Water Treatment Laboratory Workshop

Week 2

Course # 2122

Fleming Training Center

Your Partner in Clean Water

TDEC

TENNESSEE DEPARTMENT OF ENVIRONMENT AND CONSERVATION

Fleming Training Center

State of Tennessee

Water Treatment Laboratory
Week 2
Course #2122

Monday

8:30	Lab Safety and Policies	Amanda
9:30	Fluoride	Amanda
10:30	Carbon Dioxide	Amanda
11:00	Lunch	
12:00	Solids	Amanda

Tuesday

8:30	Hardness, Alkalinity	Amanda
11:30	Lunch	
12:30	TDS & Conductivity	Amanda
1:30	Langelier Index	Amanda

Wednesday

8:30	Heterotrophic Plate Count	Amanda
9:30	Metals and Organic Analysis	Amanda
11:00	Lunch	
12:00	Tour—to be announced	

Thursday

8:30	Iron	Amanda
9:30	Manganese	Amanda
11:00	Lunch	
12:00	Nitrate & Nitrite	Amanda
1:30	Taste & Odor	Amanda

Friday

8:30	Instrument & Probe Maintenance	Amanda
9:00	Review/Questions	Amanda
11:00	Lunch	
12:00	Class Exam and Evaluations	Amanda

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Water Treatment Laboratory
Week 2
Course # 2122

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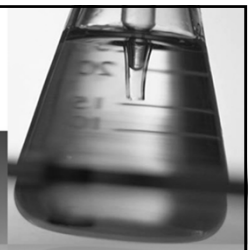
Lab Policies

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 Material Safety Data Sheets for all chemicals used in the laboratory.



Lab Safety

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

Chemical Spill

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

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

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.

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.

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.

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

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.

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.

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

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

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.

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.

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.

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

Section 1
Fluoride

Fluoride

Water Treatment Lab

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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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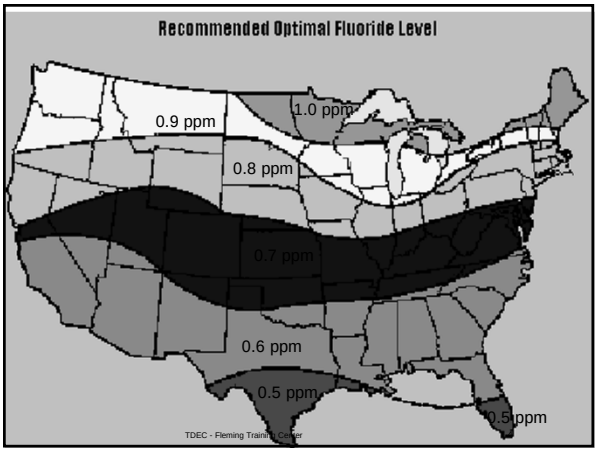

Who, What, Where, Why, How

- 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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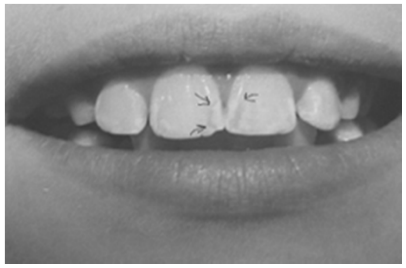
Who? (continued)

- 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)

Fluorosis

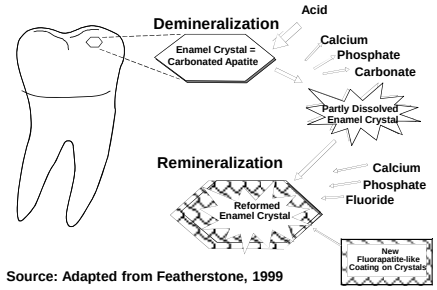


Mild Fluorosis

Fluorosis

Moderate Fluorosis w/ stains

How Fluoride Works



Source: Adapted from Featherstone, 1999

Alternatives to Fluoridated Water

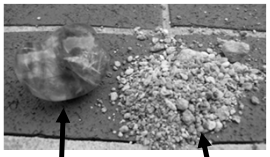
- Fluoridated water most common vehicle (various estimates of 220-300 million people worldwide)
- Fluoridated salt second most common vehicle (various estimates of 40-300 million people worldwide)
- Dietary fluoride supplements -- drops, tablets, or vitamins (60 million people-WHO 2003)
- Fluoridated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

Industrial Waste???

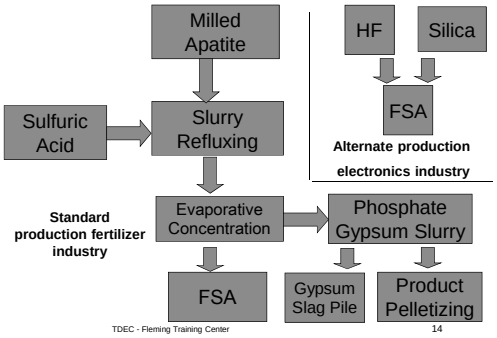
- Opposition wants us to believe it is an industrial waste by-product

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



Fluorosilicic Acid (FSA)



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.

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

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.

Fluoride Analysis

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

Fluoride Analysis

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

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

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

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.

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.

Electrode

- Calibrate with a 1 mg/L and 10 mg/L
  - Recommended daily
- Measure 25 mL of sample and 25 mL of TISAB (of half and half)
- Stir sample and measure with electrode
- Less interferences because of TISAB

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

DOC316.53.01184

USEPA[1] SPADNS 2[2] **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; see *Distillation* in this procedure).

[1] Procedure is equivalent to USEPA method 340.1 for drinking water and wastewater analysis

[2] Adapted from *Standard Methods for the Examination of Water and Wastewater, 4500-F B & D.*

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 1 Instrument-specific information

Instrument	Powder pillows		AccuVac Ampuls	
	Sample cell	Cell orientation	Sample cell	Adapter
DR 5000	2495402	Fill line faces user	2427606	—
DR 3900	2495402	Fill line faces user	2427606	LZV846 (A)
DR 3800, DR 2800, DR 2700	2495402	Fill line faces right	2122800	LZV584 (C)

Before starting the test:

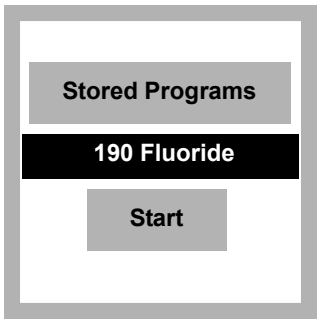
The sample and deionized water should be at the same temperature (± 1 °C). Temperature adjustments may be made before or after reagent addition.
SPADNS 2 Reagent is corrosive. Use care while handling the reagent.
For best results, measure the volume of SPADNS 2 Reagent as accurately as possible.
If the instrument displays Over Measure Range!, dilute a fresh sample with an equal volume of deionized water and repeat the test, using this solution in step 2. Multiply the result by 2.
SPADNS 2 Reagent contains a non-toxic reducing agent to prevent chlorine interference. SPADNS 2 does not contain sodium arsenite.

Collect the following items:

Description	Quantity
Solution test	
SPADNS 2 Reagent Solution	4 mL
Deionized Water	10 mL
Pipet, volumetric, 2-mL	1
Pipet, volumetric, 10-mL	1
Pipet Filler Bulb	1
Sample cells (see *Instrument-specific information*)	2
Thermometer	1
AccuVac test	
SPADNS 2 Fluoride Reagent AccuVac® Ampuls	2
Deionized Water	40 mL
Beaker, 50-mL	1

See *Consumables and replacement items* for reorder information.

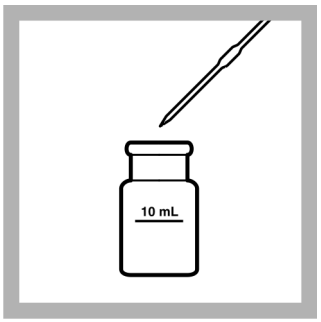
SPADNS 2 reagent solution



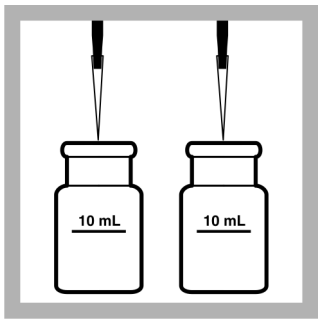
1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).

