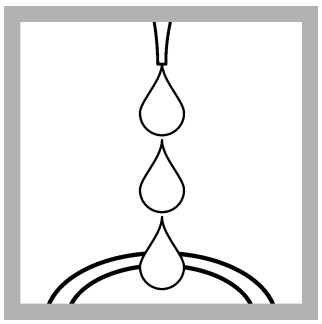
3. Prepare the sample: Fill a second sample cell with 10 mL of sample.



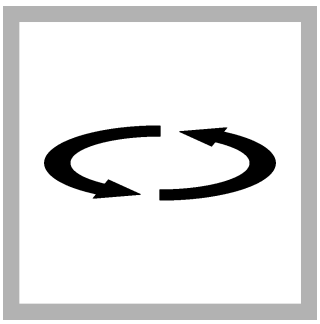
4. Add the contents of one Ascorbic Acid Powder Pillow to each sample cell.



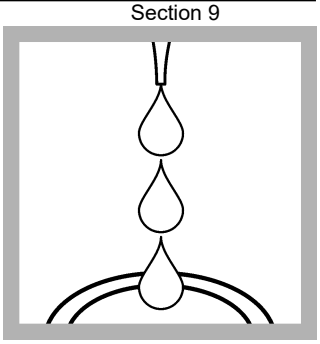
5. Put the stopper on both sample cells. Invert to dissolve the powder.



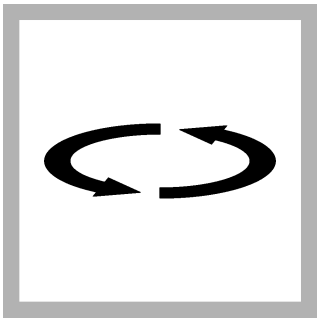
6. Add 12 drops of Alkaline Cyanide Reagent Solution to each cell.



7. Swirl to mix.
The solution may start to show turbidity. This should dissipate in the next step.

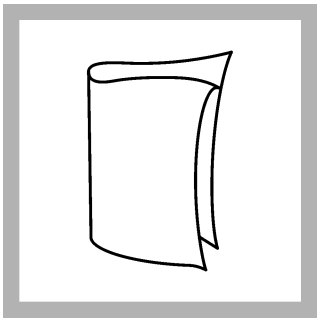


8. Add 12 drops of PAN Indicator Solution, 0.1% to each cell.

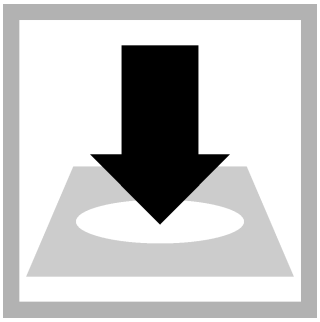


9. Swirl to mix.
The sample will show an orange color if manganese is present.

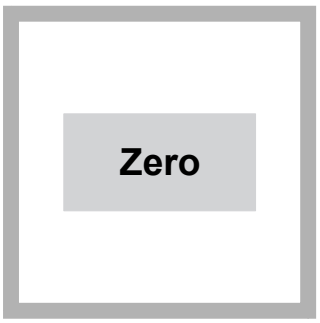
10. Start the instrument timer. A 2-minute reaction time starts.



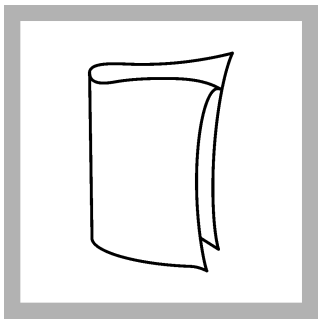
11. When the timer expires, clean the blank sample cell.



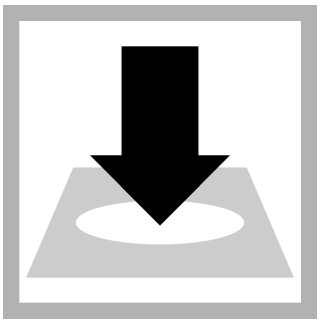
12. Insert the blank into the cell holder.



13. Push **ZERO**. The display shows 0.000 mg/L Mn.



14. Clean the prepared sample cell.



15. Insert the prepared sample into the cell holder.

16. Push **READ**. Results show in mg/L Mn.

Interferences

Interfering substance	Interference level
Aluminum	20 mg/L
Cadmium	10 mg/L
Calcium	1000 mg/L as $CaCO_3$
Cobalt	20 mg/L
Copper	50 mg/L
Hardness	For samples that contain more than 300 mg/L hardness as $CaCO_3$, add 4 drops of Rochelle Salt Solution to the sample after the Ascorbic Acid Powder Pillow is added.
Iron	25 mg/L (If the sample contains more than 5 mg/L iron, increase the reaction time to 10 minutes.)

Interfering substance	Interference level
Lead	0.5 mg/L
Magnesium	300 mg/L as $CaCO_3$
Nickel	40 mg/L
Zinc	15 mg/L

Accuracy check

Standard additions method (sample spike)

Use the standard additions method (for applicable instruments) to validate the test procedure, reagents and instrument and to find if there is an interference in the sample.

Items to collect:

- Manganese Standard Solution, 10 mg/L Mn, PourRite Ampule
- Ampule breaker
- Pipet, TenSette, 0.1–1.0 mL and tips

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 10-mL portions of fresh sample. Mix well.
6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

Items to collect:

- Manganese Standard Solution, 25 mg/L Mn
- 100-mL volumetric flask, Class A
- 2.0-mL volumetric pipet, Class A and pipet filler
- Deionized water

1. Prepare a 0.5-mg/L manganese standard solution as follows:
   a. Use a pipet to add 2.0 mL of the 25-mg/L manganese standard solution into the volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
2. Use the test procedure to measure the concentration of the prepared standard solution.
3. Compare the expected result to the actual result. The result should be 0.5 mg/L Mn.

   Note: *The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are small variations in the reagents or instruments.*

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
290	0.500 mg/L Mn	0.491–0.509 mg/L Mn	0.006 mg/L Mn

Summary of method

The PAN method is a highly sensitive and rapid procedure to measure low levels of manganese. The ascorbic acid reagent reduces all oxidized forms of manganese to Mn^{2+}. The alkaline-cyanide reagent masks potential interferences. PAN Indicator then forms an orange-colored complex with Mn^{2+}. The measurement wavelength is 560 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Manganese Reagent Set, 10 mL, includes:	—	50 tests	2651700
Alkaline Cyanide Reagent	12 drops	50 mL SCDB	2122326
Ascorbic Acid Powder Pillow	2	100/pkg	1457799
PAN Indicator Solution, 0.1%	12 drops	50 mL SCDB	2122426
Water, deionized	varies	4 L	27256

Recommended standards and apparatus

Description	Unit	Item no.
Manganese Standard Solution, 10 mg/L Mn, 2-mL PourRite® Ampule	20/pkg	2605820
Manganese Standard Solution, 25 mg/L Mn, 2-mL PourRite® Ampule	20/pkg	2112820
PourRite® Ampule Breaker, 2-mL	each	2484600
Metals Drinking Water Standard, HR for Cu, Fe, Mn	500 mL	2833649

Optional reagents and apparatus

Description	Unit	Item no.
Mixing cylinder, graduated, 25-mL	each	2088640
Flask, volumetric, Class A, 100 mL, glass, Certified	each	2636642
Nitric Acid, concentrated	500 mL	15249
Paper, pH, 0–14 pH range	100/pkg	2601300
Pipet filler, safety bulb	each	1465100
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet, TenSette®, 1.0–10.0 mL	each	1970010
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	1000/pkg	2185628
Pipet tips for TenSette® Pipet, 1.0–10.0 mL	50/pkg	2199796
Pipet tips for TenSette® Pipet, 1.0–10.0 mL	250/pkg	2199725
Pipet, volumetric, Class A, 2 mL	each	1451536

Optional reagents and apparatus (continued)

Description	Unit	Item no.
Rochelle Salt Solution	29 mL	172533
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	245032

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Manganese Bench Sheet

	mg/L		
Sample			
Standard Addition (r^2)			
Duplicate			
Standard			

Section 10
Nitrate and Nitrite

Nitrate and Nitrite

Water Treatment Lab

1

Maximum Contaminant Level

- Nitrate (NO_3^-) is 10 mg/L
- Nitrite (NO_2^-) is 1 mg/L
- Total Nitrate/Nitrite (NO_3^-/NO_2^-) is 10 mg/L

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Methemoglobinemia

- When MCL is exceeded, an immediate threat is posed to children under the age of 3-6 months
- Nitrate reacts with intestinal bacteria that change nitrate to nitrite
- Nitrite reacts with hemoglobin in blood (portion of blood that carries oxygen)
  - Reduces the oxygen-carrying ability of the blood and will produce the anemic condition "blue baby"
- Known as blue baby syndrome

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Carcinogen?

- Concern has been expressed about epidemiological link between nitrate and cancer
- Nitrite can react with secondary amines, amides and carbamates to form N-nitroso compounds
  - Several of these are potential human carcinogens

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Removal

- Ion exchange of chloride for nitrate is currently the simplest and least expensive method for removing nitrate from contaminated groundwaters
- Sulfate (SO_4^{2-}) can be a major interference in the removal of nitrate by the chloride ion form of strong base anion exchange resins

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Sample Collection

- Collect sample in plastic or glass bottle
- Samples may be refrigerated at 4°C for up to 24 hours
  - Should be analyzed as soon after collection as possible

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Nitrate

- Nitrate represents the most completely oxidized form of nitrogen found in water
- High levels indicate biological wastes or runoff from fertilized areas
- High levels stimulate algae growth which will degrade water quality

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Nitrate (NO_3^-) Analysis

- Hach method has a detection range of 0.1 – 10.0 mg/L NO_3^--N
- Uses NitraVer5 nitrate reagent powder pillows
- This method is technique-sensitive
  - Shaking time and technique influence color development
  - For more accurate results, make successive tests on a 10.0 mg/L Nitrate-Nitrogen standard

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Nitrite (NO_2^-) Analysis

- Hach method has a detection range of 0.002 – 0.30 mg/L NO_2^--N
- Uses NitriVer3 nitrate reagent powder pillows
- 20 minute reaction period for this test

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4500-NO_3^- NITROGEN (NITRATE)*

4500-NO_3^- A. Introduction

1. Selection of Method

Determination of nitrate (NO_3^-) is difficult because of the relatively complex procedures required, the high probability that interfering constituents will be present, and the limited concentration ranges of the various techniques.

An ultraviolet (UV) technique (Method B) that measures the absorbance of NO_3^- at 220 nm is suitable for screening uncontaminated water (low in organic matter).

Screen a sample; if necessary, then select a method suitable for its concentration range and probable interferences. Nitrate may be determined by ion chromatography (Section 4110), capillary ion electrophoresis (Section 4140), or the methods shown here. Applicable ranges are: nitrate electrode method (D), 0.14 to 1400 mg NO_3^--N/L; cadmium reduction method (E), 0.01 to 1.0 mg NO_3^--N/L; automated hydrazine reduction method (H), 0.01 to 10 mg NO_3^--N/L; automated cadmium reduction method (F), 0.1 to 10 mg NO_3^--N/L; cadmium reduction flow injection method (I), 0.000 25 to 10 mg NO_3^--N/L; second-derivative ultraviolet spectrophotometric method (C), 0.05 to 2 mg NO_3^--N/L. For higher NO_3^--N concentrations, dilute into the range of the selected method.

The colorimetric and UV second-derivative methods require an optically clear sample. Filter turbid sample through 0.45-μm membrane filter. Test filters for nitrate contamination.

2. Storage of Samples

Start NO_3^- determinations promptly after sampling. If storage is necessary, store for up to 2 d at 4°C; disinfected samples are stable much longer (at least 14 d) without acid preservation.

NOTE: If nitrite, NO_2^-, is present, then acid preservation can cause disproportionation of HNO_2 to NO_3^- and NO (nitric oxide). NO can be oxidized and hydrolyzed to nitrate. As a result, nitrate values may be the sum of nitrate and nitrite. Therefore, do not acidify samples for nitrate determination.

* Approved by Standard Methods Committee, 2000. Editorial revisions, 2011. Joint Task Group: 21st Edition—(4500-NO_3^-.C)—Thomas R. Holm (chair), Martin S. Frant, Karla Alicia Johnson, Scott Stieg; 20th Edition (4500-NO_3^-.I)—Scott Stieg (chair), Bradford R. Fisher, Owen B. Mathre, Theresa M. Wright.

4500-NO_3^- B. Ultraviolet Spectrophotometric Screening Method

1. General Discussion

a. Principle: Use this technique only for screening samples that have low organic matter contents, i.e., uncontaminated natural waters and potable water supplies. The NO_3^- calibration curve follows Beer's law up to 11 mg N/L.

Measurement of UV absorption at 220 nm enables rapid determination of NO_3^-. Because dissolved organic matter also may absorb at 220 nm and NO_3^- does not absorb at 275 nm, a second measurement made at 275 nm may be used to correct the NO_3^- value. The extent of this empirical correction is related to the nature and concentration of organic matter and may vary from one water to another. Consequently, this method is not recommended if a significant correction for organic matter absorbance is required, although it may be useful in monitoring NO_3^- levels within a water body with a constant type of organic matter. Correction factors for organic matter absorbance can be established by the method of additions in combination with analysis of the original NO_3^- content by another method. Sample filtration is intended to remove possible interference from suspended particles. Acidification with 1*N* HCl is designed to prevent interference from hydroxide or carbonate concentrations up to 1000 mg $CaCO_3$/L. Chloride has no effect on the determination.

b. Interference: Dissolved organic matter, surfactants, NO_2^-, and Cr^{6+} interfere. Various inorganic ions not normally found in natural water, such as chlorite and chlorate, may interfere. Inorganic substances can be compensated for by independent analysis of their concentrations and preparation of individual correction curves. For turbid samples, see 4500-NO_3^-A.1.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:I.

2. Apparatus

Spectrophotometer, for use at 220 and 275 nm with matched silica cells of 1-cm or longer light path.

3. Reagents

a. Nitrate-free water: Use redistilled or distilled, deionized water of highest purity to prepare all solutions and dilutions.

b. Stock nitrate solution: Dry potassium nitrate (KNO_3) in an oven at 105°C for 24 h. Dissolve 0.7218 g in water and dilute to 1000 mL; 1.00 mL = 100 μg NO_3^--N. Preserve with 2 mL $CHCl_3$/L. This solution is stable for at least 6 months.

c. Intermediate nitrate solution: Dilute 100 mL stock nitrate solution to 1000 mL with water; 1.00 mL = 10.0 μg NO_3^--N. Preserve with 2 mL $CHCl_3$/L. This solution is stable for 6 months.

d. Hydrochloric acid solution, HCl, 1*N*.

4. Procedure

a. Treatment of sample: To 50 mL clear sample, filtered if necessary, add 1 mL HCl solution and mix thoroughly.

b. Preparation of standard curve: Prepare NO_3^- calibration standards in the range 0 to 7 mg NO_3^--N/L by diluting to 50 mL the following volumes of intermediate nitrate solution: 0, 1.00, 2.00, 4.00, 7.00 . . . 35.0 mL. Treat NO_3^- standards in same manner as samples.

c. Spectrophotometric measurement: Read absorbance or transmittance against redistilled water set at zero absorbance or 100% transmittance. Use a wavelength of 220 nm to obtain NO_3^- reading and a wavelength of 275 nm to determine interference due to dissolved organic matter.

5. Calculation

For samples and standards, subtract two times the absorbance reading at 275 nm from the reading at 220 nm to obtain absorbance due to NO_3^-. Construct a standard curve by plotting absorbance due to NO_3^- against NO_3^--N concentration of standard. Using corrected sample absorbances, obtain sample concentrations directly from standard curve. NOTE: If correction value is more than 10% of the reading at 220 nm, do not use this method.

6. Bibliography

HOATHER, R.C. & R.F. RACKMAN. 1959. Oxidized nitrogen and sewage effluents observed by ultraviolet spectrophotometry. *Analyst* 84:549.

GOLDMAN, E. & R. JACOBS. 1961. Determination of nitrates by ultraviolet absorption. *J. Amer. Water Works Assoc.* 53:187.

ARMSTRONG, F.A.J. 1963. Determination of nitrate in water by ultraviolet spectrophotometry. *Anal. Chem.* 35:1292.

NAVONE, R. 1964. Proposed method for nitrate in potable waters. *J. Amer. Water Works Assoc.* 56:781.

4500-NO_3^- C. Second-Derivative Ultraviolet Spectrophotometric Method (PROPOSED)

1. General Discussion

a. Principle: Even though nitrate strongly absorbs ultraviolet (UV) light, determining nitrate by measuring the absorbance at one wavelength is not feasible because natural organic matter (NOM) and other solutes also absorb UV light. The spectra of NOM from different water sources usually are different, so the UV nitrate screening procedure (4500-NO_3^-.B) may not give reliable results. The UV spectrum of nitrate is quite different from that of NOM. In the nitrate spectrum, the absorbance increases rapidly from 230 to 210 nm, whereas in NOM spectra, the absorbance in the same wavelength range increases gradually. Computing the second derivative of a sample spectrum effectively eliminates the background NOM contribution.

b. Interferences: The nitrite UV spectrum is similar to that of nitrate. However, nitrite concentrations usually are much lower than nitrate concentrations. Bicarbonate absorbs weakly at wavelengths below 210 nm, but does not affect the second-derivative signal of nitrate. Bromide interferes at seawater concentrations (68 mg Br^-/L, salinity 35‰) so this method cannot be used to determine nitrate in seawater. Neither Fe nor Cu interferes at 2 mg/L, but both metals seriously interfere at 20 mg/L.[1] The method has been tested only for potable water. Its suitability for nitrate determination in wastewater has not been tested.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:I.

2. Apparatus

a. Spectrophotometer, capable of scanning from 250 to 200 nm. Some spectrophotometers can compute the second derivative of a spectrum. If the spectrophotometer cannot compute second-derivative spectra, then a computer interface is needed.

b. Cuvettes, matched 1-cm quartz.

c. Pipettor, adjustable 1 to 5 mL. Use a pipettor that clicks into place for volume adjustment, not one with a sliding scale.*

d. Cuvette mixer.†

e. Computer, cable, and software for transferring data from the spectrophotometer and computing second-derivative spectra. The cable and software may be available from the spectrophotometer manufacturer. These items are needed only if the spectrophotometer cannot compute second-derivative spectra.

3. Reagents

a. Nitrate stock solution, 100 mg NO_3^--N/L: Prepare as in 4500-NO_3^-.B.3*b* or obtain from a commercial source.

b. Nitrate-free water, distilled or deionized. Use to prepare standards and dilute samples if necessary.

4. Procedure

a. Sample treatment: Filter samples if turbid. Add 1 mL 1*M* H_2SO_4 or 2 mL 1*M* HCl to 100 mL sample, mix thoroughly.

b. Standards: Dilute 0.5, 1.0, 1.5, 2.0, and 2.5 mL nitrate stock solution to 100 mL to prepare standards containing 0.5, 1.0, 1.5, 2.0, and 2.5 mg N/L.

c. Measurement: Pipet 3.0 mL standard or sample into sample cuvette. Discard and pipet another 3.0 mL. Scan from 250 to 200 nm. If absorbance goes off-scale, dilute sample by withdrawing some sample with the macropipet and then pipetting same volume of nitrate-free water into the cuvette. For dilutions of 1:3, 1:5, and 1:10, withdraw 2.0, 2.4, and 2.7 mL. Mix with cuvette mixer. Alternatively, perform dilutions in volumetric glassware. Record any dilution. Compute second-derivative

* Wheaton pipet sold as Fisher #13-707-61 or VWR #53499-605, or equivalent.
† Bel-Art F37752-0000, or equivalent.

spectrum. Find maximum second derivative in the range 230 to 220 nm and record value. If spectrophotometer cannot compute second-derivative spectra, then set it to read the absorbance every 1.0 nm and transfer the spectra to the computer after each scan.

5. Calculation

a. Calibration: Compute second-derivative spectrum and find maximum for each sample, blank, or standard if the spectrophotometer cannot do this. Use the simplified least-squares procedure[2,3] to simultaneously smooth and differentiate spectra.‡ Perform least-squares linear regression using the second derivatives of the blank and standard spectra.

$$S = Int + C \times Slp$$

where:

S = maximum second derivative,
C = concentration,
Int = intercept of regression line, and
Slp = slope of regression line.

Thus,

$$C = \frac{S - Int}{Slp}$$

b. Samples: Calculate the nitrate concentration, C, from the equation above.

‡ A Microsoft Excel worksheet for this calculation can be obtained from Tom Holm, Illinois State Water Survey, trholm@illinois.edu.

6. Precision and Bias

Nitrate concentrations determined by the UV second-derivative method were compared with concentrations determined by ion chromatography for 79 potable-water samples with nitrate concentrations of up to 40 mg NO_3^--N/L.[4] The slope of the regression line was 0.94 with a standard error of 0.005. For 65 out of the 79 samples, the difference between nitrate concentrations determined by second-derivative UV spectrophotometry and ion chromatography was 0.5 mg N/L or less. The maximum difference for all samples was 1.6 mg NO_3^--N/L. The differences between the nitrate concentrations determined by the two methods appeared to be random, but they were not normally distributed.

7. References

1. Crumpton, W.G., T.M. Isenhard & P.D. Mitchell. 1992. Nitrate and organic N analyses with second-derivative spectroscopy. *Limnol. Oceanogr.* 37:907.
2. Savitsky, A. & M. Golay. 1964. Smoothing and differentiation of data by simplified least squares procedures. *Anal. Chem.* 36:1627.
3. Steinier, J., Y. Termonia & J. Deltour. 1972. Comments on smoothing and differentiation of data by simplified least squares. *Anal. Chem.* 44:1906.
4. Holm, T.R., W.R. Kelly, L.F. Sievers & D.L. Webb. 1997. A comparison of ultraviolet spectrophotometry with other methods for the determination of nitrate in water. *Spectroscopy* 12:38.

8. Bibliography

Simal, J., M.S. Lage & I. Iglesias. 1985. Second derivative ultraviolet spectroscopy and sulfamic acid method for determination of nitrates in water. *J. Assoc. Offic. Anal. Chem.* 68:962.

Suzuki, N. & R. Kuroda. 1987. Direct simultaneous determination of nitrate and nitrite by ultraviolet second-derivative spectrophotometry. *Analyst* 112:1077.

4500-NO_3^- D. Nitrate Electrode Method

1. General Discussion

a. Principle: The NO_3^- ion electrode is a selective sensor that develops a potential across a thin, porous, inert membrane that holds in place a water-immiscible liquid ion exchanger. The electrode responds to NO_3^- ion activity between about 10^{-5} and 10^{-1} *M* (0.14 to 1400 mg NO_3^--N/L). The lower limit of detection is determined by the small but finite solubility of the liquid ion exchanger.

b. Interferences: Chloride and bicarbonate ions interfere when their weight ratios to NO_3^--N are >10 or >5, respectively. Ions that are potential interferences but do not normally occur at significant levels in potable waters are NO_2^-, CN^-, S^{2-}, Br^-, I^-, ClO_3^-, and ClO_4^-. Although the electrodes function satisfactorily in buffers over the range pH 3 to 9, erratic responses have been noted where pH is not held constant. Because the electrode responds to NO_3^- activity rather than concentration, ionic strength must be constant in all samples and standards. Minimize these problems by using a buffer solution containing Ag_2SO_4 to remove Cl^-, Br^-, I^-, S^{2-}, and CN^-, sulfamic acid to remove NO_2^-, a buffer at pH 3 to eliminate HCO_3^- and to maintain a constant pH and ionic strength, and $Al_2(SO_4)_3$ to complex organic acids.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:I.

2. Apparatus

a. pH meter, expanded-scale or digital, capable of 0.1 mV resolution.

*b. Double-junction reference electrode.** Fill outer chamber with $(NH_4)_2SO_4$ solution.

* Orion Model 90-02, or equivalent.

c. Nitrate ion electrode:† Carefully follow manufacturer's instructions regarding care and storage.

d. Magnetic stirrer: TFE-coated stirring bar.

3. Reagents

a. Nitrate-free water: Prepare as described in 4500-NO_3^-.B.3*a*. Use for all solutions and dilutions.

b. Stock nitrate solution: Prepare as described in 4500-NO_3^-.B.3*b*.

c. Standard nitrate solutions: Dilute 1.0, 10, and 50 mL stock nitrate solution to 100 mL with water to obtain standard solutions of 1.0, 10, and 50 mg NO_3^--N/L, respectively.

d. Buffer solution: Dissolve 17.32 g $Al_2(SO_4)_3 \cdot 18H_2O$, 3.43 g Ag_2SO_4, 1.28 g H_3BO_3, and 2.52 g sulfamic acid (H_2NSO_3H), in about 800 mL water. Adjust to pH 3.0 by slowly adding 0.10*N* NaOH. Dilute to 1000 mL and store in a dark glass bottle.

e. Sodium hydroxide, NaOH, 0.1*N*.

f. Reference electrode filling solution: Dissolve 0.53 g $(NH_4)_2SO_4$ in water and dilute to 100 mL.

4. Procedure

a. Preparation of calibration curve: Transfer 10 mL of 1 mg NO_3^--N/L standard to a 50-mL beaker, add 10 mL buffer, and stir with a magnetic stirrer. Immerse tips of electrodes and record millivolt reading when stable (after about 1 min). Remove electrodes, rinse, and blot dry. Repeat for 10-mg NO_3^--N/L and 50-mg NO_3^--N/L standards. Plot potential measurements against NO_3^--N concentration on semilogarithmic graph paper, with NO_3^--N concentration on the logarithmic axis (abscissa) and potential (in millivolts) on the linear axis (ordinate). A straight line with a slope of +57 ± 3 mV/decade at 25°C should result. Recalibrate electrodes several times daily by checking potential reading of the 10 mg NO_3^--N standard and adjusting the calibration control until the reading plotted on the calibration curve is displayed again.

b. Measurement of sample: Transfer 10 mL sample to a 50-mL beaker, add 10 mL buffer solution, and stir (for about 1 min) with a magnetic stirrer. Measure standards and samples at about the same temperature. Immerse electrode tips in sample and record potential reading when stable (after about 1 min). Read concentration from calibration curve.

† Orion Model 93-07, Corning Model 476134, or equivalent.

5. Precision

Over the range of the method, precision of ±0.4 mV, corresponding to 2.5% in concentration, is expected.

6. Bibliography

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KEENEY, D.R., B.H. BYRNES & J.J. GENSON. 1970. Determination of nitrate in waters with nitrate-selective ion electrode. *Analyst* 95:383.

MILHAM, P.J., A.S. AWAD, R.E. PAULL & J.H. BULL. 1970. Analysis of plants, soils and waters for nitrate by using an ion-selective electrode. *Analyst* 95:751.

SYNNOTT, J.C., S.J. WEST & J.W. ROSS. 1984. Comparison of ion-selective electrode and gas-sensing electrode technique for measurement of nitrate in environmental samples. *In* Pawlowski et al., eds., Studies in Environmental Science, No. 23, Chemistry for Protection of the Environment. Elsevier Press, New York, N.Y.

4500-NO_3^- E. Cadmium Reduction Method

1. General Discussion

a. Principle: NO_3^- is reduced almost quantitatively to nitrite (NO_2^-) in the presence of cadmium (Cd). This method uses commercially available Cd granules treated with copper sulfate ($CuSO_4$) and packed in a glass column.

The NO_2^- produced thus is determined by diazotizing with sulfanilamide and coupling with *N*-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye that is measured colorimetrically. A correction may be made for any NO_2^- present in the sample by analyzing without the reduction step. The applicable range of this method is 0.01 to 1.0 mg NO_3^--N/L. The method is recommended especially for NO_3^- levels below 0.1 mg N/L where other methods lack adequate sensitivity.

b. Interferences: Suspended matter in the column will restrict sample flow. For turbid samples, see 4500-NO_3^-.A.l. Concentrations of iron, copper, or other metals above several milligrams per liter lower reduction efficiency. Add EDTA to samples to eliminate this interference. Oil and grease will coat the Cd surface. Remove by pre-extraction with an organic solvent (see Section 5520). Residual chlorine can interfere by oxidizing the Cd column, reducing its efficiency. Check samples for residual chlorine (see DPD methods in Section 4500-Cl). Remove residual chlorine by adding sodium thiosulfate ($Na_2S_2O_3$) solution (Section 4500-NH_3.B.3*d*). Sample color that absorbs at about 540 nm interferes.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:I.

2. Apparatus

a. Reduction column: Purchase or construct the column* (Figure 4500-NO_3^-:1) from a 100-mL volumetric pipet by removing the top portion. The column also can be constructed from two

* Tudor Scientific Glass Co., 555 Edgefield Road, Belvedere, SC 29841, Cat. TP-1730, or equivalent.

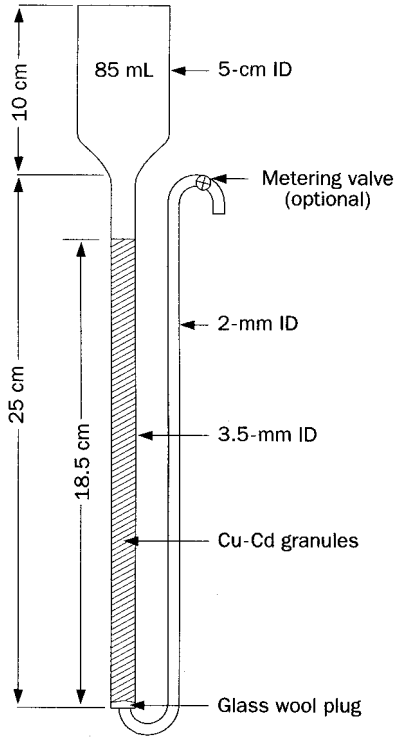

Figure 4500-NO_3^-:1. Reduction column.

pieces of tubing joined end to end: join a 10-cm length of 3-cm-ID tubing to a 25-cm length of 3.5-mm-ID tubing. Add a TFE stopcock with metering valve[1] to control flow rate.

b. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for use at 543 nm, providing a light path of 1 cm or longer.

2) *Filter photometer*, with light path of 1 cm or longer and equipped with a filter having maximum transmittance near 540 nm.

3. Reagents

a. Nitrate-free water: See 4500-NO_3^-.B.3*a*. The absorbance of a reagent blank prepared with this water should not exceed 0.01. Use for all solutions and dilutions.

b. Copper-cadmium granules: Wash 25 g new or used 20- to 100-mesh Cd granules† with 6*N* HCl and rinse with water. Swirl Cd with 100 mL 2% $CuSO_4$ solution for 5 min or until blue color partially fades. Decant and repeat with fresh $CuSO_4$ until a brown colloidal precipitate begins to develop. Gently flush with water to remove all precipitated Cu.

c. Color reagent: Prepare as directed in Section 4500-NO_2^-B.3*b*.

d. Ammonium chloride-EDTA solution: Dissolve 13 g NH_4Cl and 1.7 g disodium ethylenediamine tetraacetate in 900 mL water. Adjust to pH 8.5 with conc NH_4OH and dilute to 1 L.

e. Dilute ammonium chloride-EDTA solution: Dilute 300 mL NH_4Cl-EDTA solution to 500 mL with water.

f. Hydrochloric acid, HCl, 6*N*.

g. Copper sulfate solution, 2%: Dissolve 20 g $CuSO_4.5H_2O$ in 500 mL water and dilute to 1 L.

h. Stock nitrate solution: Prepare as directed in 4500-NO_3^-.B.3*b*.

i. Intermediate nitrate solution: Prepare as directed in 4500-NO_3^-.B.3*c*.

j. Stock nitrite solution: See Section 4500-NO_2^-.B.3*e*.

k. Intermediate nitrite solution: See Section 4500-NO_2^-.B.3*f*.

l. Working nitrite solution: Dilute 50.0 mL intermediate nitrite solution to 500 mL with nitrite-free water; 1.00 mL = 5 μg NO_2^--N.

4. Procedure

a. Preparation of reduction column: Insert a glass wool plug into bottom of reduction column and fill with water. Add sufficient Cu–Cd granules to produce a column 18.5 cm long. Maintain water level above Cu–Cd granules to prevent entrapment of air. Wash column with 200 mL dilute NH_4Cl-EDTA solution. Activate column by passing through it, at 7 to 10 mL/min, at least 100 mL of a solution composed of 25% 1.0 mg NO_3^--N/L standard and 75% NH_4Cl-EDTA solution.

b. Treatment of sample:

1) Turbidity removal—For turbid samples, see 4500-NO_3^-.A.1.

2) pH adjustment—Adjust pH to between 7 and 9, as necessary, using a pH meter and dilute HCl or NaOH. This ensures a pH of 8.5 after adding NH_4Cl-EDTA solution.

3) Sample reduction—To 25.0 mL sample or a portion diluted to 25.0 mL, add 75 mL NH_4Cl-EDTA solution and mix. Pour mixed sample into column and collect at a rate of 7 to 10 mL/min. Discard first 25 mL. Collect the rest in original sample flask. There is no need to wash columns between samples, but if columns are not to be reused for several hours or longer, pour 50 mL dilute NH_4Cl-EDTA solution on to the top and let it pass through the system. Store Cu–Cd column in this solution and never let it dry.

4) Color development and measurement—As soon as possible, and not more than 15 min after reduction, add 2.0 mL color reagent to 50 mL sample and mix. Between 10 min and 2 h afterward, measure absorbance at 543 nm against a distilled water-reagent blank. NOTE: If NO_3^- concentration exceeds the standard curve range (about 1 mg N/L), use remainder of reduced sample to make an appropriate dilution and analyze again.

c. Standards: Using the intermediate NO_3^--N solution, prepare standards in the range 0.05 to 1.0 mg NO_3^--N/L by diluting the following volumes to 100 mL in volumetric flasks: 0.5, 1.0, 2.0, 5.0, and 10.0 mL. Carry out reduction of standards exactly as described for samples. Compare at least one NO_2^- standard to a reduced NO_3^- standard at the same concentration to verify reduction column efficiency. Reactivate Cu–Cd granules as described in 4500-NO_3^-.3*b* above when efficiency of reduction falls below about 75%.

5. Calculation

Obtain a standard curve by plotting absorbance of standards against NO_3^--N concentration. Compute sample concentrations directly from standard curve. Report as milligrams oxidized N per liter (the sum of NO_3^--N plus NO_2^--N) unless the concentration of NO_2^--N is separately determined and subtracted.

† EM Laboratories, Inc., 500 Exec. Blvd., Elmsford, NY, Cat. 2001, or equivalent.

6. Precision and Bias

In a single laboratory using wastewater samples at concentrations of 0.04, 0.24, 0.55, and 1.04 mg NO_3^- + NO_2^--N/L, the standard deviations were ±0.005, ±0.004, ±0.005, and ±0.01, respectively. In a single laboratory using wastewater with additions of 0.24, 0.55, and 1.05 mg NO_3^- + NO_2^--N/L, the recoveries were 100%, 102%, and 100%, respectively.[2]

7. References

1. WOOD, E.D., F.A.J. ARMSTRONG & F.A. RICHARDS. 1967. Determination of nitrate in sea water by cadmium-copper reduction to nitrite. *J. Mar. Biol. Assoc. U.K.* 47:23.
2. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Methods for Chemical Analysis of Water and Wastes, Method 353.3. U.S. Environmental Protection Agency, Washington, D.C.

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4500-NO_3^- F. Automated Cadmium Reduction Method

1. General Discussion

a. Principle: See 4500-NO_3^-.E.1*a*.

b. Interferences: Sample turbidity may interfere. Remove by filtration before analysis. Sample color that absorbs in the photometric range used for analysis also will interfere.

c. Application: Nitrate and nitrite, singly or together in potable, surface, and saline waters and domestic and industrial wastewaters, can be determined over a range of 0.5 to 10 mg N/L.

d. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:I.

2. Apparatus

Automated analytical equipment: An example of the continuous-flow analytical instrument consists of the components shown in Figure 4500-NO_3^-:2.

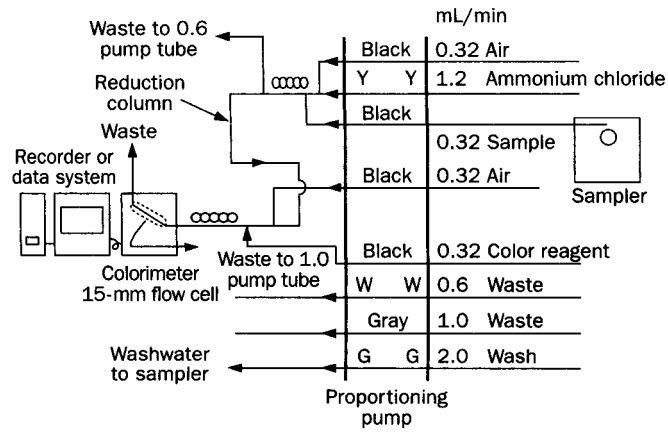

Figure 4500-NO_3^-:2. Nitrate-nitrite manifold.

3. Reagents

a. Deionized distilled water: See 4500-NO_3^-.B.3*a*.

b. Copper sulfate solution: Dissolve 20 g $CuSO_4 \cdot 5H_2O$ in 500 mL water and dilute to 1 L.

c. Wash solution: Use water for unpreserved samples. For samples preserved with H_2SO_4, add 2 mL conc H_2SO_4/L wash water.

d. Copper-cadmium granules: See 4500-NO_3^-.E.3*b*.

e. Hydrochloric acid, HCl, conc.

f. Ammonium hydroxide, NH_4OH, conc.

g. Color reagent: To approximately 800 mL water, add, while stirring, 100 mL conc H_3PO_4, 40 g sulfanilamide, and 2 g *N*-(1-naphthyl)-ethylenediamine dihydrochloride. Stir until dissolved and dilute to 1 L. Store in brown bottle and keep in the dark when not in use. This solution is stable for several months.

h. Ammonium chloride solution: Dissolve 85 g NH_4Cl in water and dilute to 1 L. Add 0.5 mL polyoxyethylene 23 lauryl ether.*

i. Stock nitrate solution: See 4500-NO_3^-.B.3*b*.

j. Intermediate nitrate solution: See 4500-NO_3^-.B.3*c*.

k. Standard nitrate solutions: Using intermediate NO_3^--N solution and water, prepare standards for calibration curve in appropriate nitrate range. Compare at least one NO_2^- standard to a NO_3^- standard at the same concentration to verify column reduction efficiency. To examine saline waters prepare standard solutions with the substitute ocean water described in Section 4500-NH_3.G.3*g*.

l. Standard nitrite solution: See Section 4500-NO_2^-.B.3*g*.

4. Procedure

Set up manifold as shown in Figure 4500-NO_3^-:2 and follow general procedure described by the manufacturer.

If sample pH is below 5 or above 9, adjust to between 5 and 9 with either conc HCl or conc NH_4OH.

5. Calculation

Prepare standard curves by plotting response of standards processed through the manifold against NO_3^--N concentration

* Brij-35, available from ICI Americas, Inc., Wilmington, DE, or equivalent.

in standards. Compute sample NO_3^--N concentration by comparing sample response with standard curve.

6. Precision and Bias

Data obtained in three laboratories with an automated system based on identical chemical principles but having slightly different configurations are given in the table below. Analyses were conducted on four natural water samples containing exact increments of inorganic nitrate:

Increment as NO_3^--N *μg/L*	Standard Deviation *μg N/L*	Bias *%*	Bias *μg N/L*
290	12	+5.75	+17
350	92	+18.10	+63
2310	318	+4.47	+103
2480	176	−2.69	−67

In a single laboratory using surface water samples at concentrations of 100, 200, 800, and 2100 μg N/L, the standard deviations were 0, ±40, ±50, and ±50 μg/L, respectively, and at concentrations of 200 and 2200 μg N/L, recoveries were 100 and 96%, respectively.

Precision and bias for the system described herein are believed to be comparable.

7. Bibliography

FIORE, J. & J.E. O'BRIEN. 1962. Automation in sanitary chemistry—Parts 1 and 2. Determination of nitrates and nitrites. *Wastes Eng.* 33:128 & 238.

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AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1987. Annual Book of ASTM Standards, Vol. 11.01. American Soc. Testing & Materials, Philadelphia, Pa.

4500-NO_3^- G. (Reserved)

4500-NO_3^- H. Automated Hydrazine Reduction Method

1. General Discussion

a. Principle: NO_3^- is reduced to NO_2^- with hydrazine sulfate. The NO_2^-(originally present) plus reduced NO_3^- is determined by diazotization with sulfanilamide and coupling with *N*-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye that is measured colorimetrically.

b. Interferences: Sample color that absorbs in the photometric range used will interfere. Concentrations of sulfide ion of less than 10 mg/L cause variations of NO_3^- and NO_2^- concentrations of ±10%.

c. Application: NO_3^- + NO_2^- in potable and surface water and in domestic and industrial wastes can be determined over a range of 0.01 to 10 mg N/L.

d. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:I.

2. Apparatus

Automated analytical equipment: An example of the continuous-flow analytical instrument consists of the components shown in Figure 4500-NO_3^-:3.

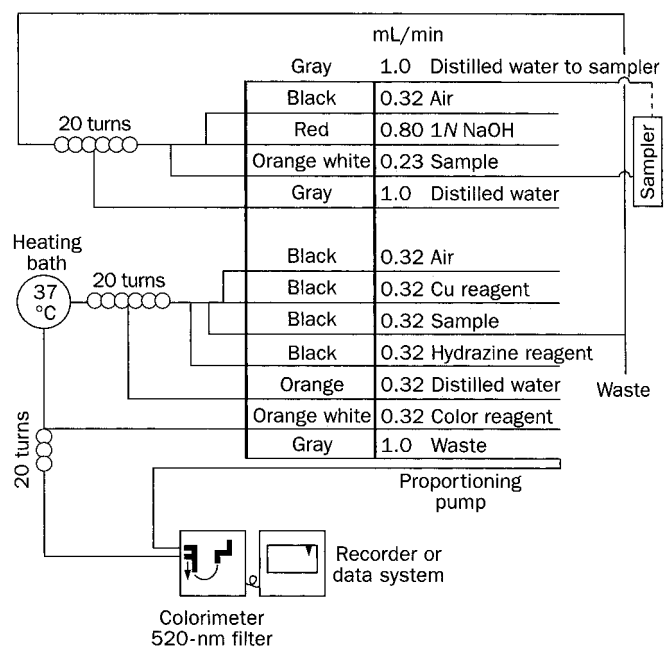


Figure 4500-NO_3^-:3. Nitrate-nitrite manifold.

3. Reagents

a. Color developing reagent: To approximately 500 mL water add 200 mL conc phosphoric acid and 10 g sulfanilamide. After sulfanilamide is dissolved completely, add 0.8 g *N*-(1-naphthyl)-ethylenediamine dihydrochloride. Dilute to 1 L with water, store

in a dark bottle, and refrigerate. Solution is stable for approximately 1 month.

b. Copper sulfate stock solution: Dissolve 2.5 g $CuSO_4 \cdot 5H_2O$ in water and dilute to 1 L.

c. Copper sulfate dilute solution: Dilute 20 mL stock solution to 2 L.

d. Sodium hydroxide stock solution, 10*N:* Dissolve 400 g NaOH in 750 mL water, cool, and dilute to 1 L.

e. Sodium hydroxide, 1.0*N:* Dilute 100 mL stock NaOH solution to 1 L.

f. Hydrazine sulfate stock solution: Dissolve 27.5 g $N_2H_4 \cdot H_2SO_4$ in 900 mL water and dilute to 1 L. This solution is stable for approximately 6 months. **CAUTION: Toxic if ingested. Mark container with appropriate warning.**

g. Hydrazine sulfate dilute solution: Dilute 22 mL stock solution to 1 L.

h. Stock nitrate solution: See 4500-NO_3^-.B.3*b*.

i. Intermediate nitrate solution: See 4500-NO_3^-.B.3*c*.

j. Standard nitrate solutions: Prepare NO_3^- calibration standards in the range 0 to 10 mg/L by diluting to 100 mL the following volumes of stock nitrate solution: 0, 0.5, 1.0, 2.0 . . . 10.0 mL. For standards in the range of 0.01 mg/L use intermediate nitrate solution. Compare at least one nitrite standard to a nitrate standard at the same concentration to verify the efficiency of the reduction.

k. Standard nitrite solution: See Sections 4500-NO_2^-.B.3*e*, *f*, and *g*.

4. Procedure

Set up manifold as shown in Figure 4500-NO_3^-:3 and follow general procedure described by manufacturer. Run a 2.0-mg NO_3^--N/L and a 2.0-mg NO_2^--N/L standard through the system to check for 100% reduction of nitrate to nitrite. The two peaks should be of equal height; if not, adjust concentration of the hydrazine sulfate solution: If the NO_3^- peak is lower than the NO_2^- peak, increase concentration of hydrazine sulfate until they are equal; if the NO_3^- peak is higher than the NO_2^-, reduce concentration of hydrazine sulfate. When correct concentration has been determined, no further adjustment should be necessary.

5. Calculation

Prepare a standard curve by plotting response of processed standards against known concentrations. Compute concentrations of samples by comparing response with standard curve.

6. Precision and Bias

In a single laboratory using drinking water, surface water, and industrial waste at concentrations of 0.39, 1.15, 1.76, and 4.75 mg NO_3^--N/L, the standard deviations were ±0.02, ±0.01, ±0.02, and ±0.03, respectively. In a single laboratory using drinking water at concentrations of 0.75 and 2.97 mg NO_3^--N/L, the recoveries were 99% and 101%.[1]

7. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Methods for Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency, Washington, D.C.

8. Bibliography

KAMPHAKE, L., S. HANNAH & J. COHEN. 1967. Automated analysis for nitrate by hydrazine reduction. *Water Res.* 1:205.