2. Prepared Sample: Pipet 10.0 mL of sample into a dry sample cell.



3. Blank Preparation: Pipet 10.0 mL of deionized water into a second dry sample cell.



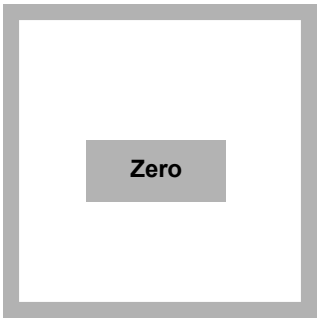
4. Carefully pipet 2.0 mL of SPADNS 2 Reagent into each cell. Swirl to mix.

SPADNS 2 reagent solution (continued)

5. Start the instrument timer.

A one-minute reaction period will begin.

6. When the timer expires, insert the blank.



7. **ZERO** the instrument.

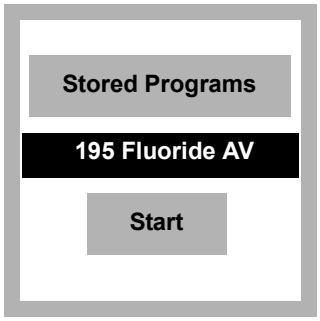
The display will show:

0.00 mg/L F^-

8. Insert the prepared sample cell.

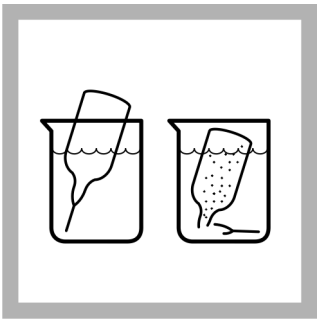
READ the results in mg/L F^-.

SPADNS 2 AccuVac® Ampuls



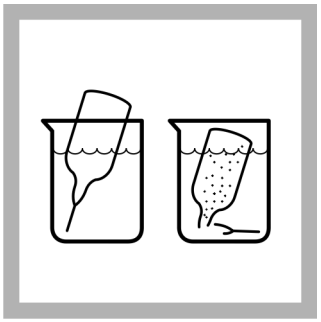
1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).



2. **Prepared Sample:** Collect at least 40 mL of sample in a 50-mL beaker.

Fill one SPADNS 2 Fluoride Reagent AccuVac Ampul with sample. Keep the tip immersed while the Ampul fills completely.



3. **Blank Preparation:** Pour at least 40 mL of deionized water into a second beaker.

Fill a second Ampul with deionized water. Keep the tip immersed while the Ampul fills completely.

4. Quickly invert both Ampuls several times to mix.

SPADNS 2 AccuVac® Ampuls (continued)

5. Start the instrument timer.

A one-minute reaction period will begin.

6. When the timer expires, insert the blank into the cell holder.

ZERO the instrument.

The display will show:

0.00 mg/L F^-

7. Insert the prepared sample into the cell holder

READ the results in mg/L F^-.

Interferences

This test is sensitive to small amounts of interference. 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.

Table 2 Interfering substances

Interfering substance	Interference level
Alkalinity (as $CaCO_3$)	At 5000 mg/L causes a - 0.1 mg/L F^- error
Aluminum	At 0.1 mg/L 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 causes a +0.1 mg/L F^- error
Chlorine	SPADNS 2 Reagent contains enough non-toxic reductant to eliminate interference up to 5 mg/L chlorine. For higher chlorine levels: **1.** Dilute sample with deionized water by a factor that will lower chlorine concentration to below 5 mg/L. **2.** Perform the SPADNS 2 reagent solution or AccuVac procedure. **3.** Multiply results by the dilution factor to obtain mg/L Fluoride.
Iron, ferric	At 10 mg/L causes a - 0.1 mg/L F^- error
Phosphate, ortho	At 16 mg/L causes a +0.1 mg/L F^- error
Sodium Hexametaphosphate	At 1.0 mg/L causes a +0.1 mg/L F^- error
Sulfate	At 200 mg/L causes a +0.1 mg/L F^- error

Distillation

Distillation Solution Preparation:

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. Allow the solution to cool before handling.***

To eliminate most interferences, dilute the sample from the acid solution as described below:

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

Note: *When distilling samples with high amounts of chloride, add 5 mg of Silver Sulfate to the sample for every mg/L of chloride in the sample.*

6. With the thermometer in place, turn the heat control to 10. The yellow pilot lamp indicates the heater is on.
7. When the temperature reaches 180 °C or when 100 mL of distillate has been collected, turn the still off (requires about 1 hour).
8. Dilute the distillate to a volume of 100 mL, if necessary. The distillate may now be analyzed by the SPADNS, SPADNS 2 or the fluoride ion-selective electrode method.

Sample collection, preservation and storage

- Samples may be stored in glass or plastic bottles for at least seven days when cooled to 4 °C (39 °F) or lower.
- Warm samples to room temperature before analysis.

Accuracy check

Standard solution method
Note: *Refer to the instrument user manual for specific software navigation instructions.*

A variety of standard solutions for the entire range of the test is available. Use standard solutions instead of sample to verify the technique.

Minor variations between lots of reagent become measurable above 1.5 mg/L. While results in this region are usable for most purposes, better accuracy may be obtained with steps 1–3.

1. Dilute a fresh sample 1:1 with deionized water.
2. Perform the test again
3. Multiply the result by 2.
4. To adjust the calibration curve with the reading obtained with the standard solution, select **Options>More>Standard Adjust** from the instrument menu.

5. Turn on the Standard Adjust feature and accept the displayed concentration. If an alternate concentration is used, enter the concentration and adjust the curve to that value.

Method performance

Program	Standard	Precision 95% Confidence Limits of Distribution	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

Safety

Follow good safety habits and laboratory techniques throughout the procedure. Consult the *Material Safety Data Sheet* for information specific to the reagents used.

Pollution prevention and waste management

SPADNS 2 Reagent does not contain sodium arsenite. Instead, it contains a non-toxic species to prevent chlorine interference. Dispose of all waste safely in accordance with local and federal guidelines.

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. Test results are measured at 580 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
SPADNS 2 Reagent Solution	4 mL	500 mL	2947549
OR			
SPADNS 2 Fluoride Reagent AccuVac® Ampuls	2	25/pkg	2527025
Water, deionized	10 mL	4 L	27256

Required apparatus (solution)

Description	Quantity	Unit	Catalog number
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
Sample cell, 10 mL square, matched pair	2	2/pkg	2495402
Thermometer	1	each	2635700

Required apparatus (AccuVac)

Description	Quantity	Unit	Catalog number
Beaker, 50-mL	1	each	50041H
Sample cell, 10 mL round, 25 x 54 mm	1	each	2122800
Sample cell, 10 mL round, 25 x 60 mm	1	6/pkg	2427606

Recommended standards

Description	Unit	Catalog number
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
Standard, Drinking Water, Mixed Parameter, Inorganic for F^-, NO_3, PO_4, SO_4	500 mL	2833049

Distillation reagents and apparatus

Description	Quantity	Unit	Catalog number
Cylinder, graduated, 100-mL	1	each	50842
Cylinder, graduated, 250-mL	1	each	50846
Distillation Heater and Support Apparatus Set,115 VAC, 50/60 Hz	1	each	2274400
AND			
Distillation Heater and Support Apparatus Set,230 VAC, 50/60 Hz	1	each	2274402
OR			
Distillation Apparatus Set, General Purpose	1	each	2265300
Flask, Erlenmeyer, 125-mL	1	each	2089743
Flask, Erlenmeyer, 250 mL, Glass	1	each	50546
Glass Beads	1	100/pkg	259600
Stir Bar, magnetic	1	each	1076416
Sulfuric Acid, ACS	1	500 mL	97949

Optional reagents and apparatus

Description	Unit	Catalog number
Silver Sulfate	113 g	33414
Balance Analytical 80 g x 0.1 mg 100–240 V	each	2936701
Weighing papers	500/pkg	1473800

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Fluoride Bench Sheet

	Tap	A	B
Probe			
SPADNS 2			

Section 2
Carbon Dioxide

CO_2 Analysis

1 TDEC - Fleming Training Center

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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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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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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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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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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Calculation

- mg 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

Buret Titration Method[1]

Method 8223

0 to 250 mg/L

Buret Titration

Scope and Application: For water and seawater.