4500-NO_3^- I. Cadmium Reduction Flow Injection Method

1. General Discussion

a. Principle: The nitrate in the sample is reduced quantitatively to nitrite by passage of the sample through a copperized cadmium column. The resulting nitrite plus any nitrite originally in the sample is determined as a sum by diazotizing the nitrite with sulfanilamide followed by coupling with *N*-(1-naphthyl) ethylenediamine dihydrochloride. The resulting water-soluble dye has a magenta color; absorbance of the color at 540 nm is proportional to the nitrate + nitrite in the sample. This sum also is known as total oxidized nitrogen (TON).

Nitrite alone can be determined by removing the cadmium column, recalibrating the method, and repeating the sample analyses. A TON and a nitrite FIA method also can be run in parallel for a set of samples. In this arrangement, the concentrations determined in the nitrite method can be subtracted from the corresponding concentrations determined in the TON method to give the resulting nitrate concentrations of the samples.

Also see Section 4500-NO_2^- and Section 4130, Flow Injection Analysis (FIA).

b. Interferences: Remove large or fibrous particulates by filtering sample through glass wool. Guard against nitrate and nitrite contamination from reagents, water, glassware, and the sample preservation process.

Residual chlorine can interfere by oxidizing the cadmium reduction column. Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. Eliminate this interference by pre-extracting sample with an organic solvent.

Low results would be obtained for samples that contain high concentrations of iron, copper, or other metals. In this method, EDTA is added to the buffer to reduce this interference.

Also see Sections 4500-NO_2^-.B.1*b* and *c* and 4500-NO_3^-.A.2 and B.1*b*.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:I.

2. Apparatus

Flow injection analysis equipment consisting of:

a. FIA injection valve with sample loop or equivalent.

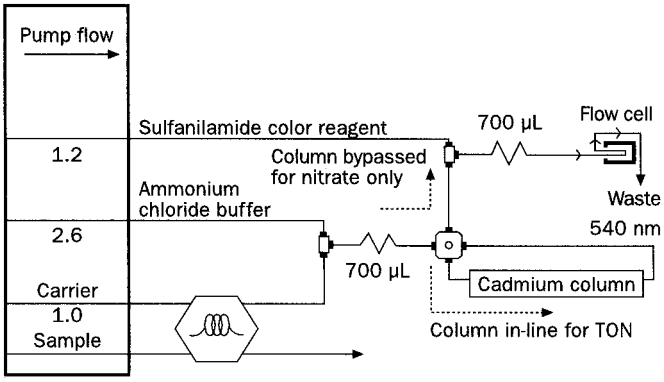


Figure 4500-NO_3^-:4. FIA nitrate + nitrite manifold.

b. Multichannel proportioning pump.

c. FIA manifold (Figure 4500-NO_3^-:4) with flow cell. Relative flow rates only are shown in Figure 4500-NO_3^-:4. Tubing volumes are given as an example only; they may be scaled down proportionally. Use manifold tubing of an inert material, such as TFE.

d. Absorbance detector, 540 nm, 10-nm bandpass.

e. Injection valve control and data acquisition system.

3. Reagents

Use reagent water (>10 megohm) to prepare carrier and all solutions. To prevent bubble formation, degas carrier and buffer with helium. Pass He at 140 kPa (20 psi) through a helium degassing tube. Bubble He through 1 L solution for 1 min. As an alternative to preparing reagents by weight/weight, use weight/volume.

a. Ammonium chloride buffer: **CAUTION: Fumes. Use a hood.** To a tared 1-L container add 800.0 g water, 126 g conc hydrochloric acid, HCl, 55.6 g ammonium hydroxide, NH_4OH, and 1.0 g disodium EDTA. Shake until dissolved. The pH of this buffer should be 8.5.

b. Sulfanilamide color reagent: To a tared, dark 1-L container add 876 g water, 170 g 85% phosphoric acid, H_3PO_4, 40.0 g sulfanilamide, and 1.0 g *N*-(1-naphthyl)ethylenediamine dihydrochloride (NED). Shake until wetted and stir with stir bar for 30 min until dissolved. This solution is stable for 1 month.

c. Hydrochloric acid, HCl, 1*M*: To a 100-mL container, add 92 g water, then add 9.6 g conc HCl. Stir or shake to mix.

d. Copper sulfate solution, 2%: To a 1-L container, add 20 g copper sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$, to 991 g water. Stir or shake to dissolve.

e. Copperized cadmium granules: Place 10 to 20 g coarse cadmium granules (0.3- to 1.5-mm-diam) in a 250-mL beaker. Wash with 50 mL acetone, then water, then two 50-mL portions 1*M* HCl (¶ *c* above). Rinse several times with water. **CAUTION: Cadmium is toxic and carcinogenic. Collect and store all waste cadmium. When handling cadmium, wear gloves and follow the precautions described on the cadmium's Material Safety Data Sheet.**

Add 100 mL 2% copper sulfate solution (¶ *d* above) to cadmium prepared above. Swirl for about 5 min, then decant the liquid and repeat with a fresh 100-mL portion of the 2% copper sulfate solution. Continue this process until the blue aqueous copper color persists. Decant and wash with at least five portions of ammonium chloride buffer (¶ *a* above) to remove colloidal copper. The cadmium should be black or dark gray. The copperized cadmium granules may be stored in a bottle under ammonium chloride buffer.

f. Stock nitrate standard, 200 mg N/L: In a 1-L volumetric flask dissolve 1.444 g potassium nitrate, KNO_3, in about 600 mL water. Add 2 mL chloroform. Dilute to mark and invert to mix. This solution is stable for 6 months.

g. Stock nitrite standard, 200.0 mg N/L: In a 1-L volumetric flask dissolve 0.986 g sodium nitrite, $NaNO_2$, or 1.214 g potassium nitrite, KNO_2, in approximately 800 mL water. Add 2 mL chloroform. Dilute to mark and invert to mix. Refrigerate.

h. Standard solution: Prepare nitrate or nitrite standards in the desired concentration range, using the stock standards (¶ *f* or *g* above), and diluting with water.

4. Procedure

Set up a manifold equivalent to that in Figure 4500-NO_3^-:4 and pack column with copperized cadmium granules. Follow methods supplied by column and instrument manufacturer or laboratory's standard operating procedure for this method.

5. Calculations

Prepare standard curves by plotting absorbance of standards processed through the manifold versus TON or nitrite concentration. The calibration curve is linear.

If TON includes measurable nitrite concentrations, it is important that the cadmium column be 100% efficient. If the efficiency is less, the nitrite in the sample will give a positive percent error equal to the difference from 100%, causing an error in TON and nitrate determinations. To measure efficiency of the cadmium column, prepare two calibration curves, one using nitrate standards and one using equimolar nitrite standards. The column efficiency is:

$$\text{Column efficiency} = 100\% \times (\text{slope of nitrate curve/slope of nitrite curve})$$

Determine column efficiency at least weekly.

6. Precision and Bias

In the studies described below, nitrate was measured. There was no significant concentration of nitrite in the samples.

a. Recovery and relative standard deviation: Table 4500-NO_3^-:I gives results of single-laboratory studies.

b. MDL: A 800-μL sample loop was used in the method described above. Using a published MDL method,[1] analysts ran 21 replicates of a 2.00-μg N/L standard. These gave a mean of 1.82 μg N/L, a standard deviation of 0.098 μg N/L, and MDL of 0.25 μg N/L. A lower MDL may be obtained by increasing the sample loop volume and increasing the ratio of carrier flow rate to reagent flow rate.

TABLE 4500-NO_3^-:I. RESULTS OF SINGLE-LABORATORY STUDIES WITH SELECTED MATRICES

Matrix	Sample/Blank Designation	Known Addition *mg NO_3^--N/L*	Recovery %	Relative Standard Deviation %
Wastewater treatment plant influent	Reference sample*	—	102	—
	Blank†	0.2	100	—
		0.4	100	—
	Site A‡	0	—	<1
		0.2	101	—
		0.4	96	—
	Site B‡	0	—	<1
		0.2	90	—
		0.4	88	—
	Site C‡	0	—	<1
		0.2	95	—
		0.4	95	—
Wastewater treatment plant effluent	Reference sample*	—	102	—
	Blank†	0.2	100	—
		0.4	95	—
	Site A‡	0	—	0.9
		0.2	95	—
		0.4	102	—
	Site B‡	0	—	0.7
		0.2	91	—
		0.4	101	—
	Site C‡	0	—	0.5
		0.2	91	—
		0.4	96	—
Landfill leachate	Reference sample*	—	98	—
	Blank†	0.2	100	—
		0.4	98	—
	Site A‡	0	—	<1
		0.2	104	—
		0.4	96	—
	Site B‡	0	—	<1
		0.2	95	—
		0.4	94	—
	Site C‡	0	—	<1
		0.2	91	<1
		0.4	93	—

* U.S. EPA QC sample, 1.98 mg N/L.
† Determined in duplicate.
‡ Samples without known additions determined four times; samples with known additions determined in duplicate. Typical difference between duplicates: influent, 2%; effluent, 1%; leachate, <1%.

7. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1984. Definition and procedure for the determination of method detection limits. Appendix B to 40 CFR 136 rev. 1.11 amended June 30, 1986. 49 CFR 43430.

Nitrite

USEPA Diazotization Method[1] — Method 8507

0.002 to 0.300 mg/L NO_2^-–N (LR, spectrophotometers) — Powder Pillows

0.005 to 0.350 mg/L NO_2^-–N (LR, colorimeters)

Scope and application: For water, wastewater and seawater.

[1] USEPA approved for wastewater analysis, Federal Register, 44(85), 25505 (May 1, 1979).

Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR6000 DR3800 DR2800 DR2700 DR1900	The fill line is to the right.	2495402
DR5000 DR3900	The fill line is toward the user.	
DR900	The orientation mark is toward the user.	2401906

Before starting

Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
For the best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to determine the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option.
UV light changes the color of the prepared sample to yellow. Keep the prepared sample out of direct sunlight.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

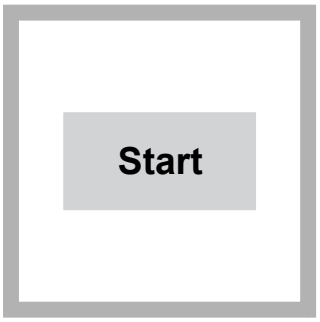
Description	Quantity
NitriVer® 3 Reagent Powder Pillows, 10 mL	1
Sample cells. (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

Refer to Consumables and replacement items on page 4 for order information.

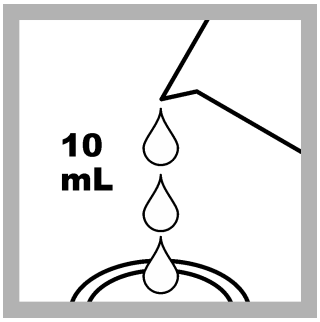
Sample collection and storage

- Collect samples in clean glass or plastic bottles.
- To preserve samples for later analysis, keep the samples at or below 6 °C (43 °F) for up to 48 hours.
- Let the sample temperature increase to room temperature before analysis.

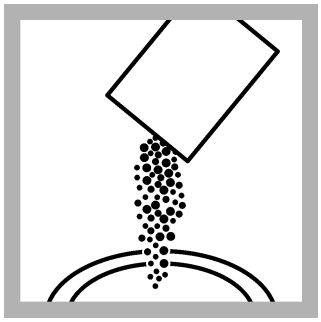
Test procedure



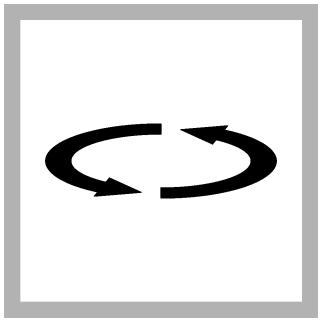
1. Start program **371 N, Nitrite LR PP**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



2. Prepare the sample: Fill a sample cell with 10 mL of sample.

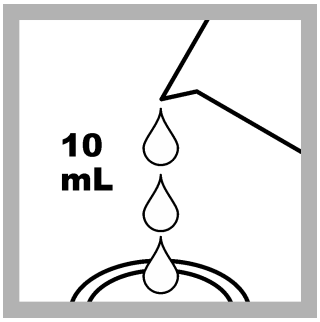


3. Add the contents of one NitriVer 3 Reagent Powder Pillow.

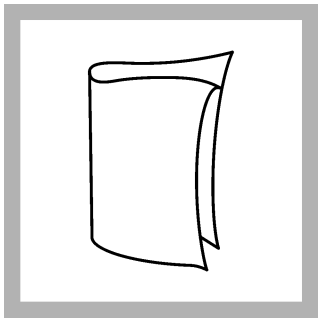


4. Swirl to mix.
A pink color shows if nitrite is present in the sample.

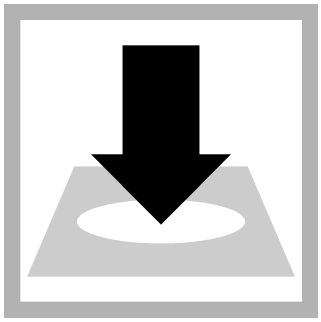
5. Start the instrument timer. A 20-minute reaction time starts.



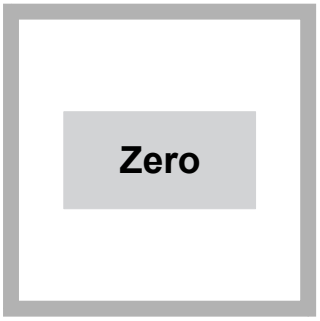
6. Prepare the blank: When the timer expires, fill a second sample cell with 10 mL of sample.



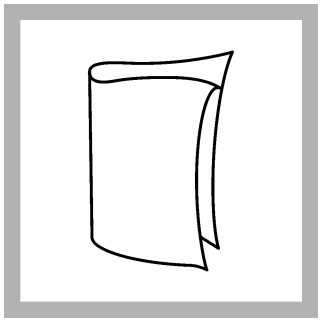
7. Clean the blank sample cell.



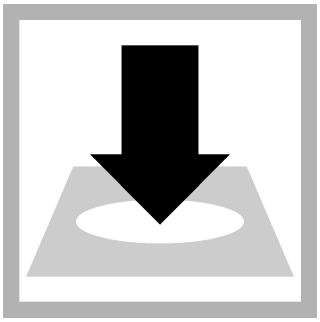
8. Insert the blank into the cell holder.



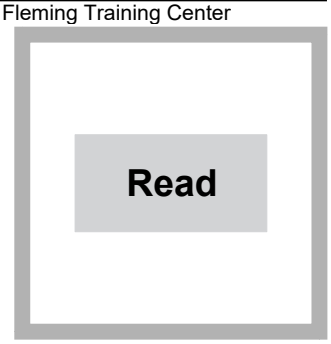
9. Push **ZERO**. The display shows 0.000 mg/L NO_2^-–N.



10. Clean the prepared sample cell.



11. Insert the prepared sample into the cell holder.



12. Push **READ**. Results show in mg/L NO_2^-–N.

Interferences

Interfering substance	Interference level
Antimonous ions	Interfere by causing precipitation
Auric ions	Interfere by causing precipitation
Bismuth ions	Interfere by causing precipitation
Chloroplatinate ions	Interfere by causing precipitation
Cupric ions	Cause low results
Ferric ions	Interfere by causing precipitation
Ferrous ions	Cause low results
Lead ions	Interfere by causing precipitation
Mercurous ions	Interfere by causing precipitation
Metavanadate ions	Interfere by causing precipitation
Nitrate	Very high levels of nitrate (>100 mg/L nitrate as N) appear to undergo a slight amount of reduction to nitrite, either spontaneously or during the course of the test. A small amount of nitrite will be found at these levels.
Silver ions	Interfere by causing precipitation
Strong oxidizing and reducing substances	Interfere at all levels
Interference from direct sunlight	UV light changes the color of the prepared sample to yellow. Keep the prepared sample out of direct sunlight.

Accuracy check

Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

Items to collect:

- 0.150 mg/L NO_2^-–N standard solution (Nitrite standard solutions are difficult to prepare. Use the instructions in Standard Methods for the Examination of Water and Wastewater, Method 4500—NO_2-B)

1. Use the test procedure to measure the concentration of the standard solution.
2. Compare the expected result to the actual result.

   Note: *The factory calibration can be adjusted slightly with the standard calibration adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are small variations in the reagents or instruments.*

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
371	0.150 mg/L NO_2^-–N	0.147–0.153 mg/L NO_2^-–N	0.002 mg/L NO_2^-–N

Summary of method

Nitrite in the sample reacts with sulfanilic acid to form an intermediate diazonium salt. This couples with chromotropic acid to produce a pink colored complex directly proportional to the amount of nitrite present. The measurement wavelength is 507 nm for spectrophotometers or 520 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
NitriVer® 3 Nitrite Reagent Powder Pillow, 10 mL	1	100/pkg	2107169

Recommended standards, reagents and apparatus

Description	Unit	Item no.
Balance, analytical, 80 g x 0.1 mg 100–240 VAC	each	2936701
Standard Methods for the Examination of Water and Wastewater (current edition)	each	2270800
Sodium Nitrite, ACS	454 g	245201
Water, deionized	4 L	27256

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TNT 839 Nitrite

0.015–0.60 mg/L NO_2^-–N or 0.05–2.00 mg/L NO_2^- Low Range

TNTplus®—Method 10207

Scope and application: For wastewater, drinking water, surface water and mineral water.

Test preparation

Reagent storage

Storage temperature: 15–25 °C (59–77 °F)

pH/Temperature

The pH of the water sample must be between pH 3–10.

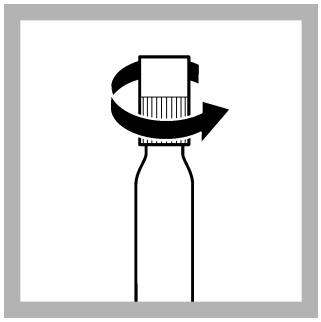
The temperature of the water sample and reagents must be between 15–25 °C (59–77 °F).

Before starting

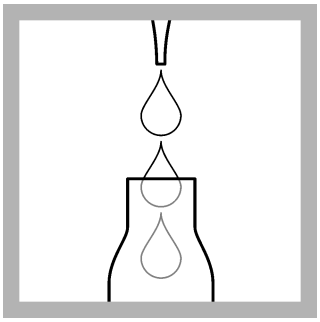
Not more than **3 hours** should elapse between sampling and analyzing the sample.
Review safety information and expiration date on the package.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Procedure

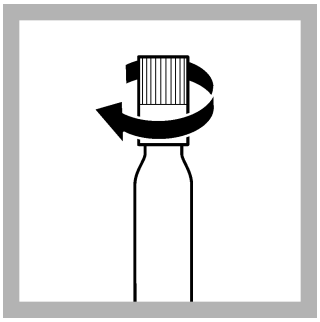
1. Carefully remove the foil from the screwed-on DosiCap Zip.



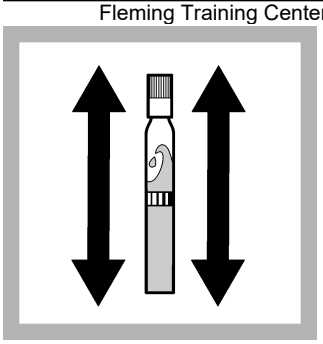
2. Unscrew the DosiCap Zip.



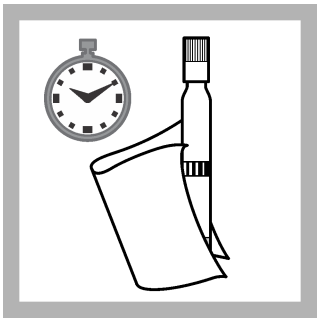
3. Carefully pipet **2.0 mL** of **sample**.



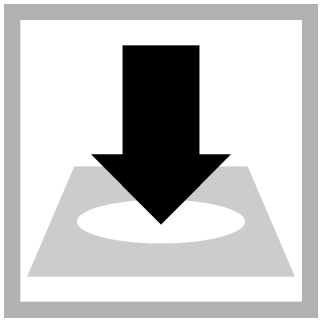
4. **Immediately** screw the DosiCap Zip back on; **fluting at the top**.



5. Shake **vigorously** until the freeze-dried contents are **completely dissolved**.



6. After **10 minutes**, thoroughly clean the outside of the vial and evaluate.



7. Insert the vial into the cell holder.
DR 1900: Go to LCK/TNTplus methods.
Select the test, push **READ**.

Interferences

The ions listed in the table have been individually checked against the given concentrations and do not cause interference. The cumulative effects and the influence of other ions have not been determined.

Chromium(VI) ions interfere with the determination. Copper(II) ions interfere with the determination even at concentrations below 1 mg/L.

The measurement results must be subjected to plausibility checks (dilute and/or spike the sample).

Interference level	Interfering substance
2000 mg/L	Cl^-, SO_4^{2-}
1000 mg/L	K^+, NO_3^-
500 mg/L	NH_4^+, PO_4^{3-}, Ca^{2+}
100 mg/L	Mg^{2+}
50 mg/L	Cr^{3+}
25 mg/L	Co^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Hg^{2+}
12 mg/L	Ni^{2+}
10 mg/L	Ag^+, Fe^{2+}
5 mg/L	Sn^{4+}, Fe^{3+}
< 1 mg/L:	Cu^{2+}

Summary of method

Nitrites react with primary aromatic amines in acidic solution to form diazonium salts. These combine with aromatic compounds that contain an amino group or a hydroxyl group to form intensively colored azo dyes.

TNTplus®

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Nitrate, MR

Cadmium Reduction Method

Method 8171

0.1 to 10.0 mg/L NO_3^-–N (MR, spectrophotometers)

0.2 to 5.0 mg/L NO_3^-–N (MR, colorimeters)

Powder Pillows or AccuVac® Ampuls

Scope and application: For water, wastewater and seawater.

Test preparation

Instrument-specific information

Table 1 shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests. Table 2 shows sample cell and adapter requirements for AccuVac Ampul tests. The tables also show all of the instruments that have the program for this test.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information for reagent addition

Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700 DR 1900	The fill line is to the right.	2495402
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The orientation mark is toward the user.	2401906

Table 2 Instrument-specific information for AccuVac Ampuls

Instrument	Adapter	Sample cell
DR 6000 DR 5000 DR 900	—	2427606
DR 3900	LZV846 (A)	
DR 1900	9609900 or 9609800 (C)	
DR 3800 DR 2800 DR 2700	LZV584 (C)	2122800

Before starting

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
For the best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to determine the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option.
This method is technique-sensitive. Shaking time and technique influence the color development. For most accurate results, use a standard solution that is within the test range and run the test several times. Increase or decrease the shaking time to get the expected result. Use the adjusted shaking time for sample measurements.
The reagents that are used in this test contain cadmium. Rinse the sample cell immediately after use to remove all cadmium particles. Collect the reacted samples for proper disposal.
A deposit of unoxidized metal will remain at the bottom of the sample cell after the reagent dissolves. The deposit will not affect results.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Powder pillows

Description	Quantity
NitraVer® Nitrate 5 Reagent powder pillow, 10-mL	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2
Stopper, Neoprene #1	2

Refer to Consumables and replacement items on page 7 for order information.