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

Test preparation

Before starting the test:

Avoid excess agitation when collecting and swirling the sample to prevent the loss of carbon dioxide. Measure the sample directly in the Erlynmeyer flask to avoid agitation.
For more accurate results, check the calibration of the Erlenmeyer flask. Fill a graduated cylinder with the sample volume of deionized water. Pour the water into the Erlenmeyer flask and mark the correct level with a wax pencil or permanent marker.
Four drops of Phenolphthalein Indicator Solution[1] can be substituted for the Phenolphthalein Indicator Powder Pillow.
The concentration of the sodium hydroxide standard solution will slowly decrease. To prevent deterioration, keep the bottle tightly sealed after use. Fill the buret immediately before the test is started and discard the remaining solution after the test. Follow the *Accuracy check* each month to make sure the solution will give accurate results.
A pH meter can be used in place of the indicators. The end point pH is 8.3.
For added convenience when stirring, use the TitraStir® stirring apparatus.

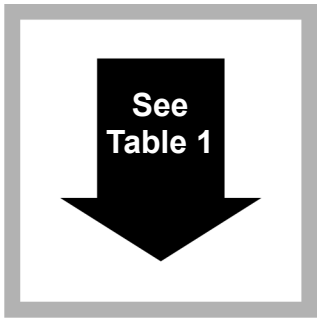
[1] See *Optional reagents and apparatus*.

Collect the following items:

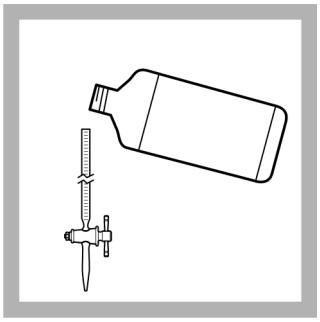
Description	Quantity
Phenolphthalein Indicator Powder Pillow	1
Sodium Hydroxide Standard Solution, 0.0227 N	1 bottle
Buret, Class A, 25-mL, with support stand	1
Erlenmeyer flask	1

See *Consumables and replacement items* for reorder information.

Buret titration

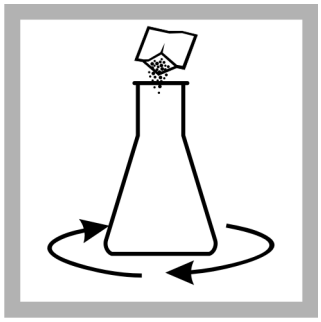


1. Select a sample volume and flask from the *Range-specific information* table.

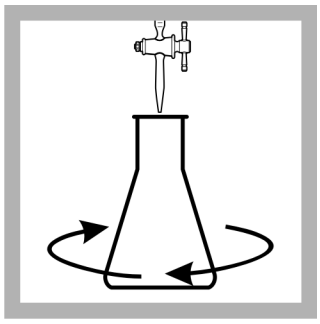


2. Fill a 25-mL buret to the zero mark with 0.0227 N Sodium Hydroxide Standard Solution.

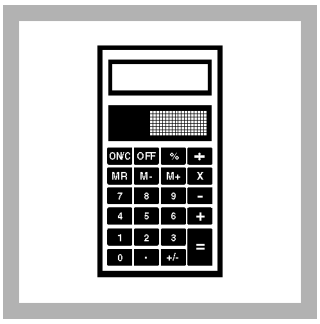
3. Fill a clean Erlenmeyer flask to the selected volume. If collected from a faucet, allow the sample to overflow several times and then pour off the excess sample.



4. Add the contents of one Phenolphthalein Indicator Powder Pillow and mix gently.



5. Titrate the sample while gently swirling the flask until a light pink color forms and persists for 30 seconds.



6. Calculate:

mL titrant used x multiplier = mg/L as CO_2

Example: 100 mL of sample was titrated and 15 mL of titrant was used to reach the endpoint. The concentration is 15 x 10 = 150 mg/L as CO_2

Table 1 Range-specific information

Range (mg/L as CO_2)	Sample volume (mL)	Flask size	Multiplier
0–125	200	250	5
100–250	100	125	10

Interferences

Interfering substances lists substances that can interfere with this test.

Table 2 Interfering substances

Interfering substance	Interference level
Color or turbidity	Color or turbidity can mask the color change of the end point. Use a pH meter instead of the phenolphthalein indicator and titrate to a pH of 8.3.
Acids	Acids other than carbonic acid will be titrated and interfere directly.

Sample collection, preservation and storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Complete the test procedure as soon as possible after collection for best accuracy. The sample can be stored for at least 24 hours if cooled.

Accuracy check

The standard additions method can be used to find if the sample has an interference. The standard solution method can be used to confirm analytical technique and reagent performance.

Standard additions method (sample spike)
Required for accuracy check:

- Carbon Dioxide Voluette® Ampule Standard Solution, 10,000-mg/L as CO_2
- Ampule breaker
- TenSette Pipet, 0.1–1.0 mL and Pipet Tips.

1. Open the standard solution ampule.
2. Use the TenSette Pipet to add 0.1 mL of the standard to the titrated sample. Swirl to mix.
3. Titrate the spiked sample to the end point. Write down the amount of titrant that was used to reach the end point.
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. Write down the amount of titrant that was used to reach the end point.
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. Write down the amount of titrant that was used to reach the end point.
8. Each 0.1 mL of standard that was added will use 1.0 mL of titrant to reach the endpoint. If more or less titrant was used, there may be an interference (see *Interferences*) or the concentration of the titrant has changed (see *Standard solution method*).

Standard solution method
A sodium hydroxide standard solution will slowly absorb carbon dioxide from the atmosphere, which forms carbonic acid and neutralizes some of the hydroxide. When sealed in plastic bottles, the sodium hydroxide concentration will decrease by approximately 1% per year. Complete the following test to make sure the concentration is accurate.

Required for accuracy check:

- Potassium Acid Phthalate Standard Solution, 100-mg/L as CO_2

1. Add 50.0-mL of Potassium Acid Phthalate Standard Solution, 100-mg/L as CO_2 to an Erlenmeyer flask.
2. Add the phenolphthalein indicator and swirl to mix.
3. Titrate the standard to the end point with the sodium hydroxide standard solution. The titration should require 5.00 mL of sodium hydroxide solution. If the volume is greater than 5.25 mL, discard the sodium hydroxide and replace it with a fresh supply.

   Note: *To correct for a reduction in strength, divide 5.00 by the number of mL required for this titration. Multiply all sample results by this factor.*

Summary of method

The analysis for dissolved carbon dioxide in water is similar to that for acidity. A water sample is titrated to a phenolphthalein end point at pH 8.3 with a sodium hydroxide standard solution. Strong mineral acids are assumed to be absent or their effect to be negligible.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
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	Catalog number
Buret, Class A, 25-mL	1	each	2636540
Buret Clamp, double	1	each	32800
Flask, Erlenmeyer, graduated, 125-mL	1	each	50543
Flask, Erlenmeyer, graduated, 250-mL	1	each	50546
Support Stand	1	each	56300

Recommended standards

Description	Unit	Catalog number
Carbon Dioxide Standard Solution, Voluette® Ampule, 10,000-mg/L as CO_2, 10-mL	16/pkg	1427510
Potassium Acid Phthalate Standard Solution, 100-mg/L as CO_2	100 mL	226142

Optional reagents and apparatus

Description	Unit	Catalog number
Phenolphthalein Indicator Solution, 5-g/L	100 mL	16232
TenSette Pipet, 0.1 to 1.0 mL	each	1970001
Pipet Tips, for TenSette Pipet 1970001[1]	50/pkg	2185696
Water, deionized	500 mL	27249
Cylinder, graduated, 250 mL	each	108146
Sampling Bottle with cap, low density polyethylene, 500 mL	12/pkg	2087079
Thermometer, Non-Mercury, -10 to 225 °C	each	2635700
Voluette Ampule breaker 10 mL	each	2196800
TitraStir Apparatus, 115 Vac	each	1940000
TitraStir Apparatus, 230 Vac	each	1940010
Stir bar, octagonal 28.6 mm x 7.9 mm	each	2095352

[1] Other sizes are available

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Section 3
Solids

Analysis of Solids

Solids Testing

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

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

Standard Methods 2540B-G

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

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

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

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 = (A – B) x 1,000
- 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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TSS Calculations

- Wt. of filter + residue = A = 1.0215 g
- Wt. of filter = B = 1.0160 g
- Sample volume = 100
- mg/L = 1.0215 – 1.0160

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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

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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]

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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!