AccuVac Ampuls

Description	Quantity
NitraVer® Nitrate 5 Reagent AccuVac® Ampul	1
Beaker, 50 mL	1
Stoppers for 18-mm tubes and AccuVac Ampuls	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	1

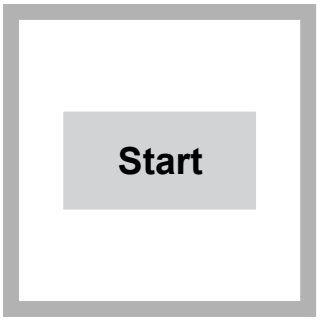
Refer to Consumables and replacement items on page 7 for order information.

Sample collection and storage

- Collect samples in clean glass or plastic bottles.
- Analyze the samples as soon as possible for best results.
- If immediate analysis is not possible, immediately filter and keep the samples at or below 6 °C (43 °F) for a maximum of 48 hours.
- To preserve samples for a maximum of 28 days, adjust the sample pH to 2 or less with concentrated sulfuric acid (approximately 2 mL per liter) and keep at or below 6 °C (43 °F). The test results then include nitrate and nitrite.
- Let the sample temperature increase to room temperature before analysis.
- Before analysis, adjust the pH to 7 with 5 N sodium hydroxide solution.

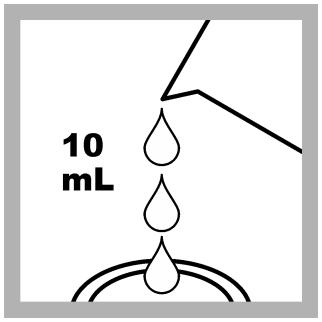
- Correct the test result for the dilution caused by the volume additions.

Powder pillow procedure

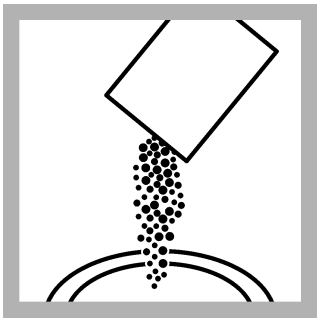


1. Start program **353 N, Nitrate MR PP**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

Note: *Although the program name can be different between instruments, the program number does not change.*

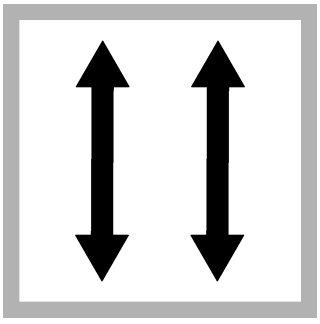


2. Prepare the sample: Fill a sample cell with 10 mL of sample.



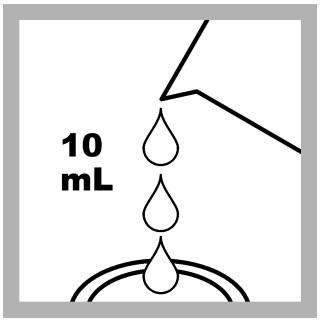
3. Add the contents of one powder pillow to the sample cell.

4. Start the instrument timer. A 1-minute reaction time starts.

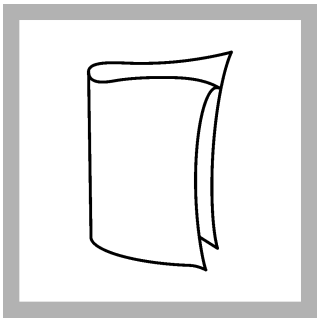


5. Put the stopper on the sample cell. Shake the sample cell vigorously until the timer expires. Some solid material will not dissolve. Undissolved powder will not affect results.

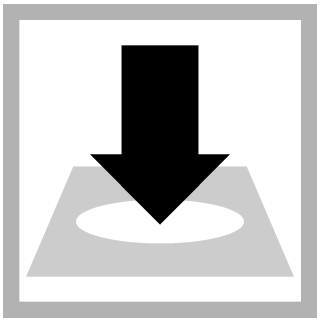
6. Start the instrument timer. A 5-minute reaction time starts.
An amber color shows if nitrate is present.



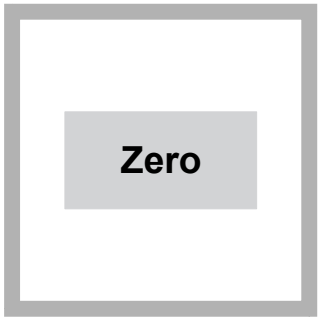
7. Prepare the blank: Fill a second sample cell with 10 mL of sample.



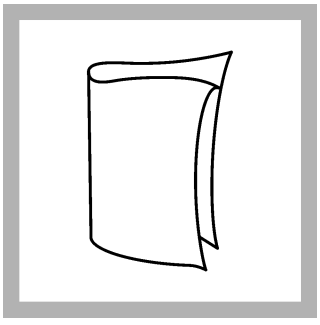
8. When the timer expires, clean the blank sample cell.



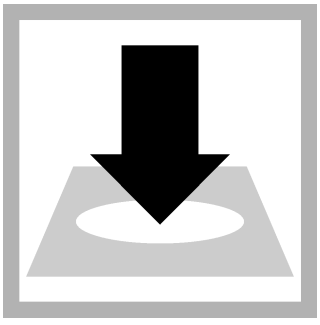
9. Insert the blank into the cell holder.



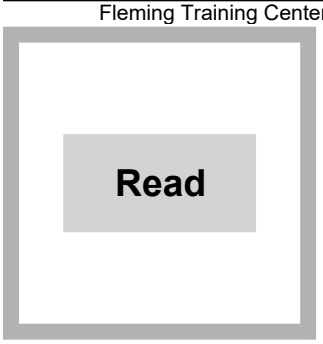
10. Push **ZERO**. The display shows 0.0 mg/L NO_3^-–N.



11. Clean the prepared sample cell.

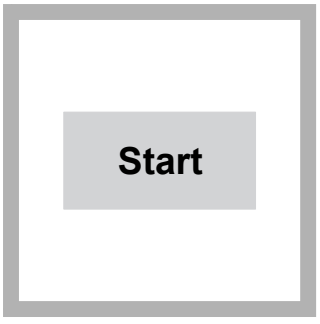


12. Within 2 minutes after the timer expires, insert the prepared sample into the cell holder.



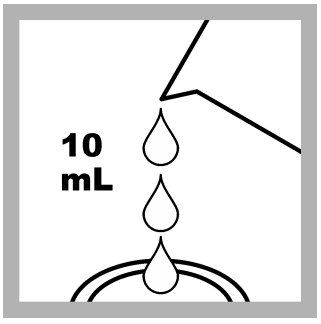
13. Push **READ**. Results show in mg/L NO_3^-–N.

AccuVac Ampul procedure

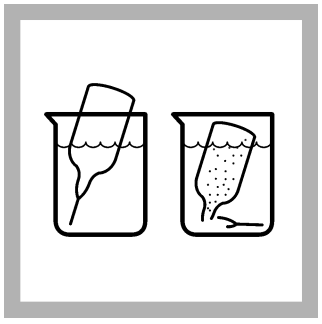


1. Start program **359 N, Nitrate MR AV**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

Note: *Although the program name can be different between instruments, the program number does not change.*

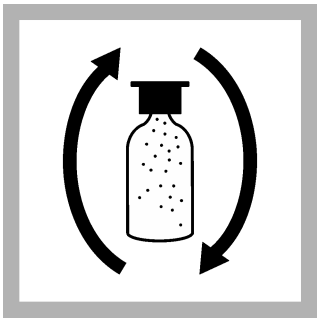


2. Prepare the blank: Fill the sample cell with 10 mL of sample.



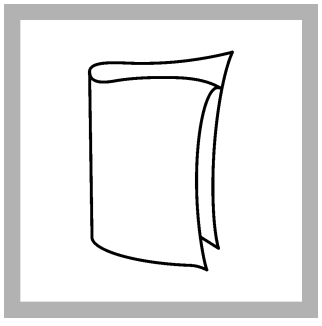
3. Prepare the sample: Collect at least 40 mL of sample in a 50-mL beaker. Fill the AccuVac Ampul with sample. Keep the tip immersed while the AccuVac Ampul fills completely.

4. Start the instrument timer. A 1-minute reaction time starts.

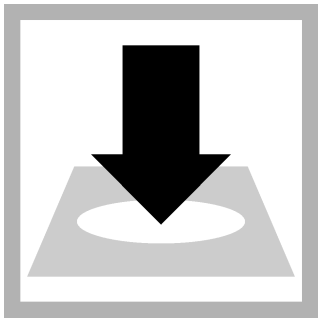


5. Use a stopper to close the Ampul tip. Invert the Ampul 48–52 times as the timer counts down.

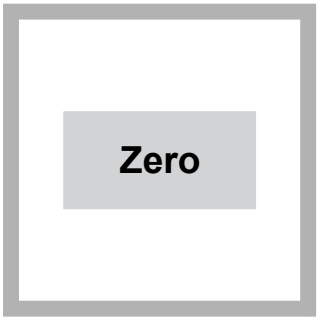
6. Start the instrument timer. A 5-minute reaction time starts.
An amber color shows if nitrate is present.



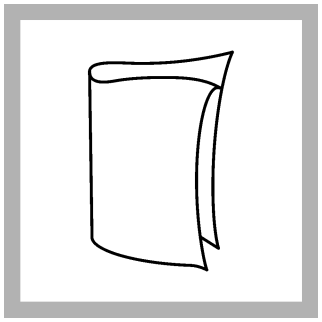
7. When the timer expires, clean the blank sample cell.



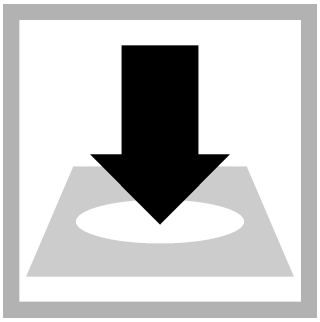
8. Insert the blank into the cell holder.



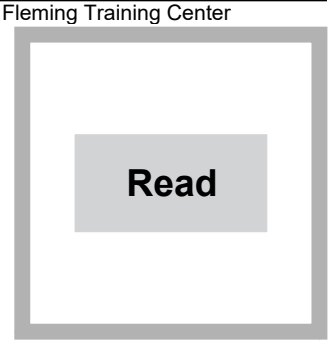
9. Push **ZERO**. The display shows 0.0 mg/L NO_3^-–N.



10. Clean the AccuVac Ampul.



11. Within 2 minutes after the timer expires, insert the prepared sample AccuVac Ampul into the cell holder.



12. Push **READ**. Results show in mg/L NO_3^-–N.

Interferences

Interfering substance	Interference level
Chloride	Chloride concentrations above 100 mg/L cause low results. The test can be used at high chloride concentrations (seawater) if a calibration is made with standards that have the same chloride concentration as the samples (refer to Seawater calibration on page 5).
Ferric iron	Interferes at all levels
Nitrite	Interferes at all levels Compensate for nitrite interference as follows: **1.** Add 30-g/L Bromine Water by drops to the sample until a yellow color remains. **2.** Add 1 drop of 30-g/L Phenol Solution to remove the color. **3.** Use the test procedure to measure the concentration of the treated sample. Report the results as total nitrate and nitrite.
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment of the sample by the reagents. Sample pre-treatment may be necessary.
Strong oxidizing and reducing substances	Interfere at all levels

Seawater calibration

Chloride concentrations above 100 mg/L cause low results. To use this method for samples with high chloride concentrations, calibrate the instrument with nitrate standard solutions that contain the same amount of chloride as the samples.
Prepare calibration standards that contain chloride and 1.0, 3.0, 5.0 and 10.0 mg/L nitrate (as NO_3^-–N) as follows:

1. Prepare 1 liter of chloride water that has the same chloride concentration as the samples.
   a. Weigh the applicable amount of ACS-grade sodium chloride: (chloride concentration of samples in g/L) x (1.6485) = g of NaCl per liter.
      Note: *18.8 g/L is the typical chloride concentration of seawater.*
   b. Add the sodium chloride to a 1-liter volumetric flask.
   c. Dilute to the mark with deionized water. Mix thoroughly. Use this water as the dilution water to prepare the nitrate standard solutions.
2. Use a pipet to add 1.0, 3.0, 5.0 and 10.0 mL of a 100 mg/L nitrate-nitrogen (NO_3^-–N) standard solution into four different 100-mL Class A volumetric flasks.
3. Dilute to the mark with the prepared chloride water. Mix thoroughly.
4. Complete the test procedure for each of the standard solutions and for the prepared chloride water (for a 0-mg/L standard solution).

5. Measure the absorbance of the standard solutions and enter a user calibration into the instrument.
6. Use the user program to measure samples that contain high concentrations of chloride.

Accuracy check

Standard additions method (sample spike)

Use the standard additions method (for applicable instruments) to validate the test procedure, reagents and instrument and to find if there is an interference in the sample.

Items to collect:

- Nitrate Nitrogen Standard Solution, 100 mg/L NO_3^-– N
- Ampule breaker
- Pipet, TenSette®, 0.1–1.0 mL and tips

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 10-mL portions of fresh sample. Mix well.

   Note: *For AccuVac® Ampuls, add 0.1 mL, 0.2 mL and 0.3 mL of a 500 mg/L NO_3^-–N standard solution to three 50-mL portions of fresh sample.*
6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

Items to collect:

- Nitrate Nitrogen Standard Solution, 100 mg/L NO_3^-– N
- 100-mL volumetric flask, Class A
- 5-mL volumetric pipet, Class A and pipet filler
- Deionized water

1. Prepare a 5.0 mg/L nitrate-nitrogen standard solution as follows:
   a. Use a pipet to add 5.0 mL of 100 mg/L nitrate-nitrogen standard solution into the volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
2. Use the test procedure to measure the concentration of the prepared standard solution.
3. Compare the expected result to the actual result.

   Note: *The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are slight variations in the reagents or instruments.*

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% Confidence Interval)	Sensitivity Concentration change per 0.010 Abs change
353	5.0 mg/L NO_3^-–N	4.8–5.2 mg/L NO_3^-–N	0.04 mg/L NO_3^-–N
359	5.0 mg/L NO_3^-–N	4.6–5.4 mg/L NO_3^-–N	0.05 mg/L NO_3^-–N

Summary of method

Cadmium metal reduces nitrate in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt. The salt couples with gentisic acid to form an amber colored solution. The measurement wavelength is 400 nm for spectrophotometers or 420 nm for colorimeters.

Pollution prevention and waste management

Reacted samples contain cadmium and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
NitraVer® 5 Nitrate Reagent Powder Pillow, 10-mL	1	100/pkg	2106169
OR			
NitraVer® 5 Nitrate Reagent AccuVac® Ampul	1	25/pkg	2511025

Required apparatus for powder pillows

Description	Quantity/test	Unit	Item no.
Stopper, Neoprene, solid, size #2	2	12/pkg	1480802

Required apparatus for AccuVac Ampuls

Description	Quantity/test	Unit	Item no.
Beaker, 50-mL	1	each	50041H
Stoppers for 18-mm tubes and AccuVac Ampuls	2	6/pkg	173106

Recommended standards

Description	Unit	Item no.
Drinking Water Standard, Mixed Parameter, Inorganic for F^-, NO_3–N, PO_4^{3-}, SO_4^{2-}	500 mL	2833049
Nitrate Nitrogen Standard Solution, 100-mg/L NH_3-N	500 mL	194749
Nitrate Nitrogen Standard Solution, Voluette® Ampule, 500-mg/L NO_3–N	16/pkg	1426010

Optional reagents and apparatus

Description	Unit	Item no.
Bromine Water, 30 g/L	29 mL	221120
Mixing cylinder, graduated, 50-mL	each	2088641

Optional reagents and apparatus (continued)

Description	Unit	Item no.
Flask, volumetric, Class A, 100-mL glass	each	1457442
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	1000/pkg	2185628
Pipet, volumetric 5.00-mL	each	1451537
Pipet filler, safety bulb	each	1465100
Phenol Solution, 30-g/L	29 mL	211220
Sodium Hydroxide Standard Solution, 5.0 N	1 L	245053
Sulfuric Acid, concentrated, ACS	500 mL	97949
Water, deionized	4 L	27256

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TNT 835 Nitrate

0.23–13.50 mg/L NO_3^-–N or
1.00–60.00 mg/L NO_3^- Low Range

TNTplus®—Method 10206

Scope and application: For wastewater, drinking water, surface water and process water.

Test preparation

Reagent storage

Storage temperature: 15–25 °C (59–77 °F)

pH/Temperature

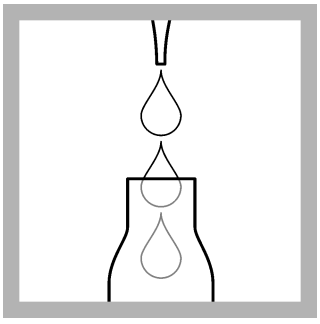
The pH of the water sample must be between pH 3–10.

The temperature of the water sample and reagents must be between 20–23 °C (68–73.4 °F).

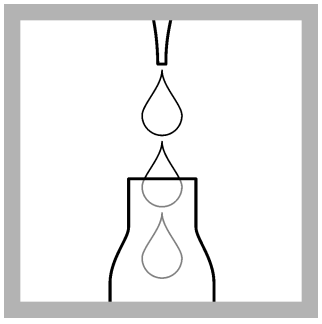
Before starting

In case of not working at the correct recommended temperature an incorrect result may be obtained.
Not more than **3 hours** should elapse between sampling and analysis. **Store in a cool place!**
Review safety information and expiration date on the package.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

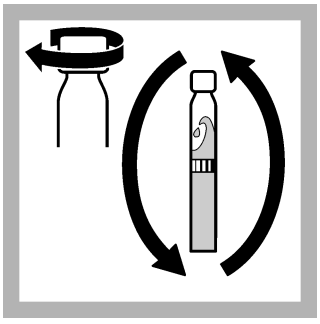
Procedure



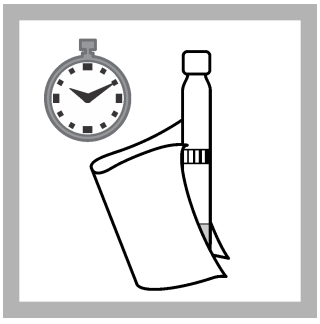
1. Carefully pipet **1.0 mL** of **sample**.



2. Carefully pipet **0.2 mL** of **solution A**.



3. Close the vial and invert a few times until **no more streaks** can be seen.



4. After **15 minutes**, thoroughly clean the outside of the vial and evaluate.

5. Insert the vial into the cell holder.
DR 1900: Go to LCK/TNTplus methods.
Select the test, push **READ**.

Interferences

The ions listed below have been individually checked up to the given concentrations and do not cause interference. We have not determined cumulative effects and the influence of other ions. High loads of oxidizable organic substances (COD) cause the reagent to change colour and to give high-bias results. The test can thus only be used for wastewater analyses if the COD is less than 200 mg/L. Measurement results can be verified using sample dilutions or standard additions.

Removal of Interferences

Nitrite concentrations of more than 2.0 mg/L interfere (high-bias results). Add 50 mg of sulfamic acid (amidosulfonic acid) to 5.0 mL of sample, dissolve and wait for 10 minutes. Analyze the prepared sample as described in the procedure above.

Interference level	Interfering substance
500 mg/L	K^+, Na^+, Cl^-
100 mg/L	Ag^+
50 mg/L	Pb^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Cd^{2+}, Sn^{2+}, Ca^{2+}, Cu^{2+}
10 mg/L	Co^{2+}, Fe^{2+}
5 mg/L	Cr^{6+}
2 mg/L	NO_2^-

Summary of method

Nitrate ions in solutions containing sulphuric and phosphoric acids react with 2.6-dimethylphenol to form 4-nitro-2.6-dimethylphenol.

TNTplus®

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Nitrate Bench Sheet

	Tap Water	Sample	
Powder Pillow			
Duplicate			
TNT			

Nitrite Bench Sheet

	Tap Water	Sample	
Powder Pillow			
Standard Addition (r^2)			
Duplicate			
TNT			

Section 11
Instrument and Probe Maintenance

Instrumentation and Probes

Water Lab week 2

Sampling

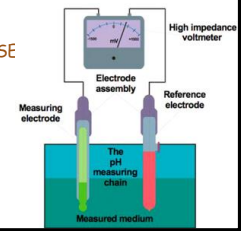
- A sample is a minute part of the whole
  - Must be representative
  - Greatest limiting factor
  - Analysis is only as good as the sample collected
- Must have a written sampling plan
  - All employees must:
    - Be trained annually
    - Agree to follow plan

Types of Samples

- Continuous (i.e. process analyzer) sampling
- Composite sample
  - Gives an average water quality
  - Not appropriate for all tests
- Grab samples
  - Gives water quality for a specific water at a specific point in time

Electrochemistry

- Electrochemistry is the science of electricity and chemistry
- Electrochemical measurements include:
  - pH
  - Ion-selective electrodes (ISE



Electrochemistry

- Advantages:
  - Wide analytical range
  - Ability to analyze turbid/colored samples directly
  - Calibrations allow user to verify performance
- Disadvantages
  - Must be calibrated before each use

pH Probes

- Thermoster measures temperature outside bulb of probe
- If able to calibrate with 4 & 7, but unable to calibrate with 7 & 10, then the 10 buffer has probably gone bad
  - 10 buffer is most unstable
    - CO_2 in air mixes with water in the buffer to create carbonic acid (H_2CO_3)
- Optimal calibration slope will be given with each probe (≈ -58 mV/decade)

Maintenance

- New Probe
  - Condition probe in pH 7 for approximately 30 minutes before initial use
- Calibrate
  - At least daily with freshly poured buffers
  - Minimum 2 buffers required; recommend 3
  - Do not stir 10 due to instability
  - Check probe documentation for ideal slope

Maintenance

- Measurement
  - Place probe into sample, stir, wait for readings
  - Rinse and dry between measurements
  - If mV jumps around when put in solution, probe is out of reference solution
    - Could be empty or clogged

Maintenance

- Storage between measurements
  - Storage solution (3M KCl)
    - Same as what is already in probe so it will prevent electrolyte from coming out of probe
  - Sample *or* solution of similar ionic strength to sample
  - pH 7 buffer
    - Similar to 3M KCl
- Store problematic probes in pH 4 for a short time
  - This may fix the problem

Troubleshooting

- mV reading in pH 7 buffer
  - Should read 0 +/- 30 mV
- Response time
  - Should be between 30 sec and 1 minute
  - May require cleaning if slow response in buffered solution
- Slope
  - Optimal slope is -59.16 +/- 5%
    - Theoretical number that will vary from probe to probe

Cleaning

- Slow response may indicate need for cleaning
  - Swish/soak probe in soapy water; Rinse; Read pH 7
  - Soak in HCl solution; Rinse; Read pH 7
    - Use less than 6N HCl to make a 1:10 dilution

Fluoride

- Alum or aluminum complexes interfere with colorimetric test
- TISAB removes most of aluminum interferences
- Probes can last 3-5 years
- Store probe in a standard
  - The higher the better

12

Fluoride

- Organics can clog pores on tip of the probe
  - Clean with toothpaste for about 5 minutes until shiny
- Crystals can build up on the tip
  - Remove cap and rinse with distilled water

13

Fluoride Troubleshooting

- Probe or Meter? Good chance it is the probe.
- To check probe, make sure pH works:
  - Use pH probe and pH buffers in fluoride mode
    - pH buffer 7 equals 1 mg/L fluoride standard
    - pH buffer 4 equals 1000 mg/L fluoride standard

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Fluoride Troubleshooting

- If good reading (good slope), then the fluoride probe is bad
- If you can read fluoride in mV, there should be about a 58 mV difference between the reading for a 10 mg/L and a 1 mg/L fluoride standard

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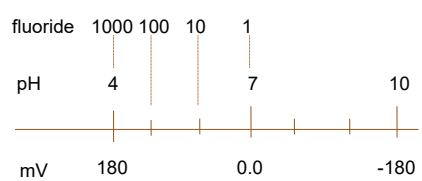
Fluoride Trouble Shooting



16

Colorimetry and Spectrophotometry

Colorimetry

- Colorimetry is using color intensity measurements to determine the amount of a substance dissolved in a solution
  - E.g. chlorine, iron, fluoride, etc.
- Measure samples with a colorimeter or spectrophotometer

Colorimetry

- Consistency in methodology is key to good data
- Clean sample cells
  - Rinse cell with sample water before collecting sample to minimize accidental dilution with DI
  - Rinse sample cell with DI water as soon as a reading is acquired

Colorimetry – Running the Test

- Add reagents to sample as instructed in procedure
  - Always read procedure thoroughly before running any test
  - Sample pH must be in range
  - Reagents contain
    - Buffer to adjust sample pH
    - Oxidizing/reducing agents
    - Masking compound for interferences
    - Indicator compound

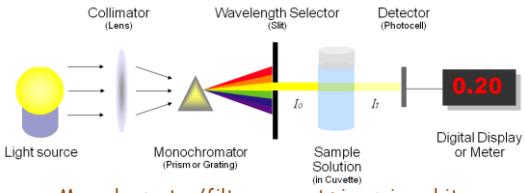
Colorimetry – Running the Test

- Reaction Time
  - Wait the amount of time specified in the procedure for reagents to react with sample and form a color
  - Example: free chlorine reaction is complete at 20 seconds
    - If more than 1 minute passes, other unwanted reactions begin to occur
  - Example: total chlorine requires a 3 minute reaction time before reading results

Colorimetry – Using the Instrument

- Zero the instrument
  - Sample blank – cell filled with sample, no reagents
  - Reagent blank – cell filled with DI water with reagents added
  - Wipe blank sample cell clean, place into instrument, and touch the Zero key
  - After appropriate reaction period, wipe sample cell clean, place into instrument, and touch the Read key

Spectrophotometer



- Monochromator/filter converts incoming white light to a single optimal wavelength
  - Prism, diffraction grating, or LED (for colorimeters)

Spectrophotometer

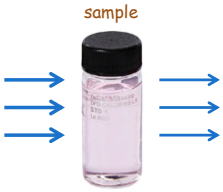
- Appropriate wavelength of light passes <u>through</u> sample cell
  - Sample cell must be clean

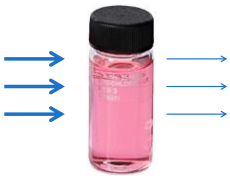
Spectrophotometer

- Light passes through sample cell, so it is vital that the cell is clean
  - Clean inside – acid or reagent
  - Clean outside – lint free cloth
    - No dust, fingerprints or scratches
  - Cells are sufficiently filled
- Sample measured by comparing the difference in intensity between the blank and the sample
  - Be consistent
    - Matched sample cells
    - Use same cell for blank and sample

Spectrophotometer

- Very little of the incident light is absorbed
  - Low concentration sample
- Most of the incident light is absorbed
  - High concentration sample





Accuracy – Standard Additions

- Prove accuracy with standards
  - Verifies testing technique, instrument performance
- Standard Additions
  - Reveals interferences and other problems
  - Step 1. Determine sample concentration
  - Step 2. Add standard addition

Accuracy – Standard Additions

- How to calculate calibration curve when not using the program in the spec

$$\frac{(Conc\ of\ std, mg/L)(Vol\ of\ added\ std, mL)}{volume\ of\ sample, mL}$$

- Example

$$\frac{(50\,mg/L)(0.2\ mL\ std)}{10\ mL\ sample} = 1.0\,mg/L\ added\ to\ sample$$

Accuracy – Standard Additions

- Results
  - New reading = sample reading +1.0 mg/L
- Calculating recovery
  - New reading – sample reading = 1.0 mg/L
- Recovery should be within +/- 5 to 10% of the standard addition
  - 1.0 +/- 0.1 mg/L
    - Acceptable range = 0.9 to 1.10 mg/L

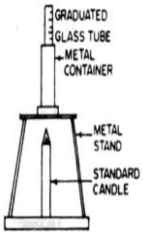
Accuracy – Standard Additions

- Original sample reading 1.00 mg/L
- Calculated increase in reading +1.00 mg/L
- Sample reading + standard addition 2.00 mg/L
  - predicted range +/- 10% = 1.80 – 2.20 mg/L

Turbidimeters

Turbidity Instrumentation

- Jackson Candle Turbidimeter
  - Utilized a whale tail candle with a wick burning at a preset length
  - Sample water poured into tube until candle flame was no longer visible when viewed from straight above
  - Depth of water in tube corresponded to a distinct JTU (jackson turbidity units) reading
  - Could not measure low concentrations reliably



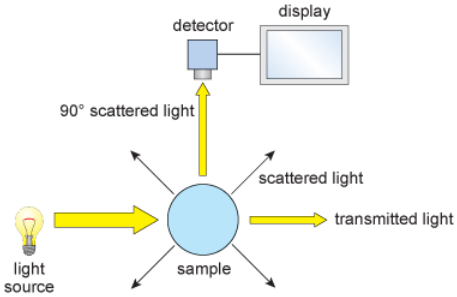
Turbidity Instrumentation

- Photometer – "transmitted light"
  - Measures amount of light transmitted through a sample
  - Could not measure low turbidities

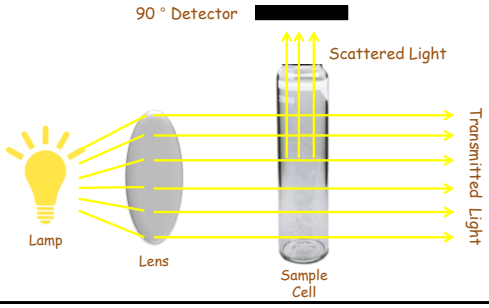
Turbidity Instrumentation

- Nephelometer – "scattered light"
  - Moved light reading from 180° to 90°
  - Measure the amount of light scattered by a sample

Schematic Diagram of a Nephelometer

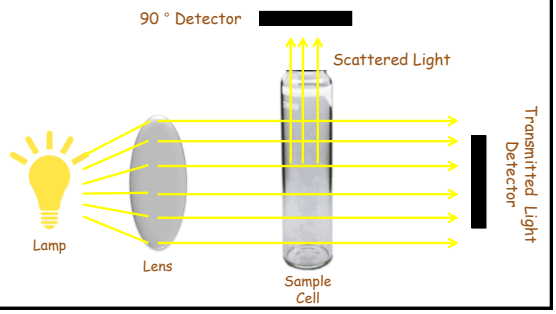


Classic 90° Nephelometer



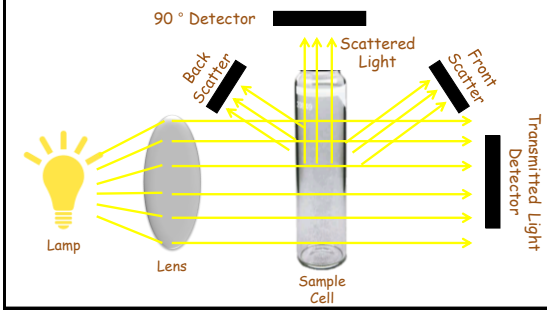
Ratio Nephelometer

Using both the 90° reading as well as the 180 ° (transmitted light) reading, we can get around color in the sample



Ratio Nephelometer

Additional detectors allows for higher measurements



Turbidity Measurement

- Sources of Error
  - Stray light
  - Improper calibration
  - Sample cells
    - Contaminated cells – give false positive
    - Scratched cells – give false positive

How to Improve Turbidity Measurement

- Sample Cells
  - Cells must be meticulously clean
    - Wash with detergent, acid (HCl)
    - Ultrasonic bath
    - Rinse with filtered deionized water
      - Very regularly
      - Rinse 5-15 times to ensure all turbidity removed
  - Hide or minimize effects of scratches with silicone oil
    - Silicone oil has same refractive properties as sample cell
    - Do NOT use silicon oil with TU5 turbidimeters!

How to Improve Turbidity Measurement

- Gas Bubbles
  - Bubbles scatter light and will give high reading
  - Degas sample
    - Draw vacuum
    - Ultrasonic bath
    - **Time – Let sample sit for a few minutes**
- Stray Light
  - Keep sample compartment and optics clean
  - Never leave sample compartment open

Turbidimeter Calibration

- Improper calibration can lead to inaccurate measurements
  - Calibrate regularly (quarterly) with primary (liquid) standards
  - Hach recommends standards no less than 20 ntu for calibration
    - Verify with lower ntu's

Turbidimeter Calibration

- After calibration, read primary standard (10 ntu or below) to verify calibration ("stray light")
  - Then use secondary (gel) standards
  - Record gel standard readings for future verifications
- If bubbles can be seen in sample cell, then the cell is probably dirty

Section 12
Taste and Odor

Taste and Odor

Significance
Sampling
Methods of Determination
Methods of Removing

1

Taste and Odor

- There are few if any enforceable regulations worldwide regarding taste and odor compounds in drinking water.
- They have the status of "Secondary Standards"

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Taste and Odor

- Customers expect their tap water to taste and smell good.
- The problem is that if there is a taste or odor problem present, your customer associates this with unsafe drinking water.

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Taste and Odor

- This lack of trust has resulted in a dramatic increase in the use of bottled water.

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Taste and Odor

- Aesthetic qualities of drinking water and their measures are dependent on human perception
- Difficult to measure
- Caused by a variety of substances
  - o Organic matter
  - o Dissolved gases
  - o Industrial waste
  - o Leached metals

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Taste and Odor

- The exact cause of taste and odor problems must be identified, whether it is source contamination, microbial metabolites, chemicals produced during treatment or chemicals produced in the distribution system, in order to minimize the problem.

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Taste and Odor

- Since researchers have been able to identify causes of taste and odor problems, control methods can be used to improve the aesthetic quality of drinking water.
- This means happier customers.

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FIGURE 1 Wheel identifying distribution system–generated tastes and odors

Courtesy of AWWA Journal, Feb. 2004

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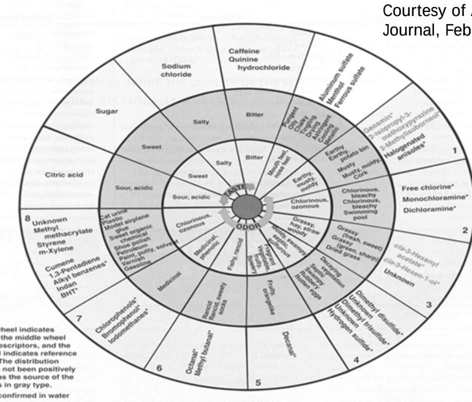


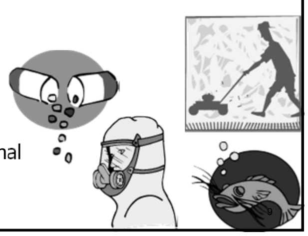
The inner wheel indicates categories, the middle wheel indicates descriptors, and the outer wheel indicates reference standards. The distribution system has not been positively confirmed as the source of the compounds in gray type.
*Presence confirmed in water

Source: D. Khiari et al, 2002. *Distribution Generated Taste-and-Odor Phenomena*. AwwaRF Report, AWWA Bookstore catalog no. 90897. AWWA, Denver. 8

Odors

- Most frequently caused by algae or decaying organic matter
- Intensity and offensiveness vary with the type of organic matter
- Classifications:

•aromatic
•grassy
•septic
•rotten egg
•fishy
•musty
•medicinal



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Odors

- Human sense of smell is more sensitive than taste, so odor tests are most commonly run in water treatment plants

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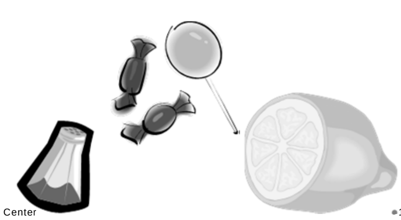
Taste

- Taste tests can only be run on water known to be safe for drinking
- Usefulness is limited
- Classifications:
  - o sweet
  - o sour
  - o bitter
  - o salty



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Significance

- Odor tests can be used to evaluate how well a plant removes taste and odor causing organic materials
- Odor tests can also be used to detect problems in the distribution system
  - o odors in dead-end water mains may have a significant bacteriological buildup
  - o chlorine odor can indicate the loss of free chlorine caused by stagnation, slime buildup and/or anaerobic conditions

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Sampling

- Water samples should be taken from raw and finished waters
- Preferably glass containers used because plastic containers may have their own odor
- Mixing of sample should be kept to a minimum, aeration may reduce odor causing compounds, until ready for analysis
- Odor tests should be run ASAP (within 24 hours)

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Methods of Determination

- Threshold odor test
  - o measured in threshold odor number (TON)
  - o determined by diluting a sample with odor-free water until the least definitely perceptible odor is achieved
  - o more accurate with more people conducting test

$$TON = \frac{A + B}{A}$$

Where A = mL sample
B = mL odor-free water

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Methods of Determination

- Flavor profile analysis
  - o can be applied for both taste and odor causing compounds
  - o panelists are trained in the proper methods of tasting and sniffing samples and are taught to identify and rate the attributes of both tastes and odors
  - o standards can be made from sucrose for sweetness, citric acid for sourness, sodium chloride for saltiness and coffee for bitterness; geranium leaves may also be used for a standard for geranium odor in a water sample

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Methods of Determination

- Quantitative Methods - how much is present
  - o Closed-Loop Stripping Analysis
  - o Solid Phase Microextraction (SPME) by GC/MS
  - o Purge and Trap (dynamic headspace)
- Complaint calls can be received with Geosmin and MIB at 10 ppt (parts per trillion)

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Removal of Taste and Odors

- There are two different areas taste and odor problems can begin:
  - o Source water
    - can be treated in source water or at the treatment plant
  - o Distribution system
    - can be caused by corrosive water leaching metals into water or low chlorine residuals resulting in bacterial growth in water

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Source Water Treatment

- Early detection of an algal bloom is best
  - o usually have to have historical data to know when blooms occur
  - o data tracking:
  - o early detection by:

•Temperature •Turbidity •Algae collection
•pH •Nutrient content •Algae ID

•Underwater visual inspection
•flavor profile analysis

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Source Water Treatment

- Copper sulfate
- Operations methods
- Operational tools
  - Aeration
  - Blending treated water with non-treated water
  - Alum
  - Ferric Salts
  - Artificial circulation - prevent lake stratification
  - Removal of fish - stir up sediments
  - Dredging of lake/reservoir - extreme
  - Selective withdrawal

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Treatment in Plant

- Most plants don't have the luxury of having protected reservoirs they can treat to prevent problems before they come into the plant.
- Best way to prevent is to look at historical data: if algal blooms occur when water reaches certain temperature.

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Treatment in Plant

- Oxidizers
  - o Ozone
    - removes 90% of Geosmin and MIB
  - o Chlorine Dioxide
    - removes phenolic and medicinal odors
  - o Potassium Permanganate
    - removes grassy and cucumber odors
- PAC
- Biological Filtration

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Distribution System

- Look at historical data
  - o what time of the year are complaints made?
  - o where are there breaks, repairs or replacement on the water main?
  - o was there a possibility of cross-connection and backflow?
- Always remember, as temperature increases during the summer, chlorine residual drops
  - o chlorine can mask a taste or odor
  - o bacteria can grow with low/no residual chlorine
  - o either of these problems can create taste and odor problems

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Distribution System

- Problems
  - o getting a good description from your customer; one person may say the water has a metallic taste and another may say it tastes like sewage
- Getting sample
  - o take at customer's house, make sure customer checks sample to see if taste or odor problem is present in the sample you just collected - if not, no need to send to lab

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Distribution System

- Once a problem has been identified, work upstream from the customers tap to find the source of the problem
- Once you have solved a customer's problem, you learn more about your distribution system and you increase customer confidence
- Operational Tools
  - o flushing mains
  - o reconfiguring mains
  - o cross-connection control

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Taste and Odor

- Some treatment methods may remove taste and odor problems, by doing so, they may add new taste and odors that are offensive
- For the treated water industry to move forward, more effort is needed to:
  - o characterize taste and odors
  - o develop analytical procedures
  - o to detect and identify causes of taste and odor problems
  - o develop economical solutions for minimizing taste and odor problems

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2150 ODOR*

2150 A. Introduction

1. Discussion

Odor, like taste, depends on contact of a stimulating substance with the appropriate human receptor cell. The stimuli are chemical in nature and the term "chemical senses" often is applied to odor and taste. Water is a neutral medium, always present on or at the receptors that perceive sensory response. In its pure form, water is odor-free. Man and other animals can avoid many potentially toxic foods and waters because of adverse sensory response. These senses often provide the first warning of potential hazards in the environment.

Odor is recognized[1] as a quality factor affecting acceptability of drinking water (and foods prepared with it), tainting of fish and other aquatic organisms, and esthetics of recreational waters. Most organic and some inorganic chemicals contribute taste or odor. These chemicals may originate from municipal and industrial waste discharges, from natural sources such as decomposition of vegetable matter, or from associated microbial activity, and from disinfectants or their products.

The potential for impairment of the sensory quality of water has increased as a result of expansion in the variety and quantity of waste materials, demand for water disposal of captured air pollutants, and increased reuse of available water supplies by a growing population. Domestic consumers and process industries such as food, beverage, and pharmaceutical manufacturers require water essentially free of tastes and odors.

Some substances, such as certain inorganic salts, produce taste without odor and are evaluated by taste testing (Section 2160). Many other sensations ascribed to the sense of taste actually are odors, even though the sensation is not noticed until the material is taken into the mouth. Because some odorous materials are detectable when present in only a few nanograms per liter, it is usually impractical and often impossible to isolate and identify the odor-producing chemical. The human nose is the practical odor-testing device used in this method. Odor tests are performed to provide qualitative descriptions and approximate quantitative measurements of odor intensity. The method for intensity measurement presented here is the *threshold odor* test, based on a method of limits.[2] This procedure, while not universally preferred,[3] has definite strengths.[4]

Sensory tests are useful as a check on the quality of raw and finished water and for control of odor through the treatment process.[2,3,5] They can assess the effectiveness of different treatments and provide a means of tracing the source of contamination.

Section 6040 provides an analytical procedure for quantifying several organic odor-producing compounds including geosmin and methylisoborneol.

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* Approved by Standard Methods Committee, 1997. Editorial revisions, 2011.
Joint Task Group: 20th Edition—Irwin H. (Mel) Suffet, (chair), John A. Arrington, Larry D. Benefield, Larry David Cole, Thomas S. Gittelman, James P. Kizer, Shundar Lin, Gerald L. Mahon, Morten C. Meilgaard, James R. Nugent.

https://doi.org/10.2105/SMWW.2882.019

2150 B. Threshold Odor Test

1. General Discussion

a. Principle: Determine the threshold odor by diluting a sample with odor-free water until the least definitely perceptible odor is achieved. There is no absolute threshold odor concentration, because of inherent variation in individual olfactory capability. A given person varies in sensitivity over time. Day-to-day and within-day differences occur. Furthermore, responses vary as a result of the characteristic, as well as concentration, of odorant. The number of persons selected to measure threshold odor will depend on the objective of the tests, economics, and available personnel. Larger-sized panels are needed for sensory testing when the results must represent the population as a whole or when great precision is desired. Under such circumstances, panels of no fewer than five persons, and preferably ten or more, are recommended.[1] Measurement of threshold levels by one person is often a necessity at water treatment plants. Interpretation of the single tester result requires knowledge of the relative acuity of that person. Some investigators have used specific odorants, such as *m*-cresol or *n*-butanol, to calibrate a tester's response.[2] Others have used the University of Pennsylvania Smell Identification Test to assess an individual's ability to identify odors correctly.[3]

b. Application: This threshold method is applicable to samples ranging from nearly odorless natural waters to industrial wastes with threshold numbers in the thousands. There are no intrinsic difficulties with the highly odorous samples because they are reduced in concentration proportionately before being presented to the test observers.

c. Qualitative descriptions: A fully acceptable system for characterizing odor has not been developed despite efforts over more than a century. Nevertheless, Section 2170 (Flavor Profile Analysis) specifies a set of 23 odor reference standards that may be used if qualitative descriptions are important. These descriptors can be used with the Threshold Odor Test to standardize methods for sensory analysis.

d. Sampling and storage: Collect samples for odor testing in glass bottles with glass or TFE-lined closures. Complete tests as soon as possible after sample collection. If storage is necessary, collect at least 500 mL of sample in a bottle filled to the top; refrigerate, making sure that no extraneous odors can be drawn into the sample as it cools. Do not use plastic containers.

e. Dechlorination: Most tap waters and some wastewaters are chlorinated. Often it is desirable to determine the odor of the chlorinated sample as well as that of the same sample after dechlorination. Dechlorinate with thiosulfate in exact stoichiometric quantity as described under Nitrogen (Ammonia), Section 4500-NH_3.

f. Temperature: Threshold odor values vary with temperature. For most tap waters and raw water sources, a sample temperature of 60°C will permit detection of odors that otherwise might be missed; 60°C is the standard temperature for hot threshold odor tests. For some purposes—because the odor is too fleeting or there is excessive heat sensation—the hot odor test may not be applicable; where experience shows that a lower temperature is needed, use a standard test temperature of 40°C. For special purposes, other temperatures may be used. *Report temperature at which observations are made.*

g. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 2020:II.

2. Apparatus

To assure reliable threshold measurements, use odor-free glassware. Clean glassware shortly before use with nonodorous soap and acid cleaning solution and rinse with odor-free water. Reserve this glassware exclusively for threshold testing. Do not use rubber, cork, or plastic stoppers. Do not use narrow-mouth vessels.

a. Sample bottles, glass-stoppered or with TFE-lined closures.

b. Constant-temperature bath: A water bath or electric hot plate capable of temperature control of ±1°C for odor tests at elevated temperatures. The bath must not contribute any odor to the odor flasks.

c. Odor flasks: Glass-stoppered, 500-mL (ST 32) Erlenmeyer flasks, to hold sample dilutions during testing.

d. Pipets:

1) *Transfer and volumetric pipets or graduated cylinders*—200-, 100-, 50-, and 25-mL.

2) *Measuring pipets*—10-mL, graduated in tenths.

e. Thermometer: Zero to 110°C, chemical or metal-stem dial type.