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

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

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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.

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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)**

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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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TSS

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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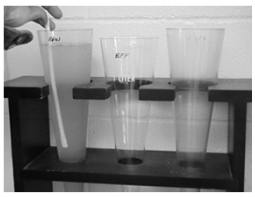
SS SM2540 F – 1997 Settleable Solids

- Dup
- Corrective Action
- Batch Size
- QC Frequency



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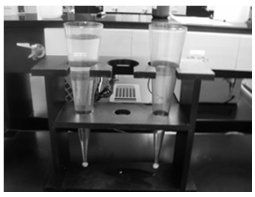
SS SM2540 F – 1997 Settleable Solids

- 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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TSS Sample Worksheet

Sample	Dish Number	Filter Weight, g (B)	Sample Volume, mL (C)	Filter + dried sample, g (A)	Filter + dried sample, g (2nd)	TSS = A-B/C
Dup						
Blank			100			

Solids, Nonfilterable Suspended Solids; Total and Volatile

DOC316.53.001204

USEPA[1] Gravimetric Method[2]

Methods 8158 and 8164

Scope and Application: For water and wastewater.

[1] USEPA accepted.

[2] Adapted from *Standard Methods for the Examination of Water and Wastewater* Section 2450

Test preparation

Before starting the test:

The Total Nonfilterable Solids are the same as the Total Suspended Solids (TSS)

Collect the following items:

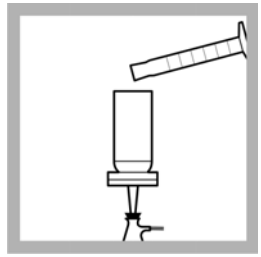
Description	Quantity
Filter flask	1
Filter holder	1
Filter, 47-mm	1
Graduated cylinder, 100-mL	1
Tongs	1
Tweezers	1
Watch glass	1
Desiccator with desiccant	1
Muffle Furnace	1
Drying Oven	1
Deionized Water	varies

See *Consumables and replacement items* for reorder information.

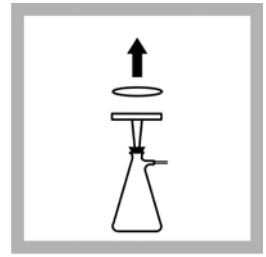
Gravimetric Method—Total Nonfilterable Residue, Method 8158

1. Use tweezers to place a 47-mm glass fibre filter disc in the filter holder. Always use tweezers to handle filter discs.

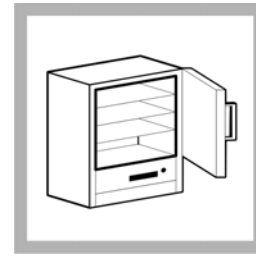
Moisture from fingers can add moisture to the disc and cause a weighing error.



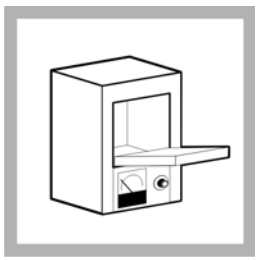
2. Place the filter holder assembly in the filtering flask and add 100 mL of deionized water. Apply vacuum to the flask until all the water is drawn through the filter.



3. Slowly release the vacuum from the filtering system and remove the disc from the filter holder and transfer to a watch glass.



4. Place the disc in a preheated drying oven at 103 °C for one hour.

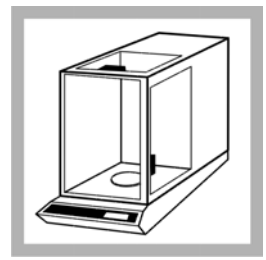


5. If volatile nonfilterable solids are also being measured, use tongs to place the watch glass with the disc into a muffle furnace and ignite at 550 °C for 15 minutes. If not, omit this step.

Partially preheat the muffle furnace before inserting the watch glass. Placing the watch glass in a 550 °C furnace could cause it to shatter. Bring the temperature up to 550 °C 15 minutes after placing the filter and watch glass in the furnace.

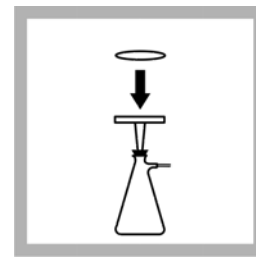
6. Use metal tongs to remove the disc and watch glass from the oven or furnace and place in a desiccator. Cover immediately. Allow the watch glass to cool slightly before sealing the desiccator as pressure from the heated air inside the desiccator can force the cover off.

Allow the filter and glass to cool to room temperature.



7. Remove the watch glass and disc from the desiccator as a unit and place beside the analytical balance.

Use plastic tweezers to remove the disc from the watch glass and weigh to the nearest 0.1 mg (0.0001 g). Record this value as B.



8. Again, place the disc in the filter holder/flask assembly. Wet the disc with deionized water to ensure adhesion to the holder.

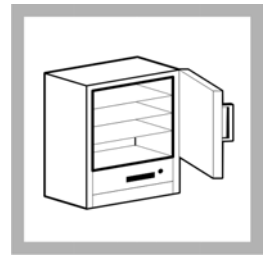
Gravimetric Method—Total Nonfilterable Residue, Method 8158 (continued)

9. Filter 100 mL (or more, if solids content is low) of well-mixed, representative water sample by applying vacuum to the flask. Follow with three separate 10-mL washings of deionized water.

For greatest accuracy, filter as much sample as possible. However, using a sample that contains more than 15 mg of solids will clog the filter prematurely. Adjust the exact volume of the water sample to achieve the optimum condition. Several completed tests will show whether any adjustment is necessary.

10. Remove any residue that remains on the sides or bottom lip of the filter holder. A rubber policeman on the end of a stirring rod is very helpful to scrape the residue loose. Small amounts of deionized water will help wash the residue down onto the filter disc.

Slowly release the vacuum from the filtering system and gently remove the filter disc from the holder. Place the disc on a watch glass. Inspect the filtrate (filtered water in flask) to make sure that the solids are properly trapped on the disc.

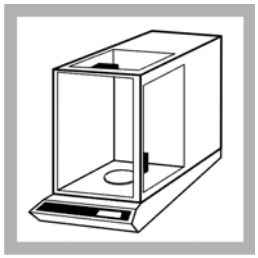


11. Place the watch glass and filter in a drying oven at 103 °C for one hour.

12. Use metal tongs to remove the disc and watch glass from the oven or furnace and place in a desiccator. Cover immediately. Allow the watch glass to cool slightly before sealing the desiccator as pressure from the heated air inside the desiccator can force the cover off.

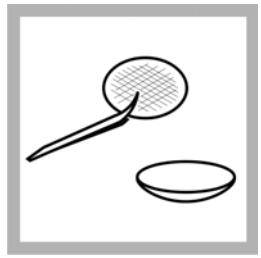
Allow the filter and glass to cool to room temperature.

Gravimetric Method—Total Nonfilterable Residue, Method 8158 (continued)



13. Remove the watch glass and disc from the desiccator as a unit and place beside the analytical balance.

Use plastic tweezers to remove the disc from the watch glass and weigh to the nearest 0.1 mg (0.0001 g). Record this mg value as A.



14. Return the disc to the watch glass if the mg/L Volatile Nonfilterable Residue is to be determined. If not, discard the disc.

If Volatile Nonfilterable Residue is to be determined, do not lose any of the suspended matter on the disc.