3. Odor-Free Water

a. Sources: Prepare odor-free water by passing distilled, deionized, or tap water through activated carbon. If product water is not odor-free, rebuild or purify the system. In all cases verify quality of product water daily.

b. Odor-free-water generator (Figure 2150:1):* Make the PVC generator from a 2-ft length of 4-in. PVC pipe approved for use for drinking water purposes (e.g., Schedule 80, or National Water Council-approved in U.K.). Thread pipe end to accept threaded caps. Have a small threaded nipple in the cap center for water inlet or outlet. To retain the activated carbon, place coarse glass wool in top and bottom of generator. Regulate water flow to generator by a needle valve and a pressure regulator to provide the minimum pressure for the desired flow. Use activated carbon of approximately 12 to 40 mesh grain size.†

c. Generator operation: Pass tap or purified water through odor-free-water generator at rate of 100 mL/min. When generator is started, flush to remove carbon fines and discard product, or pre-rinse carbon.

Check quality of water obtained from the odor-free-water generator daily at 40 and 60°C before use. The life of the carbon will vary with the condition and amount of water filtered. Subtle odors of biological origin often are found if moist carbon filters stand idle

* For approximate metric dimensions in centimeters, multiply dimensions in inches by 2.54.

† Nuchar WV-G, Westvaco, Covington, VA; Filtrasorb 200, Calgon Carbon Corporation, Pittsburgh, PA; or equivalent.

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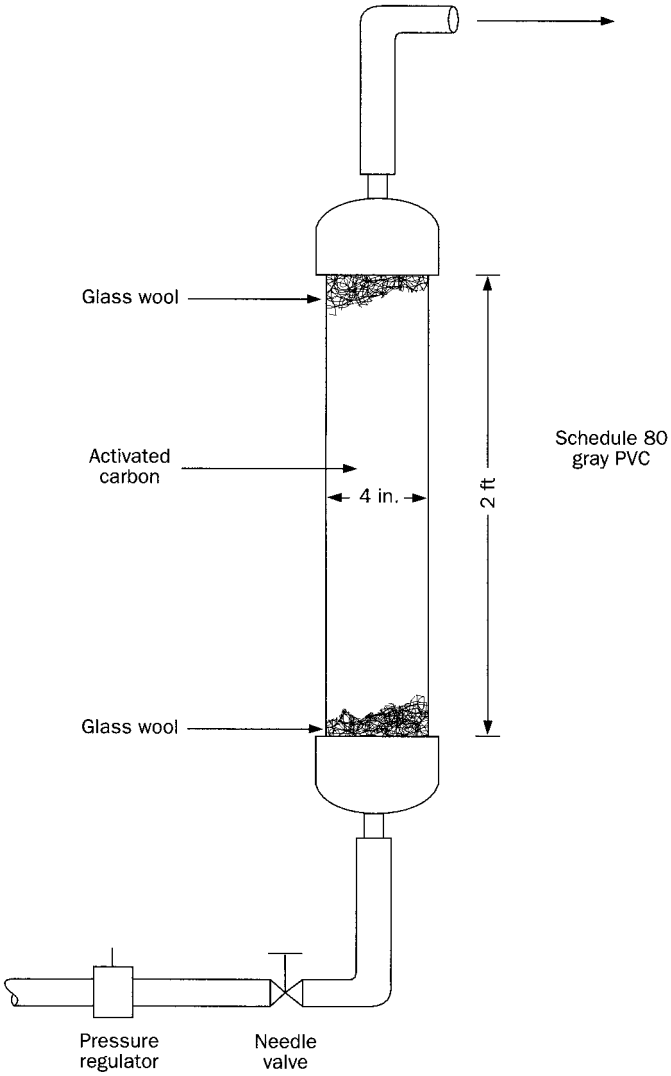

Figure 2150:1. Odor-free-water generator.

between test periods. Detection of odor in the water coming through the carbon indicates that a change of carbon is needed.

4. Procedure

a. Precautions: Carefully select by preliminary tests the persons to make taste or odor tests. Although extreme sensitivity is not required, exclude insensitive persons and concentrate on observers who have a sincere interest in the test. Avoid extraneous odor stimuli such as those caused by smoking and eating before the test or those contributed by scented soaps, perfumes, and shaving lotions. Ensure that the tester is free from colds or allergies that affect odor response. Limit frequency of tests to a number below the fatigue level by frequent rests in an odor-free atmosphere. Keep room in which tests are conducted free from distractions, drafts, and odor.[2] If necessary, set aside a special odor-free room ventilated by air that is filtered through activated carbon and maintained at a constant comfortable temperature and humidity.[4]

TABLE 2150:I. THRESHOLD ODOR NUMBERS CORRESPONDING TO VARIOUS DILUTIONS

Sample Volume Diluted to 200 mL *mL*	Threshold Odor No.	Sample Volume Diluted to 200 mL *mL*	Threshold Odor No.
200	1	12.0	17
140	1.4	8.3	24
100	2	5.7	35
70	3	4.0	50
50	4	2.8	70
35	6	2.0	100
25	8	1.4	140
17	12	1.0	200

For precise work use a panel of five or more testers. Do not allow persons making odor measurements to prepare samples or to know dilution concentrations being evaluated. Familiarize testers with the procedure before they participate in a panel test. Present most dilute sample first to avoid tiring the senses with the concentrated sample. Keep temperature of samples during testing within 1°C of the specified temperature.

Because many raw and waste waters are colored or have decided turbidity that may bias results, use opaque or darkly colored odor flasks, such as red actinic Erlenmeyer flasks.

b. Characterization: As part of the threshold test or as a separate test, direct each observer to describe the characteristic sample odor using odor reference standards (see Section 2170). Compile the consensus that may appear among testers and that affords a clue to the origin of the odorous component. The value of the characterization test increases as observers become more experienced with a particular category of odor (e.g., earthy, musty, chlorine).

c. Threshold measurement:‡ The "threshold odor number," designated by the abbreviation TON, is the greatest dilution of sample with odor-free water yielding a definitely perceptible odor. Bring total volume of sample and odor-free water to 200 mL in each test. Follow dilutions and record corresponding TON presented in Table 2150:I. These numbers have been computed thus:

$$\text{TON} = \frac{A + B}{A}$$

where:

A = mL sample and
B = mL odor-free water.

1) Place proper volume of odor-free water in the flask first, add sample to water (avoiding contact of pipet or sample with lip or neck of flask), mix by swirling, and proceed as follows.

Determine approximate range of the threshold number by adding 200 mL, 50 mL, 12 mL, and 2.8 mL sample to separate 500-mL glass-stoppered Erlenmeyer flasks containing odor-free

‡ There are numerous methods of arranging and presenting samples for odor determinations. The methods offered here are practical and economical of time and personnel. If extensive tests are planned and statistical analysis of data is required, become familiar with the more accurate methods that have been used extensively by flavor and allied industries.[5]

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TABLE 2150:II. DILUTIONS FOR VARIOUS ODOR INTENSITIES

Sample Volume in Which Odor Is First Noted *mL*	Volumes to Be Diluted to 200 mL *mL*
200	200, 140, 100, 70, 50
50	50, 35, 25, 17, 12
12	12, 8.3, 5.7, 4.0, 2.8
2.8	Intermediate dilution

water to make a total volume of 200 mL. Use a separate flask containing only odor-free water as reference for comparison. Heat dilutions and reference to desired test temperature.

2) Shake flask containing odor-free water, remove stopper, and sniff vapors. Test sample containing least amount of odor-bearing water in the same way. If odor can be detected in this dilution, prepare more dilute samples as described in ¶ *c*5) below. If odor cannot be detected in first dilution, repeat above procedure using sample containing next higher concentration of odor-bearing water, and continue this process until odor is detected clearly.

3) Based on results obtained in the preliminary test, prepare a set of dilutions using Table 2150:II as a guide. Prepare the five dilutions shown on the appropriate line and the three next most concentrated on the next line in Table 2150:II. For example, if odor was first noted in the flask containing 50 mL sample in the preliminary test, prepare flasks containing 50, 35, 25, 17, 12, 8.3, 5.7, and 4.0 mL sample, each diluted to 200 mL with odor-free water. This array is necessary to challenge the range of sensitivities of the entire panel of testers.

Insert two or more blanks in the series near the expected threshold, but avoid any repeated pattern. Do not let tester know which dilutions are odorous and which are blanks. Instruct tester to smell each flask in sequence, beginning with the least concentrated sample, until odor is detected with certainty.

4) Record observations by indicating whether odor is noted in each test flask. For example:

mL Sample Diluted to 200 mL	12	0	17	25	0	35	50
Response	−	−	−	+	−	+	−

5) If the sample being tested requires more dilution than is provided by Table 2150:II, prepare an intermediate dilution consisting of 20 mL sample diluted to 200 mL with odor-free water. Use this dilution for the threshold determination. Multiply TON obtained by 10 to correct for the intermediate dilution. In rare cases more than one tenfold intermediate dilution step may be required.

5. Calculation

The threshold odor number is the dilution ratio at which odor is just detectable. In the example above, 2150B.4*c*4), the first detectable odor occurred when 25 mL sample was diluted to 200 mL. Thus the threshold is 200 divided by 25, or 8. Table 2150:I lists the threshold numbers corresponding to common dilutions.

The smallest TON that can be observed is 1, as in the case where the odor flask contains 200 mL undiluted sample. If no odor is detected at this concentration, report "No odor observed" instead of a threshold number. (In special applications, fractional threshold numbers have been calculated.[6])

Anomalous responses sometimes occur; a low concentration may be called positive and a higher concentration in the series may be called negative. In such a case, designate the threshold as the point after which no further anomalies occur. For instance:

Increasing Concentration →

Response − − + − + + + +

↓

Threshold

where:

− signifies negative response and
+ signifies positive response.

Occasionally a flask contains residual odor or is contaminated inadvertently. For precise testing repeat entire threshold odor test to determine if the last flask marked " − " was actually a mislabelled blank of odor-free water or if the previous " + " was a contaminated sample.

Use appropriate statistical methods to calculate the most probable average threshold from large numbers of panel results. For most purposes, express the threshold of a group as the geometric mean of individual thresholds.

6. Interpretation of Results

A threshold number is not a precise value. In the case of the single observer it represents a judgment at the time of testing. Panel results are more meaningful because individual differences have less influence on the result. One or two observers can develop useful data if comparison with larger panels has been made to check their sensitivity. Do not make comparisons of data from time to time or place to place unless all test conditions have been standardized carefully and there is some basis for comparison of observed intensities.

7. References

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2150 C. Total Intensity of Odor (PROPOSED)*

1. General Discussion

a. Principle: Total Intensity of Odor (TIO) is a technique for numerically rating the strength (intensity) of a sample's total odor based on comparisons to prescribed odor intensity reference standards. This TIO method is considered complementary to the method of Section 2170 and follows the specific recommendations provided by Section 2170. Each TIO is established by a panel as follows:

- a minimum of four panelists smell the headspace above a sample;
- each panelist makes an initial, independent assessment of the sample; and
- then panel members discuss their findings and reach a consensus.

This method is not performed on diluted samples because TIO only applies to a sample's condition representative of when it was collected. Samples typically contain mixtures of compounds, and dilution alters these compounds' influence on total odor intensity. The TIO method is successful because samples are evaluated at full strength and reference standards allow panelists to rate overall odor strength consistently and agree on a numerical odor intensity.

b. Application: This method can be used to evaluate samples from drinking water sources, various points in the water treatment train, and finished drinking water. Its results can be used as an indicator of changes that could lead to consumer complaints. While this method focuses on the rating of odor intensity and is economically efficient in that it does not require extensive training or advanced laboratory techniques, Flavor Profile Analysis (Section 2170) remains the preferred method for both qualitative and quantitative analysis.

TABLE 2150:III. DOSING CHART FOR DECHLORINATING AGENT

Chemical	Strength	Cl_2 Concentration *mg/L as* Cl_2	Dosage AA
Ascorbic Acid	6 g/L	1	1.0 mL
		2	2.0 mL
		3	3.0 mL
		4	4.0 mL

Adapted from: WORLEY, J., A.M. DIETRICH & R. HOEHN. 2002. Dechlorination techniques to improve sensory odor testing of geosmin and 2-MIB. *J. Am. Water Works Assoc.* 95(3):109.

c. Sample collection and storage: Collect samples in 1-L amber glass bottles with polytetrafluoroethylene (PTFE)-lined closures. When sampling from a tap, remove all screens and aerators to minimize turbulence. Ensure that the sample collected is representative of the water of interest, flushing the line if appropriate. Reduce flow rate during sampling. Rinse the bottle once with sample water, then fill bottle to the top and replace cap without any headspace. After collection, store sample at approximately 4°C to minimize loss of odors before testing. To obtain the most accurate results, analyze samples as soon as possible after collection. Do not analyze samples >24 h after collection.

d. Dechlorination: Chlorinated water samples should be dechlorinated with ascorbic acid (Table 2150:III) before analysis, unless the chlorine residual needs to be evaluated for its odor impact.

e. Temperature: For routine drinking-water analyses, conduct TIO at 25 ± 2°C. For some applications, such as when evalu-

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Joint Task Group: Melissa S. Dale (chair), Gary A. Burlingame, Roy D. Desrochers, Sr., Andrea M. Dietrich, Wilbur A. Frehner, Allison Jacobsen-Garcia, Peggy Singley Moylan.

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TABLE 2150:IV. HEXANAL ODOR REFERENCE STANDARD CONCENTRATIONS AND TOTAL INTENSITY OF ODOR RATING SCALE

Code	Hexanal Conc $\mu g/L$	TIO Rating	TIO Description
H0	0	0	Odor-free
H2	5	2	Very Weak
H4	30	4	Weak
H6	100	6	Weak to Moderate
H8	1600	8	Moderate

SOURCE: OMUR-OZBEK, P. & A.M. DIETRICH. 2008. Developing Hexanal as an Odor Reference Standard for the Sensory Analysis of Drinking Water. *Water Res.* 42(10-11):2598.

ating/troubleshooting odor complaints occurring when using heated water or cooking, testing at 45 ± 2°C may be preferred. Note the testing temperature on the report.

Allow adequate time for sample to reach the testing temperature after removing it from refrigeration. Ideally, place samples in a water bath set to the testing temperature and leave them there for 30 minutes.

f. Safety: Do not use this method for industrial or domestic wastes or other samples suspected to contain hazardous levels of chemical or biological contaminants.

2. Apparatus

a. Sample and standard bottles: 1-L narrow-mouth amber glass, with PTFE-lined closure. (NOTE: 500-mL bottles can also be used.)

b. Glass graduated cylinders: 100-, 500-, and 1000-mL.

c. Odor-free testing room: TIO sessions should take place in a clean, odor-free room with minimal distractions.

d. Water bath: Capable of bringing samples to testing temperature within 30 min.

3. Reagents

a. Odor-free water: Bottled water determined by panelists to be odor-free before use. If a noticeable odor is present, obtain a different lot or brand of water. Alternatively, prepare odor-free water using the procedure described in 2150B.3.

b. n-Hexanal, 96% purity (CAS 66-25-1): Hexanal has been demonstrated as a chemical reference standard for odor intensity.[1]

c. Ascorbic acid, reagent grade (CAS 50-81-7): Ascorbic acid (vitamin C) is a known dechlorinating agent that has no inherent odor, is relatively safe, and has little effect on pH.[2]

4. Odor Reference Standards

A series of odor reference standards is prepared and used to provide reference points for odor-intensity ratings; panelists compare the water samples' odor intensity to the reference standards' intensities. Table 2150:IV shows the concentrations of prepared hexanal odor-reference standards to represent "odor-free," "very weak," "weak," "weak to moderate," and "moderate" intensities.

5. Panelist Orientation

Before assessing samples for TIO, panelists should become familiar with the odor-intensity scale by participating in an orientation session. Prepare reference standard solutions according to Table 2150:IV and bring them to testing temperature. Measure 250-mL aliquots of each solution into separate 1-L amber bottles, minimizing water turbulence/agitation when pouring, and tightly cap. Prepare one set of standards for each panelist.

Begin with the no-odor blank and then continue with each reference standard from the lowest to highest intensity. Gently shake the bottle to ensure that volatile compounds are released into the headspace. Remove cap and smell headspace using short sniffs (avoid long, drawn-out sniffs). Repeat with each reference standard. Allow adequate time for panelists to become familiar with the reference standards and their corresponding intensities. Avoid odor fatigue by limiting the number of sniffs per standard.

6. Procedure

a. Sample preparation: Bring sample to testing temperature. Measure and transfer a 250-mL aliquot of sample into a 1-L glass bottle, minimizing water turbulence/agitation when pouring. Tightly cap bottle. Repeat until each panelist has an aliquot.

b. Odor analysis: Before each session begins, prepare the reference standard solutions (Table 2150:IV) and bring them to testing temperature. Measure a 250-mL aliquot of each solution into separate 1-L amber bottles and tightly cap. Have each panelist sniff the H4 reference standard to calibrate their sensory perception to the intensity of 4 ("slight"). Wait at least 30 s before analyzing sample(s).

Working independently, each panelist gently shakes their sample bottle, removes the cap, and sniffs the headspace. They then each assign the sample a TIO based on their familiarity with the intensity scale. If evaluating additional samples, panelists then sniff odor-free water and rest for ≥1 min between samples.

c. Recording and discussion: One panel member compiles all results on one sheet. If the difference in individual TIO values is >2 for any sample (e.g., one panelist reports TIO of 2, and another reports TIO of 6), then the panel discusses sample and may retest, again using the reference standards for calibration, so a closer consensus may be obtained.

d. Reporting: After individual results are discussed and recorded, the panel reaches a consensus via discussion and reports it. Report results as TIO at the testing temperature used [e.g., WTP_A Filter Effluent TIO = 2 (at 25°C)].

7. Quality Control

Include odor-free water samples periodically as a blind control. Include duplicate samples occasionally to check individual panelists' reproducibility. A known addition of an odor reference standard can also be used to check reproducibility and accurate use of the intensity scale. (See Section 2170 for references for odorants and their concentrations.)

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8. Method Validation

Researchers conducted a method-validation study that directly compared overall odor-intensity results when using TIO and Flavor Profile Analysis (Section 2170).[3] The two methods agreed 100% of the time for five drinking water treatment plant effluents sampled over two compliance cycles (a total of 10 samples). They agreed 92% of the time for 13 source water samples analyzed during the same compliance cycles. They agreed 83% of the time for four replicate samples of a drinking water treatment plant effluent that were separately fortified with six common drinking water odorants (a total of 24 fortified samples).

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2160 TASTE*

2160 A. Introduction

1. General Discussion

Taste refers only to gustatory sensations called bitter, salty, sour, and sweet that result from chemical stimulation of sensory nerve endings located in the papillae of the tongue and soft palate. Flavor refers to a complex of gustatory, olfactory, and trigeminal sensations resulting from chemical stimulation of sensory nerve endings located in the tongue, nasal cavity, and oral cavity.[1] Water samples taken into the mouth for sensory analysis always produce a flavor, although taste, odor, or mouthfeel may predominate, depending on the chemical substances present. Methods for sensory analysis presented herein require that the sample be taken into the mouth, that is, be tasted, but technically the sensory analysis requires evaluation of the complex sensation called flavor. As used here, taste refers to a method of sensory analysis in which samples are taken into the mouth but the resultant evaluations pertain to flavor.

Three methods have been developed for the sensory evaluation of water samples taken into the mouth: the flavor threshold test (FTT), the flavor rating assessment (FRA), and the flavor profile analysis (FPA) (Section 2170). The FTT is the oldest. It has been used extensively and is particularly useful for determining if the overall flavor of a sample of finished water is detectably different from a defined standard.[2] The FRA is especially valuable for determining if a sample of finished water is acceptable for daily consumption,[3] and the FPA is most useful for identifying and characterizing individual flavors in a water sample.[4]

Make flavor tests only on samples known to be safe for ingestion. Do not use samples that may be contaminated with bacteria, viruses, parasites, or hazardous chemicals, that contain dechlorinating agents such as sodium arsenite or that are derived from an unesthetic source. Do not make flavor tests on wastewaters or similar untreated effluents. Observe all sanitary and esthetic precautions with regard to apparatus and containers contacting the sample. Properly clean and sterilize containers before using them. Conduct analyses in a laboratory free from interfering background odors and if possible provide non-odorous carbon-filtered air at constant temperature and humidity. Use the procedure described in Section 2150B.3 with respect to taste- and odor-free water to prepare dilution water and reference samples.

2. References

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* Approved by Standard Methods Committee, 2010. Editorial revisions, 2011.

2160 B. Flavor Threshold Test (FTT)

1. General Discussion

Use the FTT to measure detectable flavor quantitatively. More precisely, use the method to compare the sample flavor objectively with that of specified reference water used as diluent.

The flavor threshold number (FTN) is the greatest dilution of sample with reference water yielding a definitely perceptible difference. The FTN is computed as follows:

$$\text{FTN} = \frac{A + B}{A}$$

where:

A = sample volume, mL, and
B = reference water (diluent) volume, mL.

T1 Table 2160:I gives the FTNs corresponding to various dilutions.

The QC practices considered to be an integral part of each method are summarized in Table 2020:II.

2. Procedure

a. Panel selection: Carefully select by preliminary trials interested persons to make flavor tests. Exclude insensitive persons and ensure that the testers are free from colds or allergies. Familiarize testers with the procedure before they participate in a panel test, but do not let them prepare samples or know dilution concentrations being evaluated. For precise work use a panel of five or more testers.

b. Taste characterization: Have each observer describe the characteristic sample flavor of the most concentrated sample. Compile the consensus that may appear among testers. The value of characterization increases as observers become more experienced with a particular flavor category such as chlorophenolic, grassy, or musty.

c. Preliminary test: To determine approximate range of the FTN, add 200-, 50-, 12-, and 4-mL sample portions to volumes of reference water (see Section 2150B.3) designated in Table

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TABLE 2160:I. FLAVOR THRESHOLD NUMBERS CORRESPONDING TO VARIOUS DILUTIONS

Sample Volume *mL*	Diluent Volume *mL*	Flavor Threshold No. *FTN*
200	0	1
100	100	2
70	130	3
50	150	4
35	165	6
25	175	8
17	183	12
12	188	17
8	192	25
6	194	33
4	196	50
3	197	67
2	198	100
1	199	200

2160:I in separate 300-mL glass beakers to make a total of 200 mL in each beaker, and mix gently with clean stirrer. Use separate beaker containing only reference water for comparison. Keep sample temperature during testing within 1°C of specified temperature. Present samples to each taster in a uniform manner, with the reference water presented first, followed by the most dilute sample. If a flavor can be detected in this dilution, prepare an intermediate sample by diluting 20 mL sample to 200 mL with reference water. Use this dilution for threshold determination and multiply FTN obtained by 10 to correct for intermediate dilution. In rare cases a higher intermediate dilution may be required.

If no flavor is detected in the most dilute sample, repeat using the next concentration. Continue this process until flavor is detected clearly.

T2 *d. FTN determination:* Based on results obtained in the preliminary test, prepare a set of dilutions using Table 2160:II as a guide. Prepare the seven dilutions shown on the appropriate line. This array is necessary to challenge the range of sensitivities of the entire panel of testers. If the sample being tested requires more dilution than is provided by Table 2160:II, make intermediate dilutions as directed in ¶ *c* above.