15. Calculate Total Non-filterable Residue (TNR):

$$\frac{A - B}{\text{Sample Volume in Liters}} = \text{mg/L TNR}$$

Where:

A = Weight (mg) of disc with residue

B = Weight (mg) of disc

Example:

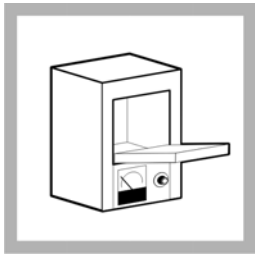
A = 95.5 mg

B = 81.5 mg

Volume of sample = 0.1 L

$$\frac{95.5\text{ mg} - 81.5\text{ mg}}{0.1\text{ L}} = 140\text{ mg/L TNR}$$

Gravimetric Method—Volatile Nonfilterable Solids, Method 8164

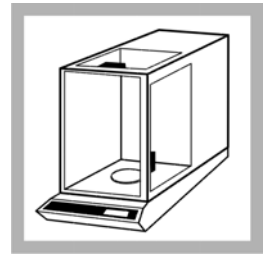


1. Place the watch glass and filter disc from the Total Nonfilterable Residue procedure (step 14) in the muffle furnace and ignite at 550 °C for 15 minutes.

Partially preheat the muffle furnace before inserting the watch glass. However, placing the watch glass in a 550 °C furnace could cause it to shatter. Bring the temperature up to 550 °C 15 minutes after placing the filter and watch glass in the furnace.

2. Use metal tongs to remove the disc and watch glass from the oven or furnace and place in a desiccator. Cover immediately. Allow the watch glass to cool slightly before sealing the desiccator as pressure from the heated air inside the desiccator can force the cover off.

Allow the filter and glass to cool to room temperature.



3. Remove the watch glass and disc from the desiccator as a unit and place beside the analytical balance.

Use plastic tweezers to remove the disc from the watch glass and weigh to the nearest 0.1 mg (0.0001 g). Record this mg value as C.

4. Calculate Volatile Non-filterable Residue (VNR):

$$\frac{A - C}{\text{Sample Volume in Liters}} = \text{mg/L VNR}$$

where:

A = Weight (mg) of disc with residue

C = Weight (mg) of disc and residue after ignition

Example:

A = 95.5 mg

C = 91.2 mg

Volume of sample = 0.1 L

$$\frac{95.5\text{ mg} - 91.2\text{ mg}}{0.1\text{ L}} = 43\text{ mg/L VNR}$$

Sample collection, preservation and storage

- Collect samples in clean plastic or glass bottles.
- Samples should be analyzed as soon as possible after collection but can be stored up to seven days by cooling to 4 °C (39 °F).

Consumables and replacement items

Required apparatus

Description	Unit	Catalog number
Aspirator, vacuum	each	213100
Balance, Analytical, 115 VAC, 60 Hz	each	2936701
Bottle, wash, 500-mL	each	62011
Cylinder, graduated, 100-mL	each	50842
Desiccant, indicating Drierite	each	2088701
Desiccator, without stopcock	each	1428500
Desiccator Plate, ceramic	each	1428400
Filter disc, glass fiber, 47-mm	100/pkg	253000
Filter Holder, magnetic	each	1352900
Flask, filtering, 1000-mL	each	54653
Furnace, muffle 240 VAC, 50/60 Hz	each	1429624
Furnace, muffle, 120 VAC, 50/60 Hz	each	1429600
Oven, laboratory, 240 VAC, 50 Hz	each	1428902
Oven, laboratory, 120 VAC, 60 Hz	each	1428900
Stopper, rubber, one-hole, No. 8	6/pkg	211908
Tongs	each	56900
Tubing, rubber, 7.9 x 2.4 mm	3.6 m	56019
Tweezers, plastic	each	1428200
Watch Glass, 100-mm	each	57870
Water, deionized	4 L	27256

Optional reagents and apparatus

Description	Unit	Catalog number
Ammonium Hydroxide, approx.. 58% ACS	500 mL	10649
Bottle, w/cap, wide mouth 500 mL poly	12/pkg	2087079
Brush	each	68700
Pump, vacuum, hand-operated	each	1428300
Pump, vacuum, 1.2 CFM, 220 VAC, w/Europeon plug	each	—
Pump, vacuum, 1.2 CFM, 115 VAC, 60 Hz	each	2824800
Rubber policeman for 3/16" rod	each	1430900
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
  - $\text{Average} = \frac{\text{Sample Conc + Dup Conc}}{2}$
  - 5% of Average = (Average Concentration)(0.05)
  - Acceptable Range = (Avg. – 5% of Avg) & (Avg + 5% of Avg)

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

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

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.

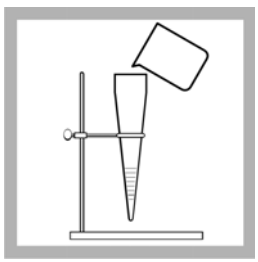
Test preparation

Collect the following items:

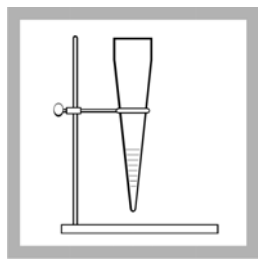
Description	Quantity
Imhoff Cone	2
Imhoff Cone Brush	1
Imhoff Cone Support	1

See *Consumables and replacement items* for reorder information.

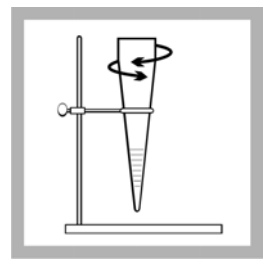
Direct Measurement



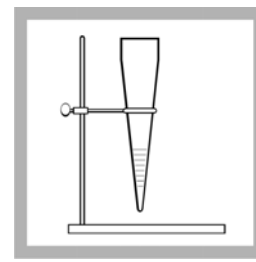
1. Fill an Imhoff cone to the 1-liter mark with a thoroughly mixed sample.



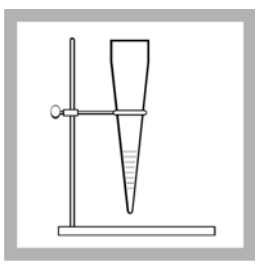
2. Wait 45 minutes for the undisturbed sample to settle.



3. Spin the cone forward and backward several times to dislodge materials on the inclined side of the cone.



4. Wait 15 minutes for the sample to settle.



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

Sampling and storage

- Collect samples in clean plastic or glass bottles.
- Refrigerate at 4 °C up to the time of analysis to minimize microbiological decomposition of solids.
- Analyze within 24 hours. Bring to room temperature before analysis.

Summary of method

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

Consumables and replacement items

Required apparatus

Description	Quantity/Test	Unit	Catalog number
Imhoff Cone	2	each	206700
Imhoff Cone Brush	1	each	68800
Imhoff Cone Support	1	each	57200

Optional apparatus

Description	Quantity/Test	Unit	Catalog number
Beaker, Glass, low form	2000 mL	each	50054
Gloves, Chemical resistant, size 9–9 1/2	pair	each	2410104
Pitcher, Graduated	2000 mL	each	2612854
Sampler, Dipper	3–9 ft handle	each	2929501

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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
  - $= \frac{\text{Difference between sample and duplicate}}{\text{Average of the sample and duplicate}} \times 100\%$

Section 4
Hardness, Alkalinity, TDS & Conductivity

Alkalinity, Hardness, TDS & Conductivity

Laboratory Workshop

TDEC - Fleming Training Center

1

Alkalinity

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2

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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3

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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4

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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5

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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6

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

8

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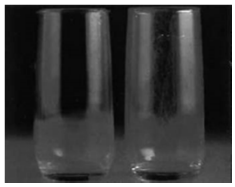
Hardness

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



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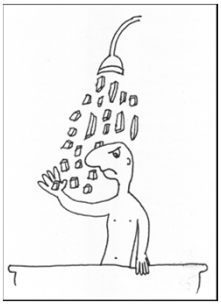
9

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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10

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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11

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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12

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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13

Total Dissolved Solids

14

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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 precipation 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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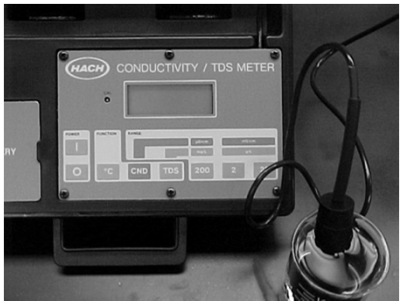
CONDUCTIVITY/TDS METER