Use a clean 50-mL beaker filled to the 25-mL level or use an ordinary restaurant-style drinking glass for each dilution and reference sample. Do not use glassware used in sensory testing for other analyses. Between tests, sanitize containers in an automatic dishwasher supplied with water at not less than 60°C.

TABLE 2160:II. DILUTIONS FOR DETERMINING THE FTN

Sample Volume in Which Taste Is First Noted *mL*	Volumes to be Diluted to 200 mL *mL*
200	200, 100, 70, 50, 35, 25, 17
50	50, 35, 25, 17, 12, 8, 6
12	12, 8, 6, 4, 3, 2, 1
4	Intermediate dilution

Maintain samples at 15 ± 1°C. However, if temperature of water in the distribution system is higher than 15°C, select an appropriate temperature. Specify temperature in reporting results.

Present series of samples to each tester in order of increasing concentration. Pair each sample with a known reference. Have tester taste sample by taking into the mouth whatever volume is comfortable, moving sample throughout the mouth, holding it for several seconds, and discharging it without swallowing. Have tester compare sample with reference and record whether a flavor or aftertaste is detectable. Insert two or more reference blanks in the series near the expected threshold, but avoid any repeated pattern. Do not let tester know which samples have flavor and which are blanks. Instruct tester to taste each sample in sequence, beginning with the least concentrated sample, until flavor is detected with certainty.

Record observations by indicating whether flavor is noted in each test beaker. For example:

mL Sample Diluted to 200 mL	6	8	12	0	17	25	35	0	50
Response	−	−	−	−	−	+	+	−	+

where:

− signifies negative response and
+ signifies positive response.

3. Calculation

The flavor threshold number is the dilution ratio at which flavor is just detectable. In the example above, the first detectable flavor occurred when 25 mL sample was diluted to 200 mL yielding a threshold number of 8 (Table 2160:I). Reference blanks do not influence calculation of the threshold.

The smallest FTN that can be observed is 1, where the beaker contains 200 mL undiluted sample. If no flavor is detected at this concentration, report "No flavor observed" instead of a threshold number.

Anomalous responses sometimes occur; a low concentration may be called positive and a higher concentration in the series may be called negative. In such cases, designate the threshold as that point after which no further anomalies occur. The following illustrates an approach to an anomalous series (responses to reference blanks are excluded):

Increasing Concentration →

Response:	−	+	−	+	+	+	+

↓
Threshold

Calculate mean and standard deviation of all FTNs if the distribution is reasonably symmetrical; otherwise, express the threshold of a group as the median or geometric mean of individual thresholds.

4. Interpretation of Results

An FTN is not a precise value. In the case of the single observer it represents a judgment at the time of testing. Panel

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results are more meaningful because individual differences have less influence on the test result. One or two observers can develop useful data if comparison with larger panels has been made to check their sensitivity. Do not make comparisons of data from time to time or place to place unless all test conditions have been standardized carefully and there is some basis for comparison of observed FTNs.

5. Bibliography

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2160 C. Flavor Rating Assessment (FRA)

1. General Discussion

When the purpose of the test is to estimate acceptability for daily consumption, use the flavor rating assessment described below. This procedure has been used with samples from public sources in laboratory research and consumer surveys to recommend standards governing mineral content in drinking water. Each tester is presented with a list of nine statements about the water ranging on a scale from very favorable to very unfavorable. The tester's task is to select the statement that best expresses his or her opinion. The individual rating is the scale number of the statement selected. The panel rating for a particular sample is an appropriate measure of central tendency of the scale numbers for all testers for that sample.

2. Samples

Sample finished water ready for human consumption or use experimentally treated water if the sanitary requirements given in 2160A.1 are met fully. Use taste- and odor-free water as described in Section 2150B.3 and a solution of 2000 mg NaCl/L prepared with taste- and odor-free water as criterion samples.

3. Procedure

a. Panel selection and preparation: Give prospective testers thorough instructions and trial or orientation sessions followed by questions and discussion of procedures. In tasting samples, testers work alone. Select panel members on the basis of performance in these trial sessions. Do not let testers know the composition or source of specific samples.

b. Rating test: A single rating session may be used to evaluate up to 10 samples, including the criterion samples mentioned in 2160C.2. Allow at least 30 min rest between repeated rating sessions.

For glassware requirements, see 2160B.2*d*.

Present samples at a temperature that the testers will find pleasant for drinking water; maintain this temperature throughout testing. A temperature of 15°C is recommended, but in any case, do not let the test temperature exceed tap water temperatures customary at the time of the test. Specify test temperature in reporting results.

Independently randomize sample order for each tester. Instruct each to complete the following steps:

1) Taste about half the sample by taking water into the mouth, holding it for several seconds, and discharging it without swallowing;
2) Form an initial judgment on the rating scale;
3) Make a second tasting in a similar manner;
4) Make a final rating and record result on an appropriate data form;
5) Rinse mouth with reference water;
6) Rest 1 min before repeating Steps 1 through 5 on next sample.

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c. Characterization: If characterization of flavor also is required, conduct a final rating session wherein each tester is asked to describe the flavor of each sample rated (see 2160B.2*b*).

4. Calculation

Use the following scale for rating. Record ratings as integers ranging from one to nine, with one given the highest quality rating. Calculate mean and standard deviation of all ratings if the distribution is reasonably symmetrical, otherwise express the most typical rating of a group as the median or geometric mean of individual ratings.

Action tendency scale:

1) I would be very happy to accept this water as my everyday drinking water.
2) I would be happy to accept this water as my everyday drinking water.
3) I am sure that I could accept this water as my everyday drinking water.
4) I could accept this water as my everyday drinking water.
5) Maybe I could accept this water as my everyday drinking water.
6) I don't think I could accept this water as my everyday drinking water.
7) I could not accept this water as my everyday drinking water.
8) I could never drink this water.
9) I can't stand this water in my mouth and I could never drink it.

5. Interpretation of Results

Values representing the central tendency and dispersion of quality ratings for a laboratory panel are only estimates of these values for a defined consuming population.

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2170 FLAVOR PROFILE ANALYSIS*

2170 A. Introduction

1. Discussion

Flavor profile analysis (FPA) is one of several techniques for identifying water sample taste(s) and odor(s).[1] (For general information on taste, see Section 2160; for information on odor, see Section 2150.)

FPA is designed to evaluate the tastes and odors important in drinking water. It is not used to judge a sample, to determine preferences between samples, or to determine acceptance of a water sample for public consumption. FPA is used to define a water sample's taste and odor attributes, which then could be related to, or associated with, consumer perceptions (e.g., customer complaints[2]).

One of FPA's strengths is its use of well-trained panelists who use specific, standardized terminology and can discern and express small differences between samples. Each panelist assigns to each sample descriptors that characterize the taste(s) and/or odor(s) detected. Each descriptor is given an intensity (relative to standards) that indicates the strength of each taste and odor. After individual evaluations, panelists share results and attempt to come to a consensus of descriptors and intensities for each sample. The quality of training and data interpretation determine the value of FPA results.

Because dilution may change measured descriptors,[3,4] FPA determines the strength or intensity of each perceived taste or odor without sample dilution.

2. FPA Can Also Be Used for Odor Threshold Measurements

FPA measures two types of thresholds: recognition thresholds and detection thresholds. A *recognition threshold* is the lowest concentration at which a stimulus can be identified and recognized. A *detection threshold* is "a concentration range . . . below which the odor or taste of a substance will not be detectable under any practical circumstances, and above which individuals with a normal sense of smell or taste would readily detect the presence of the substance."[5] Generally, odor detection threshold concentrations are lower than odor recognition threshold concentrations.

Sensory detection thresholds are similar in concept to method detection levels for chemical analyses. As with a method detection level, a sensory threshold is a point where quantification and accuracy are weakest; small changes in testing conditions, or small levels of contamination or background interference, greatly affect results. Moreover, sensory thresholds usually have much greater variability than method detection levels.[6]

Thresholds can be determined for individuals or for a group. Thresholds across individuals are much more variable than group thresholds, although even group thresholds can vary by two orders of magnitude for the same chemical in water. In the sensory threshold region, the effects of human test variability are significant, so reporting a threshold value as a single number can sometimes be misleading.[7,8] Practice and training can produce lower, more consistent thresholds.

Several standardized tests are available[5,9] for detection threshold measurement by individuals and groups. These forced-choice methods use a series of concentrations selected to bracket the expected threshold level. At each concentration, a panelist typically evaluates three samples: one with the odor in it and two without. Each panelist must choose which sample has the odor. The FPA presented here also can be used to estimate individual or group odor thresholds. Typically, an FPA intensity rating of 2 (see 2170B.6) is equated with a recognition threshold. Depending on the concentration range selected, the results occasionally must be extrapolated to achieve the rating of 1. A Weber–Fechner plot[4] of FPA rating versus log concentration can be used for this purpose.

Both analytical and sensory detection thresholds are statistical interpretations of measured data. This may be why a practical method for estimating odor thresholds in drinking water has not yet been widely used by drinking water utilities. Any report of a threshold value must include a description of the panelists, their level of training, the threshold measurement technique, and the statistical analysis used, because these variables can profoundly affect results, and the details are important when evaluating the reported threshold's reliability and context.

3. Safety

See 2170B.2.

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2170 B. Flavor Profile Analysis

1. General Discussion

a. Principle:[1] FPA uses a group of four or five trained panelists to examine the sensory characteristics of samples. Flavor attributes are determined by tasting; odor attributes are determined by sniffing the sample. The method allows more than one flavor, odor, or feeling (e.g., drying, burning) attribute to be determined per sample and each attribute's intensity to be measured. Figure 2170:1 shows

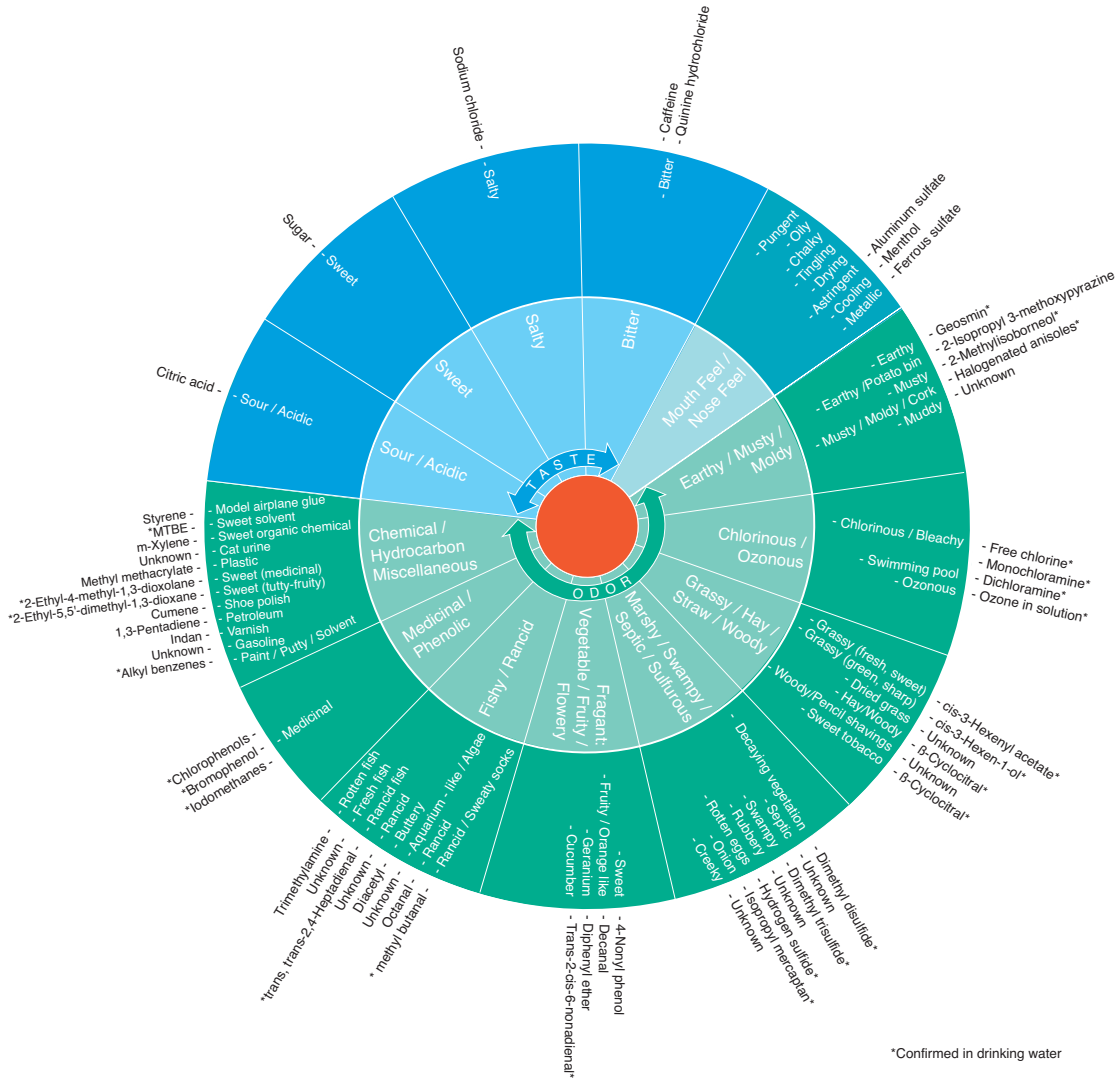

Figure 2170:1. Taste and odor wheel, showing flavor and odor attributes and example compounds. Source: SUFFET, I.H., J. HO, D. CHOU, D. KHIARI & J. MALLEVIALLE 1995. Taste-and-odor problems observed during drinking water treatment. In I.H. Suffet, J. Mallevialle & E. Kawczynski, eds. Advances in Taste and Odor Treatment and Control. American Water Works Assoc. Research Foundation & Lyonnaise des Eaux, Denver, Colo., p.6. (modified 2006). For a color version of this figure, contact *Standard Methods* technical information manager at www.standardmethods.org/contact/.

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the relationships among these attributes and factors, as well as specific compounds that exemplify them.

Initially, panelists record their perceptions without discussion. Individual results are considered important, even though the reported result is a consensus. Individual results might alert the panel to a "new" odor or to a change. Once each individual has made an independent assessment of a sample, the panel discusses its findings and reaches a consensus without changing individual results.

b. Interference: Background odors present during analysis affect results. Analyst illness (e.g., cold or allergy) and a recent history of eating, drinking, or smoking can diminish or otherwise alter perception.

c. Application:[1–4] FPA has been applied to drinking water sources, finished drinking water, sampling points in the drinking water treatment train, and bottled waters. It also has been used to investigate customer complaints.

d. Quality control (QC): The QC steps considered to be an integral part of each method are summarized in Tables 2020:I and II.

2. Safety

a. Samples: Some substances are health hazards when inhaled or ingested. Do not use this method for industrial wastes or other samples suspected to contain high concentrations of hazardous substances. Chemically analyze suspect samples to determine whether hazardous chemicals are present before making FPA. Do not taste untreated drinking water unless certain that no health threat (biological or chemical) exists.

b. Standards: Avoid human exposure to known or probable human carcinogens. An exposure assessment of chemicals that could be used in FPA[5] revealed that, in most cases, the levels and duration of exposure to chemical standards for training and calibration are well below levels of concern and should pose no known health risks when properly used for FPA.

3. Panel Selection and Training

Carefully select and train a group of panelists according to procedures available from the American Water Works Association.[6] Because four or five panelists are needed to conduct a test, training of additional panelists may be desirable to allow for unavailability of individuals. Because FPA includes discussions during which panelists reach consensus on sample descriptions, avoid including on the panel a person with a dominating personality. The opinions of a senior member or panel leader also may have this undesired effect.

Panelists must be able to detect and recognize various odors present. The training of panelists using odor reference standards is important for developing a consistent terminology within the panel and over time.[7] Trained panelists have been shown to produce more reliable sensory data.[8] FPA requires well-trained panelists and data interpreters. Reproducibility of results depends on the panelists' training and experience.

4. Apparatus[3,4,7,9,10]

Reserve apparatus and glassware exclusively for FPA.

a. Sample bottles: Glass, 1-L, with TFE-lined closure.

b. Containers for odor analysis:[3,4,7,10] Select containers for odor analysis depending on panelists' preference, sample temperature, and container availability.

1) Panel preference—Plastic cups, 7-, 8-, or 16-oz (207-, 237-, or 473-mL), disposable, are convenient. Do not use waxed-lined paper cups. Some panels have found that plastic cups impart a plastic and/or floral odor to samples and therefore prefer wide-mouth, 500-mL Erlenmeyer flasks with ST32 ground-glass stoppers. The panel should determine the acceptable, odor-free test container (glass or plastic) most suitable to its use.

2) Temperature[3,9–11]—If odor samples are tested at 45°C, do not use plastic containers. If odor samples are tested at 25°C, use the same plastic cup and sample for both odor and flavor analysis. Temperature is known to affect the intensity of an odor. For most compounds, the odor will increase as the temperature increases because more molecules of the odor-producing substance (*odorant*) will volatilize from the water sample and enter the nose. Testing at 45°C will produce a greater odor intensity and more likely chance of detection by panelists than testing at 25°C. (NOTE: There are a few exceptions, such as dissolved calcium carbonate, where the compound is less volatile or more soluble as temperature increases).

3) Availability[3]—Containers must be consistently available because panel responses may change when different containers are used.

c. Containers for flavor analysis:[3,7,9,10] Use either disposable odor- and taste-free plastic cups, or glass containers. Do not use wax-lined or paper cups. If using glass containers, verify that they contribute no taste to the sample. Wash glass containers as directed in 2170B.7*a*.

d. Watch glasses to cover the plastic cups.

e. Constant-temperature water bath capable of maintaining a temperature ±1°C. The bath must not contribute any odor to the sample containers or testing room.

f. Thermometer, graduated 0 to 110°C, chemical or metal-stem dial type.

g. Syringes.

h. Ice chest for storing samples.

i. Odor-free testing room:[3,7,9,10] Hold FPA sessions in a clean, well-lit, quiet, odor-free, and temperature-controlled room. The room should have an area with a table and chairs set up so panelists can first perform the tests individually and then hold a group discussion. Place an easel pad in the room so all panelists can see it. Use an easel pad with odor-free markers (e.g., a wax, china marker).

j. Refrigerator capable of maintaining a temperature of 4°C.

5. Reagents

a. Odor-free water: See Section 2150B.3.

b. Crackers: Use salt- and flavor-free crackers* to cleanse the palate during taste testing. Before tasting anything, use the crackers and taste-free water to cleanse the palate. Use crackers between samples to reduce carryover of perceptions.

c. Odor and flavor standards:[3,4,7,9,10,12–14] Odor and flavor reference standards have been developed for use as a guide for qualitative descriptors (names for odors). Odor reference standards help panelists agree on the descriptor for specific odors.

* Carr's Table Water Crackers—plain, or equivalent.

TABLE 2170:I. CONFIRMED ODOR REFERENCES*

Compound	Odor Characteristics	Stock Solution Concentration *mg/L*	Amount Placed into 200 mL Pure Water at 25°C for Presentation
Geosmin	Earthy, red beets	0.2†	300 μL for 300 ng/L
2-Methylisoborneol	Earthy, peat-like, Brazil nut, soil	0.2†	200 μL for 200 ng/L
Free chlorine	Chlorinous	1000 (0.1% solution) @ pH 7	0.1 mL for 0.5 mg/L
Dichloramine	Swimming pool chlorine	1000 (0.1% solution) @ pH 7	0.1 mL for 0.5 mg/L
Monochloramine	Chlorinous	1000 (0.1% solution) @ pH 7	0.1 mL for 0.5 mg/L
trans,2-*cis*,6-Nonadienal	Cucumber, green vegetation	1000	1 μL for 5 μg/L
cis-3-Hexenyl-1-acetate	Grassy	1000	100 μL for 500 μg/L
cis-3-Hexene-1-ol	Grassy, green apple	1000	100 μL for 500 μg/L

NOTE: These compounds have actually been identified as causes of odors in raw and finished drinking water.
* Adapted from AMERICAN WATER WORKS ASSOCIATION. 1993. Flavor Profile Analysis: Screening and Training of Panelists. AWWA Manual. Denver, Colo.
† Compounds are typically dissolved in methanol.

Tables 2170:I, II, and III list some of the odor references for training FPA panelists, with their descriptive names and preparations. Table 2170:I shows Confirmed Odor References, which are odorants that actually occur in water. Table 2170:II shows Representative Odor References, odorants that can occur in the environment in general but have not yet been documented in drinking water or would not be expected to occur in most drinking waters. Table 2170:III shows Substitute Odor References, or ways to reproduce the odor qualities that can occur in water. (Figure 2170:1 is based on these tables.) Unlisted reference standards can be added to suit the panel's needs, provided that safety considerations have been adequately addressed (see 2170B.2). For convenience in odor identification and training, place several drops of stock solutions (producing moderately strong odors) onto sterile cotton moistened with pharmaceutical-grade mineral oil and inserted in 25-mL amber-colored vials with TFE-lined caps.

d. Taste standards:[3,4,7,9,10,13] The chemicals used for taste standards are sucrose (sweet), citric acid (sour), sodium chloride (salt), and caffeine (bitter). Table 2170:IV lists the chemicals used and their concentrations for basic taste standards at "slight," "moderate," and "strong" levels. The taste standards provide reference points for both taste and odor training, as well as intensity ratings. The panelists compare the intensity of what they smell or taste in the samples to the intensity of the standards they have tasted. In general, tastes from all but the sweet standard tend to overpower any subsequent tasting; only the sweet taste standard is recommended for use during actual sample analysis. However, in some instances (due to cultural or lifestyle differences), the use of the salty or another taste standard is preferred for training to recognize the intensities of tastes. If the panel meets as seldom as once a week, make sweet standards available so panelists can "recalibrate" themselves. Panels that meet more than once a week may not need to "recalibrate" as often. Make standards fresh each time they are used.[3]

6. Scale

The strength of a taste or odor is judged according to the following scale:

— (odor- or taste-free)
T (threshold)
2 (very weak)
4 (weak)
6
8 (moderate)
10
12 (strong)

The rating scale has been modified from the terms "slight to strong"[1,15] to use numbers corresponding to the ordinal categories. Points (other than threshold) on the scale can be anchored by the use of taste standards. Thus, a certain concentration of a taste standard is defined as a certain point on the rating scale, thereby anchoring numerical ratings for non-threshold intensities. Threshold ratings are not defined by any standards. Their meaning is different from that of the other ratings, and they are difficult to manipulate mathematically.

7. Procedure

a. Glassware preparation: Prepare sample bottles by washing bottle and cap with detergent. Rinse 10 times with hot water. Optionally rinse with HCl (1:1). In either case, provide a final rinse with odor-free water (see Section 2150B.3) multiple times. If there is residual odor (e.g., chalky), repeat cleaning.

Prepare 500-mL Erlenmeyer flasks by either of the two methods described below, provided that the method imparts no odor to the sample. Make tests with freshly cleaned containers.

1) Without wearing rubber gloves, wash flask with soapy water. Additionally, scrub outside of flask with scouring pad to

TABLE 2170:II. REPRESENTATIVE ODOR REFERENCE STANDARDS*

Compound	Odor Characteristics	Stock Solution Concentration *mg/L*	Amount Placed Into 200 mL Pure Water at 25°C for Presentation
2,3,6-Trichloroanisole	Leather, earthy	1000	4 μL for 20 μg/L
2,3-Diethylpyrazine	Mildew, damp basement	1000	2 μL for 10 μg/L
2-Isopropyl-3-methoxypyrazine	Potato bin, musty	1000	40 μL for 200 μg/L
Nonanal	Hay, sweet	1000	40 μL for 200 μg/L
Dimethyl sulfide	Decaying vegetation, canned corn	1000	1 μL for 5 μg/L
Dimethyl disulfide	Septic	1000	2 μL for 10 μg/L
Dimethyltrisulfide	Garlicky, oniony, septic	0.2	50 μL for 50 ng/L
Butyric acid	Putrid, sickening	1000	200 μL for 1 mg/L
trans,2-Nonenal	Cucumber with skin	1000	40 μL for 200 μg/L
Diphenyl ether	Geranium	1000†	20 μL for 100 μg/L
D-Limonene	Citrusy	1000	400 μL for 2 mg/L
Hexanal	Lettuce heart, pumpkin, green pistachio	1000	40 μL for 200 μg/L
2-Isobutyl-3-methoxypyrazine	Green/bell pepper, musty	1000	40 μL for 200 μg/L
trans,2-*trans*,4-Decadienal	Rancid, oily	1000	1000 μL for 5 mg/L
Butanol	Alcohol, solventy	1000	200 μL for 1 mg/L
Pyridine	Sweet, alcohol, organic	1000	400 μL for 2 mg/L

NOTE: Possible causes of odors or chemical substitutes for causes of odors.
* Adapted from AMERICAN WATER WORKS ASSOCIATION. 1993. Flavor Profile Analysis: Screening and Training of Panelists. AWWA Manual. Denver, Colo.
† Compounds are typically dissolved in methanol.

TABLE 2170:III. SUBSTITUTE ODOR REFERENCE STANDARDS*

Compound	Odor Characteristic	Preparation
Cloves	Spicy (like cloves)	Use supermarket brand of dried clove buds (spice). Add 3 clove buds to 200 mL pure water and swirl 1–2 min. Allow to stand overnight at room temperature, then discard the buds.
Dried grass	Hay	Place dried cut grass in Erlenmeyer flask until half full.
Geranium	Trichloramine	Break geranium stems and place in dry stoppered flask
Grass	Decaying vegetation	Weigh 2 g fresh grass and mix into 200 mL pure water and let stand at room temperature. In 1–3 d, the odor will appear.
Grass	Septic	Allow the solution above for decaying vegetation to stand for an additional 1–2 weeks.
Milk of magnesia	Chalky	Place 4 tablets milk of magnesia in 200 mL pure water
Oil of cade	Smokey	Place 1–2 drops in 200 mL pure water in stoppered container
Rubber hose	Rubber hose	Boil a short section of rubber hose in 200 mL pure water for 5 min. Allow to cool and remove the hose.
Soap	Soapy	Place 5 g of chipped, nonscented bar soap in 200 mL pure water.
Pencil shavings	Woody	Instruct panel member to sharpen a wood pencil and sniff the freshly exposed wood.

NOTE: Standards made from materials rather than chemicals.
* Adapted from AMERICAN WATER WORKS ASSOCIATION. 1993. Flavor Profile Analysis: Screening and Training of Panelists. AWWA Manual. Denver, Colo.

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TABLE 2170:IV. BASIC TASTE STANDARDS

Chemical for Basic Tastes	Food or Beverage Corresponding to Intensity	Concentration %	Intensity Scale (1 to 12)*
Sweet: sugar	Canned fruit or vegetables	5.00	4 W
	Carbonated soda	10.00	8 M
	Syrup, jelly	15.00	12 S
Sour: citric acid	Fresh fruit jelly	0.05	4 W
	Some carbonated sodas	0.10	8 M
	Lemon juice	0.20	12 S
Salt: sodium chloride	Level in bread	0.40	4 W
	Dehydrated soup mix	0.70	8 M
	Soy sauce	1.00	12 S
Bitter: caffeine	Strong coffee	0.05	4 W
		0.10	8 M
		0.20	12 S
or quinine		0.001	4 W
hydrochloride		0.002	8 M
dihydrate		0.004	12 S

* W = weak; M = moderate; S = strong.

remove body oils. Rinse 10 times with hot water and 3 times with odor-free water. To store flask, add 100 to 200 mL odor-free water and ST32 ground-glass stopper. Before use, rinse with 100 mL odor-free water. If there is residual odor, repeat cleaning.

2) Do not handle with rubber gloves. Before use, add 200 mL odor-free water and heat to boiling; lightly lay ST32 ground-glass stopper over flask opening, permitting water vapor to escape. Discard boiled water, and let flask cool to room temperature. If there is residual odor, repeat this procedure or use cleaning alternative 1) above. After analyzing a sample, discard it, rinse flask 10 times with hot tap water, add 200 mL odor-free water and ST32 ground-glass stopper, and store.

For flasks with persistent odor, use commercial glassware cleaning mixture or HCl (1:1).

b. Sample collection: Collect sample in cleaned container. When sampling from a tap, remove all screens and aerators to minimize turbulence. Flush tap at least 5 min, unless a sample indicative of the standing water from the tap is desired. In that case, take an immediate sample from it (i.e., do not flush first). Reduce flow rate during sampling. Rinse bottle with sample, then fill it to the top (no headspace). Chill or refrigerate sample immediately, and analyze as soon after collection as possible—preferably within 24 h but no longer than 48 h.

c. Sample preparation: Pour samples into properly prepared glassware or acceptable disposable containers. Analyze samples at the same temperature. Adjust sample temperatures by placing samples in a water bath 15 min before analysis. Prepare a sample for each panelist. Examine odor samples before flavor samples.

1) Odor analysis—When using 500-mL Erlenmeyer flasks for odor analysis, place 200 mL sample in the flask. Make transfer carefully to avoid loss of volatile components. When 7- to 8-oz (207- to 237-mL) plastic cups are used, place 60-mL sample portions in cups and cover with watch glasses. When 16-oz (473-mL) plastic cups are used, place 200-mL portions in cups and cover with watch glasses.

2) Taste analysis—Bring sample to 25°C before pouring into containers for tasting. Cover each container with a watch glass if samples are not tasted immediately. If samples are tested at 25°C for odor, use the same sample for flavor analysis.

d. Pre-test considerations: Notify panelists (see 2170B.3) well in advance of panel session so a substitute can be found if necessary. The panel consists of at least four or five members. If fewer than four panelists are available, store the sample until a full panel can meet. Panelists who have colds or allergic attacks on the day of the panel are unacceptable; they should ask the panel coordinator to find a substitute. Panelists must not smoke or eat for 30 min before the session. Wearing cologne or perfume or washing hands with scented soap before the session is not permitted.

e. Sample analysis:

1) Odor analysis—Heat samples to proper temperature. If Erlenmeyer flasks are used, sample temperature is 45°C. If plastic cups are used, sample temperature is 25°C. Give each panelist his/her own sample. If a flask is used, hold it with one hand on the bottom and the other on the ST32 ground-glass stopper. Do not touch flask neck. Gently swirl (do not shake) flask circularly to ensure that volatile compounds are released into the headspace. Bring flask close to nose, remove ST32 ground-glass stopper, and sniff at flask opening. Record impressions of odor attributes (in the order perceived) and assessment of each attribute's intensity. If a cup is used, gently swirl the cup for a few seconds without lifting it off the tabletop. Remove watch glass and, keeping hands away from the cup, sniff sample and record perceptions. **CAUTION: Only sniff samples known to be toxicologically safe.** For both the flask and the plastic cup method, smell all samples before going on to the taste test. Do not discuss or interact with other panelists until the time for discussion.

2) Flavor analysis—When tasting, take sample into the mouth and roll it over the entire surface of the tongue. Slurping enhances the odor aspect of flavor. **CAUTION: If samples are of**

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unknown, untested water, do not taste. Only taste samples that have been verified by microbiological and organic/inorganic chemical tests to be safe for human consumption. Do not discuss or interact with other panelists until the time for discussion.

3) Intensity—In both taste and odor analysis, each panelist determines intensity ratings by matching the intensity of the flavor or odor perceived with the defined intensities of the basic taste (sweet) standard. This may be difficult initially. Some panels have found it helpful to make a basic taste standard available throughout the analysis so any panelist who wishes to "recalibrate" may do so.

4) Re-examination of samples—First impressions are most important, particularly for intensity. The intensity rating may diminish upon re-examination because of fatigue [see ¶ *e*6) below] and odorant volatility. However, if an odor or flavor is difficult for a panelist to describe, the panelist may go back and re-evaluate the sample before recording results.

5) Individual results—As soon as a sample is tasted or smelled, record individual results. Information recorded includes a description of odors or flavors perceived, their intensity, and the order in which they were perceived.

6) Rest interval—Sniff odor-free water and rest at least 2 min between samples. *Fatigue* (more properly called *adaptation)* is a decrease in a panelist's sensitivity to a given taste- or odor-producing substance (tastant or odorant) because the person has previously been exposed to that substance. Put simply, a panelist is no longer responsive to a taste or odor because that person has had too much sensory stimulation. Geosmin and 2-methylisoborneol are two compounds known to produce fatigue; after exposure to four samples, a person begins to have difficulty smelling these odorants and cannot assess intensity accurately. Other compounds (e.g., sugar) do not seem to produce fatigue. Because odor mixtures are more complex than taste mixtures, olfactory adaptation is more serious.[6]

Because the odorants or tastants in water samples are frequently unknown in advance, it is prudent to give panelists only 4 to 5 samples per FPA testing session and ask them to rest between samples. The rest interval also is important because it prevents carryover of odors between samples. If the samples are known to contain geosmin or 2-methylisoborneol, then definitely limit the session to four samples and ask panelists to wait 3 min between samples and clear their noses or palates with taste- and odor-free water.

Factors that can induce fatigue include odor intensity, type of odorants (some compounds, such as geosmin and chlorine, induce more fatigue than others), number of samples tested during a session, and rest interval between samples.[1,7] The panel leader also may try to order samples so those known to cause fatigue are placed near the end of the sample row.[16] Avoid juxtaposing such samples. Also, use taste- and odor-free blanks between samples.

7) Dechlorination of samples[17]—The odor of chlorine is distinctive and may mask other odors in a sample. If it is desirable to assess odors other than the chlorinous odor, remove the chlorine species via a reducing agent, such as sodium thiosulfate or sodium sulfite (see Section 4500-NH_3). Hydrogen peroxide and ascorbic acid also can be used to reduce chlorine; appropriate quantities are presented in Tables 2170:V and VI. Hydrogen peroxide is not efficient for reducing chloramines, however, because the kinetics are too slow. Take special care not to overdose these chemicals because overdosage can affect the water's flavor. For example, adding too much hydrogen peroxide can impart a sweet odor. Use caution with sodium thiosulfate because adding more than the stoichiometric dose could result in a "sulfur" odor from production of reduced sulfur compounds.

TABLE 2170:V. STOICHIOMETRIC DOSAGES OF DECHLORINATING AGENTS

Dechlorination Agent	Stoichiometric Dose *mg agent/mg Cl as Cl_2*	Effective Dose *mg agent/mg Cl as Cl_2*
Ascorbic acid	2.48	3.0
Hydrogen peroxide	0.48	0.6
Oxalic acid	1.27	45.0
Sodium nitrite	0.97	1.1
Sodium thiosulfate	0.56	2.2

SOURCE: WORLEY, J.L., A.M. DIETRICH & R.C. HOEHN. 2003. Dechlorination techniques to improve sensory odor testing of geosmin and 2–MIB. *J. Amer. Water. Works Assoc.* 95(3):109.

8) Consensus development[7,10,13,16]—When all panelists have had an opportunity to examine the sample, hold a discussion period. Each panelist states his/her impression of the sample, which the panel leader records for everyone to see. On examining the order of appearance, intensity, and descriptors of tastes and odors, the panel leader attempts to group responses together, soliciting comments from panel members as to whether they agree. Sometimes panelists detect an odor that they cannot describe; in the discussion, they may see what another panelist called it and decide to agree with that description. With inexperienced panels, several descriptors may be used for one taste or odor. As the panel gains more experience, these differences tend to be reconciled. It is the panel leader's responsibility to ensure that panelists are provided with standards that duplicate the sample tastes and odors. Descriptions that fewer than 50% of the panelists use are called "other notes" and are listed separately or not included in group results.

9) Recording panel results—Record the following: sample description; time of sampling; identity of each panel member; taste, odor, and feeling descriptors; intensity rating; order of perception; and range and average for each descriptor.

TABLE 2170:VI. DECHLORINATING AGENT DOSAGE CHART FOR CHLORINE

Dechlorinating Agent	Strength of Dechlorinating Agent	Approximate Total Chlorine Concentration *mg/L as Cl_2*	Dosage of Dechlorinating Agent
Ascorbic acid	5 g/L	1	1.2 mL
		2	2.4 mL
		3	3.6 mL
		4	4.8 mL
Hydrogen peroxide	3% (drug-store grade)	1	40 μL
		2	80 μL
		3	120 μL
		4	160 μL

SOURCE: WORLEY, J.L., A.M. DIETRICH & R.C. HOEHN. 2003. Dechlorination techniques to improve sensory odor testing of geosmin and 2–MIB. *J. Amer. Water. Works Assoc.* 95(3):109.

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8. Calculation and Interpretation[7,16]

Calculate intensity means (and standard deviations) if at least 50% of panelists agree on a given descriptor or if descriptors can be grouped together (e.g., plastic and vinyl). If a panelist does not give that description, assign an intensity value of zero. For example, FPA of a drinking water sample could produce the following data:

	Intensity				
	Report by Individual Panelist				
Descriptor	I	II	III	IV	Mean
Musty	2	4	0	2	2.0
Chlorinous	2	4	4	4	3.5

Acceptability of the water to consumers should be the underlying guideline for any interpretation of panel results. For example, if plant effluent has an odor or taste intensity average of 5 or higher, and the descriptor is "earthy," this would indicate a potential for consumer complaints. Levels of intensities and descriptors that would constitute a possible problem need to be determined in advance. Panelists should know when results would be atypical for the samples that were analyzed and should notify the proper person(s) immediately for follow-up action. Only experienced and trained panelists should interpret panel results.

9. Quality Control[16]

Expose panelists to samples of known composition, such as odor-free samples (blanks), samples with known additions, and duplicates, as frequently as possible. Analyze blind, coded samples periodically to prevent overfamiliarity with routine samples. The odor-free sample serves to detect guessing. Duplicates check reproducibility. A standard concentration of an odor reference standard in odor-free water or a matrix sample also can be used to check odor recognition and reproducibility of the intensity scale.

Counterbalance samples so each panelist receives them in a different order. This prevents error due to order effects, such as fatigue, carryover, and expectation. When possible, samples should be coded and split within panels from the same laboratory or other laboratory FPA panels, and their results compared (intralaboratory and intrapanel comparsions). This ensures acceptable, reproducible results, as well as confidence in panels' results.

10. Precision and Bias

Initial studies of precision and bias have been completed,[16] including a reproducibility study on the use of reference materials.[15]

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Examples of Customer Complaints

Customer Complaint	Possible Cause
Red water or reddish-brown staining of fixtures and laundry	Corrosion of iron pipes or presence of natural iron in raw water
Bluish stains on fixtures	Corrosion of copper lines
Black water	Sulfide corrosion of copper or iron lines or precipitations of natural manganese
Foul tastes and/or odors	Byproducts from microbial activity
Loss of Pressure	Excessive scaling, tubercule (buildup from pitting corrosion), leak in system from pitting or other type of corrosion
Lack of hot water	Buildup of mineral deposits in hot water system (can be reduced by setting thermostats to under 140°F [60°C])
Short service life of household plumbing	Rapid deterioration of pipes from pitting or other types of corrosion

Odor (TON) Analysis

Odor, like taste, depends on contact of a stimulating substance with the appropriate human receptor cell. The stimuli are chemical in nature and the term "chemical senses" often is applied to odor and taste. Water is a natural medium, always present on or at the receptors that perceive sensory response. In its pure form, water is odor-free. Man and other animals can avoid many potentially toxic foods and waters because of adverse sensory response. These senses often provide the first warning of potential hazards in the environment.

Odor is recognized as a quality factor affecting acceptability of drinking water (and foods prepared with it), tainting fish and other aquatic organisms, and esthetics of recreational waters. Most organics and some inorganic chemicals contribute taste or odor. These chemicals may originate from municipal and industrial waste discharges, from natural sources such as decomposition of vegetable matter, or from associated microbial activity, and from disinfectants or their products.

Some odorous materials are detectable when present in only a few nanograms per liter. Due to this fact, it is usually impractical and often impossible to isolate and identify the odor-producing chemical. The human nose is the practical odor-testing device used in this method. Odor tests are performed to provide qualitative descriptions and approximate quantitative measurements of odor intensity. The method for intensity measurement presented here is the threshold odor test.

The principle for threshold odor testing is to dilute a sample with odor-free water until the least definitely perceptible odor is achieved. There is no absolute threshold odor concentration, because of inherent variation in individual olfactory capability. A given person varies in sensitivity over time. Day-to-day and within-day differences occur.

Sampling and Storage

Collect samples in glass bottles, plastic bottles can leave a plastic smell. Complete tests as soon as possible. If storage is necessary, collect at least 500 mL of sample in a bottle filled to the top; refrigerate, making sure no extraneous odors can be drawn into the sample as it cools. Often is it desirable to determine the odor of the water with and without chlorine. Dechlorinate with sodium thiosulfate.

❖ Threshold Odor Number (TON) Test

- Temperature
  - Values vary with temperature
  - For most tap waters and raw water sources, a sample temperature of 60°C will permit detection of odors that otherwise might be missed
  - 40°C can also be used as the test temperature
  - Report temperature at which observations are made
- Apparatus
  - Constant temperature bath: either water bath or electric hot plate capable of temperature control of ± 1°C
- Procedure
  - Insure tester is free from allergies or colds that affect odor response

- Measurement:
  - Place proper volume of odor-free water in the flask first, add sample to water
  - Shake flask containing odor-free water, remove stopper and sniff vapors
  - Test sample with least amount of odor-bearing water in the same way
    - If odor can be detected in this dilution, prepare more dilutions
    - If odor can't be detected in first dilution, repeat above procedure using sample containing next higher concentration of odor-bearing water, continue until odor is detected clearly

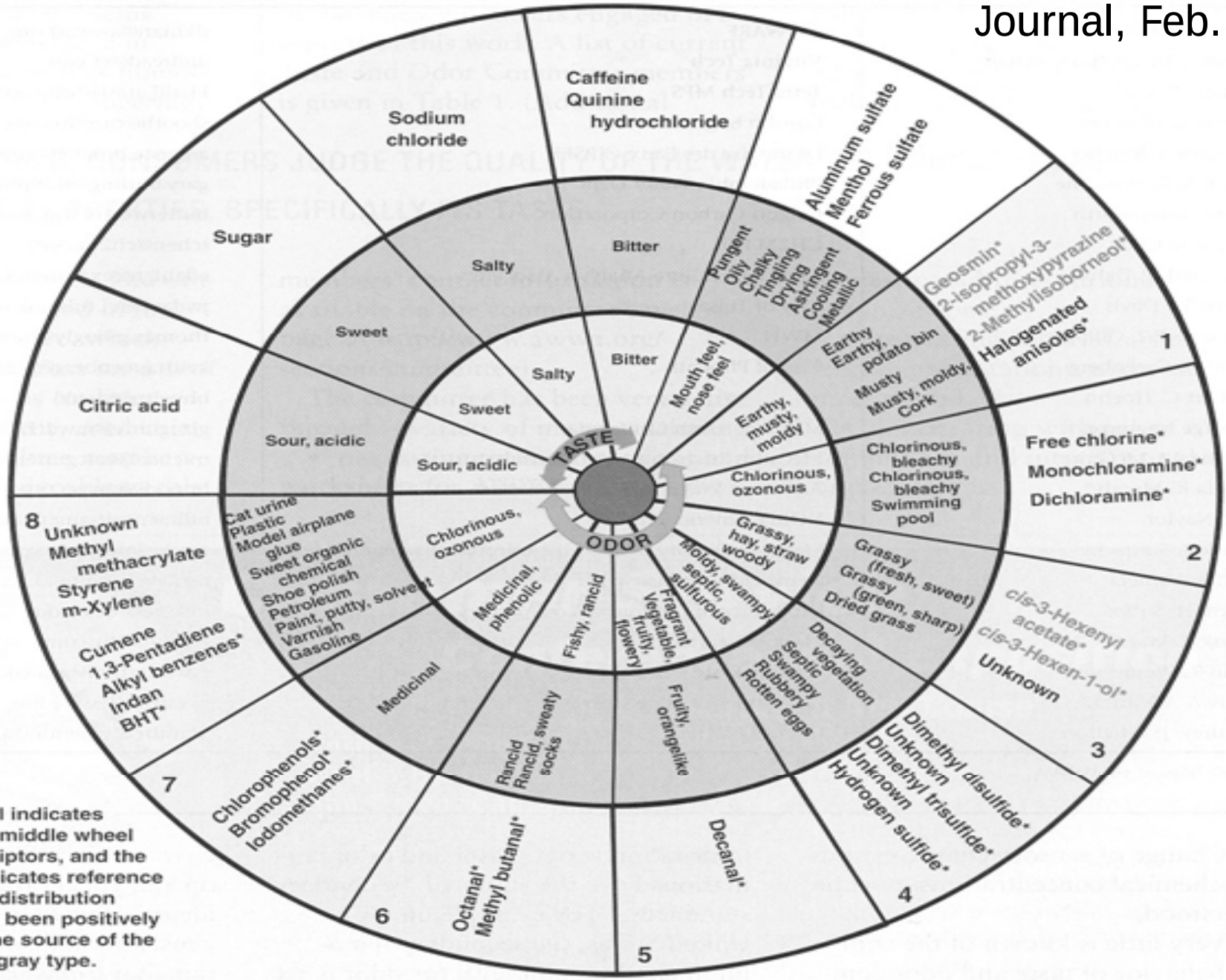
➢ Calculation

- The threshold odor number is the dilution ratio at which odor is just detectable.
- $TON = \frac{A + B}{A}$

- where: A = mL of sample
  B = mL of odor-free water

Courtesy of AWWA Journal, Feb. 2004

FIGURE 1 Wheel identifying distribution system–generated tastes and odors



The inner wheel indicates categories, the middle wheel indicates descriptors, and the outer wheel indicates reference standards. The distribution system has not been positively confirmed as the source of the compounds in gray type.

*Presence confirmed in water

Source: D. Khiari et al, 2002. *Distribution Generated Taste-and-Odor Phenomena.* AwwaRF Report, AWWA Bookstore catalog no. 90897. AWWA, Denver.