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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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Alkalinity

DOC316.53.01151

USEPA[1] Buret Titration Method[2]

Method 8221

(0 to 5,000 mg/L as $CaCO_3$)

Buret Titration

Scope and Application: For water, wastewater and seawater

[1] USEPA Accepted

[2] Adapted from *Standard Methods for the Examination of Water and Wastewater, 2320 B*

Test preparation

Before starting the test:

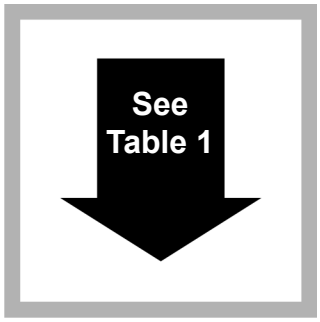
Read the entire procedure before starting the test.
A pH meter is required for NPDES reporting and is recommended for best results.
Substitute six drops of Phenolphthalein Indicator Solution for the Phenolphthalein Indicator Powder Pillow if necessary
Substitute six drops of Bromcresol Green-Methyl Red Indicator Solution for the Bromcresol Green-Methyl Red Powder Pillow if necessary.
Results in mg/L as $CaCO_3$ Ó 17.12 = grains per gallon

Collect the following items:

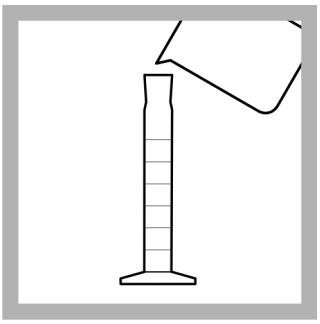
Description	Quantity
Bromcresol Green-Methyl Red indicator powder pillow	1
Phenolphthalein indicator powder pillow	1
Sulfuric acid standard solution, 0.020 N	varies[1]
Buret clamp, double	1
Buret, Class A, 25-mL	1
Graduated cylinder	varies[1]
Erlenmeyer flask, 250-mL	1
Funnel, Micro	1
Support Stand	1

[1] See *Consumables and replacement items* on page 6.

Buret titration (Method 8221)

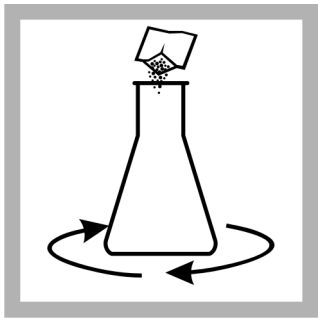


1. Select a sample volume from the *Sample volume selection for expected concentration* table that corresponds to the expected alkalinity concentration in mg/L as calcium carbonate ($CaCO_3$).

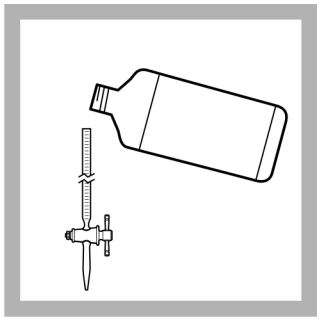


2. Use a graduated cylinder or pipet to measure the sample volume.

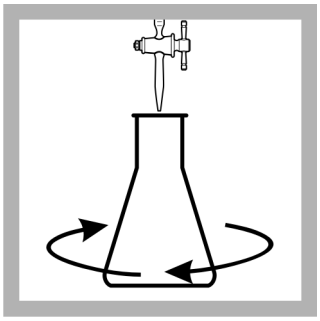
3. Transfer the sample into a 250-mL Erlenmeyer flask. Dilute to about 50-mL with deionized water if necessary.



4. Add the contents of one Phenolphthalein Indicator Powder Pillow. Swirl to mix. (Omit this step when using a pH meter.)

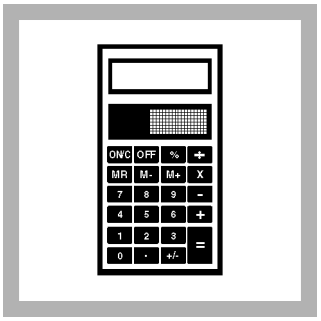


5. Fill a 25-mL buret to the zero mark with 0.020 N Sulfuric Acid standard solution.



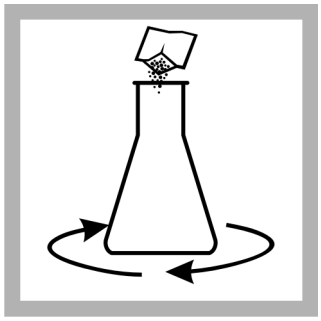
6. While swirling the flask, titrate the sample until the solution color changes from pink to colorless (pH 8.3).

If the solution is colorless before titrating with sulfuric acid, the phenolphthalein alkalinity is zero.



7. Calculate:

mL Titrant Ì multiplier used = mg/L phenolphthalein alkalinity as $CaCO_3$.

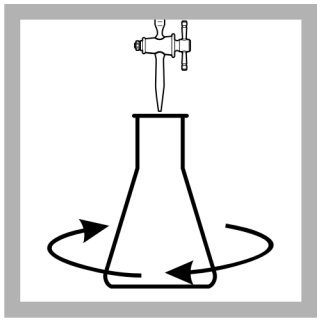


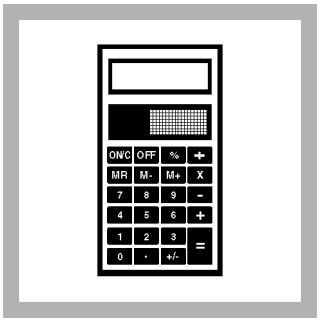
8. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow to the titrated sample. Swirl to mix.

Do not add indicator if a pH meter is used.

Specific sample composition may require titration to a specific pH (see the *Alkalinity relationship* table).

Buret titration (Method 8221)





9. Continue the titration until a light pink end point is reached.

10. Calculate:

mL Titrant Ì multiplier used = mg/L total alkalinity as $CaCO_3$.

Table 1 Sample volume selection for expected concentration

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Sulfuric Acid	Multiplier
0–500	50	20353	20
400–1000	25	20353	40
1000–2500	10	20353	100
2000–5000	5	20353	200

The end points in the *Alkalinity endpoints* table are recommended for determining total alkalinity in water samples of various compositions and alkalinity concentrations.

Table 2 Alkalinity endpoints

Sample composition	End point pH	
	Total Alkalinity	Phenolphthalein Alkalinity
Alkalinity about 30 mg/L	pH 4.9	pH 8.3
Alkalinity about 150 mg/L	pH 4.6	pH 8.3
Alkalinity about 500 mg/L	pH 4.3	pH 8.3
Silicates or phosphates present	pH 4.5	pH 8.3
Industrial wastes or complex system	pH 4.5	pH 8.3
Routine or Automated Analyses	pH 4.5	pH 8.3

Total alkalinity primarily includes hydroxide, carbonate, and bicarbonate alkalinities. The concentration of these types in a sample may be determined when the phenolphthalein and total alkalinities are known (*Alkalinity relationship* table).

Table 3 Alkalinity relationship

Row	Result of Titration	Hydroxide Alkalinity Equals:	Carbonate Alkalinity Equals:	Bicarbonate Alkalinity Equals:
1	Phenolphthalein Alkalinity equal to 0	0	0	Total Alkalinity
2	Phenolphthalein Alkalinity equal to Total Alkalinity	Total Alkalinity	0	0
3	Phenolphthalein Alkalinity less than one-half of Total Alkalinity	0	Phenolphthalein Alkalinity times 2	Total Alkalinity minus two times Phenolphthalein Alkalinity
4	Phenolphthalein Alkalinity equal to one-half of Total Alkalinity	0	Total Alkalinity	0
5	Phenolphthalein Alkalinity greater than one-half of Total Alkalinity	2 times Phenolphthalein Alkalinity minus Total Alkalinity	2 times the difference between Total and Phenolphthalein Alkalinity	0

Use the *Alkalinity relationship* table with the following procedure:

1. Does the phenolphthalein alkalinity equal zero? If yes, use Row 1.
2. Does the phenolphthalein alkalinity equal total alkalinity? If yes, use Row 2.
3. Divide the total alkalinity by 2 to calculate one-half the total alkalinity.
4. Select Row 3, 4 or 5 based on comparing the result of step c (one-half total alkalinity) with the phenolphthalein alkalinity.
5. Perform the required calculations if any.
6. Check your results. The sum of the three alkalinity types will equal the total alkalinity.

Example:
A sample has 170 mg/L as $CaCO_3$ phenolphthalein alkalinity and 250 mg/L as CaCO3 total alkalinity. What is the concentration of hydroxide, carbonate, and bicarbonate alkalinities?

a. The phenolphthalein alkalinity does not equal zero but 170 mg/L.
b. The phenolphthalein alkalinity does not equal total alkalinity (170 mg/L vs. 250 mg/L).
c. One-half of the total alkalinity equals 125 mg/L.
d. Because the phenolphthalein alkalinity of 170 mg/L is greater than one-half the total alkalinity of 125 mg/L, select Row 5.

The hydroxide alkalinity is equal to:

$2 \times 170 = 340$

$340 - 250 = 90$ mg/L hydroxide alkalinity

The carbonate alkalinity is equal to:

$250 - 170 = 80$

$80 \times 2 = 160$ mg/L carbonate alkalinity

The bicarbonate alkalinity is equal to zero mg/L.

Check:

90 mg/L hydroxide alkalinity + 160 mg/L carbonate alkalinity + 0 mg/L bicarbonate alkalinity = 250 mg/L

The answer is correct.

The sum of each type equals the total alkalinity (250 mg/L).

Interferences

Chlorine at levels above 3.5 mg/L cause a yellow-brown color upon the 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 Standard Solution* before adding the indicator.

Highly colored or turbid samples may mask the color change at the end point. Use a pH meter for these samples, titrating to pH 8.3 for phenolphthalein alkalinity and the appropriate pH (see the *Alkalinity endpoints* table) for total alkalinity.

Sampling and storage

Collect samples in plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation and prolonged exposure to air. Samples should be analyzed as soon as possible after collection but can be stored at least 24 hours by cooling to 4 °C (39 °F) or below. Warm to room temperature before analyzing.

Accuracy check

End point confirmation

- To accurately determine the phenolphthalein alkalinity end point, mix the contents of one Phenolphthalein Indicator Powder Pillow and the contents of one pH 8.3 Buffer Powder Pillow with 50 mL of deionized water in a 250-mL Erlenmeyer flask. The resulting color is the end point.
- To accurately determine the total alkalinity end point, mix the contents of one pH 4.5 Buffer Powder Pillow and the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow with 50 mL of deionized water in a 250-mL Erlenmeyer flask. Titrate to a light pink color change.

Standard additions method (Sample Spike)

Perform the standard additions method check as follows:

1. Break the top 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 in step 6 or step 9. 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 2.5 mL for each 0.1 mL increment of standard added.

Summary of method

Alkalinity is expressed as P (phenolphthalein) alkalinity or as T (total) alkalinity. Both types are determined by titration with a Sulfuric Acid Standard Solution to an end point evidenced by the color change of an indicator solution or determined with a pH meter. The P alkalinity is determined by titration to a pH of 8.3 and registers the total hydroxide and one half the carbonate present. The T alkalinity is determined by titration to a pH of 4.5. The total alkalinity includes all carbonate, bicarbonate and hydroxide alkalinity. Alternatively, total alkalinity end points may be determined by using a pH meter and titrating to the specific pH required for the sample composition.

* See *Consumables and replacement items* on page 6.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Catalog number
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

Required apparatus

Description	Quantity/test	Unit	Catalog number
Buret Clamp, double	1	each	32800
Buret, Class A, 25-mL	1	each	2636540
Select one or more based on sample volume:			
Cylinder, graduated, 5-mL	—	each	50837
Cylinder, graduated, 10-mL	—	each	50838
Cylinder, graduated, 25-mL	—	each	50840
Cylinder, graduated, 50-mL	—	each	50841
Flask, Erlenmeyer, 250-mL	1	each	50546
Pipet, volumetric, Class A, 5-mL,	—	each	1451537
Pipet, volumetric, Class A, 10-mL	—	each	1451537
Pipet Filler, Safety Bulb	—	each	1465100
Ampule Breaker	—	each	2196800
Funnel, Micro	1	each	2584335
Support Stand	1	each	56300

Required standards

Description	Unit	Catalog number
Alkalinity Standard Solution, Voluette® Ampules, 0.500 N, 10-mL	16/pkg	1427810
Buffer Powder Pillows, pH 4.5	25/pkg	89568
Buffer Powder Pillows, pH 8.3	25/pkg	89868
Water, deionized	4 L	27256

Optional items

Description	Unit	Catalog number
Sodium Thiosulfate Standard Solution, 0.1 N	—	32332
TenSette Pipet, 0.1–1.0 mL	—	1970001
Tips for Tensette Pipet	50/pkg	2185696

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	Tap Water - sample volume = 100 mL		Unknown - sample volume = mL	
	pH Meter	Color Method	pH Meter	Color Method
Bench 1	mL to pH 4.5 =			mL to colorless = total mL to pink =
Bench 2		mL to pink =	mL to 8.3 = total mL to pH 4.5=	
Bench 3	mL to pH 4.5 =			mL to colorless = total mL to pink =
Bench 4		mL to pink =	mL to 8.3 = total mL to pH 4.5=	
Bench 5a	mL to pH 4.5 =			mL to colorless = total mL to pink =
Bench 5b		mL to pink =	mL to 8.3 = total mL to pH 4.5=	

Unknown Sample Only

Phenolphthalein Alkalinity - Titrate to pH 8.3

$$\text{Phenolphthalein Alkalinity} = \frac{(\text{mL titrant used to reach pH of 8.3})(0.02\ N\ H_2SO_4)(50{,}000)}{\text{mL sample}}$$

$$\text{Phenolphthalein Alkalinity} = \frac{(_____)(0.02\ N\ H_2SO_4)(50{,}000)}{_____\ \text{mL sample}} =$$

Tap & Unknown Sample

Total Alkalinity - Titrate to pH 4.5

$$\text{Total Alkalinity} = \frac{(\text{total mL titrant used to reach pH of 4.5})(0.02\ N\ H_2SO_4)(50{,}000)}{\text{mL sample}}$$

$$\text{Total Alkalinity} = \frac{(_____)(0.02\ N\ H_2SO_4)(50{,}000)}{_____\ \text{mL sample}} =$$

Orion Alkalinity Method =

Hardness, Calcium

USEPA[1] Buret Titration Method[2]

Method 8222

0 to 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 the test:

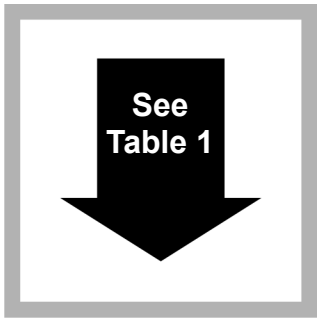
A 0.1-g scoop of CalVer® 2 Calcium Indicator Powder can be used in place of the CalVer 2 Calcium Indicator Powder Pillow.
Magnesium is not included in the results but must be present for a sharp end point. If magnesium is not present, add one to two drops of Magnesium Standard Solution, 10-g/L as $CaCO_3$ to the sample before the test is started.

Collect the following items:

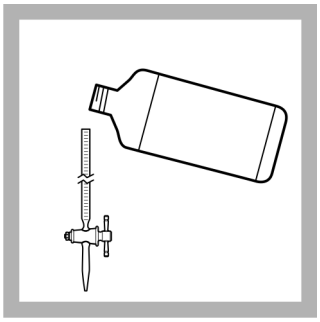
Description	Quantity
CalVer 2 Calcium Indicator Powder Pillow	1
Potassium Hydroxide Standard Solution, 8 N	1 mL
TitraVer Hardness Titrant (see *Range-specific information*)	1 bottle
Buret, Class A, 25-mL, with support stand	1
Erlenmeyer flask, 250 mL	1
Graduated cylinder	1

See *Consumables and replacement items* for reorder information.

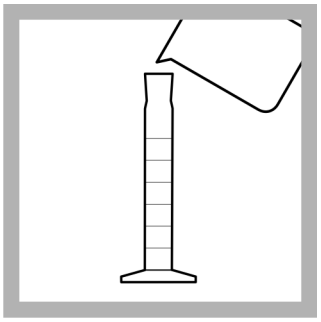
Buret titration



1. Select the sample volume and titrant concentration from the *Range-specific information* table.

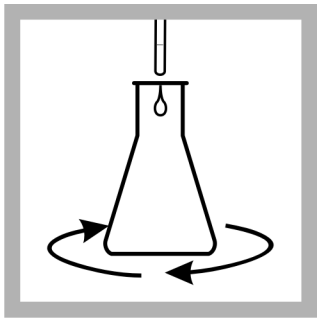


2. Fill a 25-mL buret to the zero mark with the TitraVer Hardness Titrant.

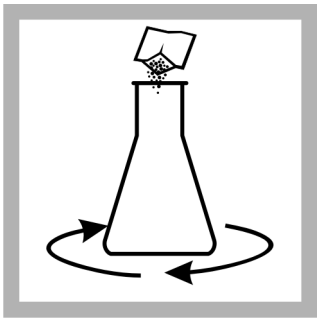


3. Use a graduated cylinder or pipet to measure the sample volume from the *Range-specific information* table.

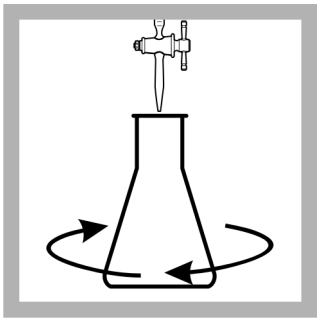
4. Transfer the sample into a 250-mL Erlenmeyer flask. If the sample volume is less than 50 mL, dilute to approximately 50 mL with deionized water. If magnesium is known to be absent, add one or two drops of Magnesium Standard Solution, 10-g/L as $CaCO_3$.



5. Add 1 mL of 8 N Potassium Hydroxide Standard Solution using the 1-mL dropper. Swirl to mix.

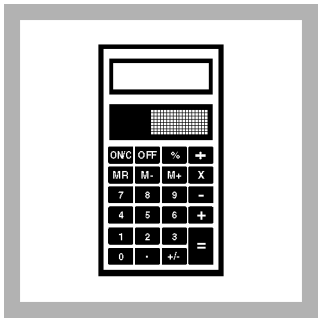


6. Add the contents of one CalVer 2 Calcium Indicator Powder Pillow. Swirl to mix.



7. Titrate the sample while swirling the flask until the color changes from red to pure blue.

Magnesium must be present (and usually is in natural waters) for a sharp end point, although it is not measured in the titration.



8. Use the multiplier in *Range-specific information* to calculate the concentration:

mL titrant used x multiplier = mg/L calcium as $CaCO_3$

Example: 50 mL of sample was titrated with the 0.020 N titrant solution and 15 mL of titrant was used to reach the endpoint.
The calcium concentration is: 15 x 20 = 300 mg/L as $CaCO_3$

Table 1 Range-specific information

Range (mg/L as $CaCO_3$)	Sample volume (mL)	Hardness titrant concentration	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

Table 2 Hardness conversions

To convert from	To	Multiply by
mg/L as $CaCO_3$	mg/L as Ca	0.400
	grains per gallon (gpg)	0.058
	German degrees hardness (Gdh)	0.056

Interferences

WARNING
Chemical hazard. Potassium cyanide is toxic. Always add it after the potassium hydroxide. Dispose of all cyanide containing wastes according to local regulations.

An interfering substance can prevent the color change at the titration end point. A dilution can reduce the interference to a level at which the substance does not interfere. If an interference is suspected, decrease the sample volume, dilute to 50 mL and repeat the test. *Interfering substances* lists substances that can interfere with this test.

Table 3 Interfering substances

Interfering substance	Interference level
Acidity	The test can tolerate 10,000 mg/L acidity.
Alkalinity	The test can tolerate 10,000 mg/L alkalinity.
Aluminum	Interferes by causing a slow end point but up to 200 mg/L aluminum can be tolerated by allowing sufficient time for the color change.
Barium	Barium is titrated along with calcium but is seldom found in natural waters in significant amounts.
Chloride	Saturated solutions do not give a distinct end point, but the test can be run directly under sea water.
Cobalt	Interferes at all levels. 0.5 grams of potassium cyanide can be added after the potassium hydroxide solution to remove interference from up to 20 mg/L cobalt.
Copper	Interferes at 0.1 mg/L copper. 0.5 grams of potassium cyanide can be added after the potassium hydroxide solution to remove interference from up to 100 mg/L copper.
Iron	Interferes above 8 mg/L by causing an orange-red to green end point. Accurate results can still be obtained up to approximately 20 mg/L iron with this end point.
Magnesium	Interference from magnesium is prevented up to 200 mg/L by the formation of magnesium hydroxide at the high test pH but higher levels prevent a distinct end point.
Manganese	Interferes above 5 mg/L.
Nickel	Interferes at 0.5 mg/L nickel. 0.5 grams of potassium cyanide can be added after the potassium hydroxide solution to remove interference from up to 200 mg/L nickel.

Table 3 Interfering substances (continued)

Interfering substance	Interference level
Orthophosphate	Causes a slow end point but does not interfere if the calcium phosphate that forms is allowed to redissolve during the titration.
Polyphosphates	Interfere directly and must be absent.
Strontium	Strontium is titrated along with calcium but is seldom found in natural waters in significant amounts.
Temperature	Samples at about 20 °C (68 °F) or colder should be titrated slowly near the end point to allow sufficient time for the color change.
Zinc	Interferes at 5 mg/L zinc. 0.5 grams of potassium cyanide can be added after the potassium hydroxide solution to remove interference from up to 100 mg/L zinc.
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents. Adjust the pH before starting the test (see *Sample collection, preservation and storage*).

Sample collection, preservation and storage

Collect samples in plastic or glass bottles that have been washed with a detergent and rinsed with tap water. Then rinse the bottles in 1:1 nitric acid solution and deionized water.

The following storage instructions are necessary only when immediate analysis is not possible. To preserve the sample, add 1.5 mL of nitric acid per liter (or quart) of sample. Mix. Measure the sample pH to make sure that the pH is 2 or less. Add more nitric acid in 0.5-mL increments if necessary. Mix thoroughly and check the pH after each addition until the pH is 2 or less. Preserved samples can be stored at least six months at room temperature.

Before running the test, adjust the sample to pH 7 by adding potassium hydroxide standard solution and mixing thoroughly. Correct the test result for volume additions.

Accuracy check

Use the standard additions method to find if the sample has an interference. Use the standard solution method to confirm anaytical technique and reagent performance.

Standard additions method (sample spike)
Required for accuracy check:

- Hardness Voluette Ampule Standard Solution, 10,000-mg/L as $CaCO_3$
- Ampule breaker
- TenSette Pipet, 0.1–1.0 mL or 1.0–10.0 mL and Pipet Tips.

Procedure for use with the **0.020 N** titrant:

1. Open the standard solution ampule.
2. Use the TenSette Pipet to add 0.1 mL of the standard to the titrated sample. Swirl to mix.
3. Titrate the spiked sample to the end point. Write down the amount of titrant that was used to reach the end point.
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. Write down the amount of titrant that was used to reach the end point.
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. Write down the amount of titrant that was used to reach the end point.

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 (see *Interferences*) or the concentration of the titrant has changed (see *Accuracy check*).

Procedure for use with the **0.200 N** titrant:

1. Open the standard solution ampule.
2. Use the TenSette Pipet to add 1.0 mL of the standard to the titrated sample. Swirl to mix.
3. Titrate the spiked sample to the end point. Write down the amount of titrant that was used to reach the end point.
4. Use the TenSette Pipet to add 2.0 mL of standard to the titrated sample. Swirl to mix.
5. Titrate the spiked sample to the end point. Write down the amount of titrant that was used to reach the end point.
6. Use the TenSette Pipet to add 3.0 mL of standard to the titrated sample. Swirl to mix.
7. Titrate the spiked sample to the end point. Write down the amount of titrant that was used to reach the end point.
8. Each 1.0 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 (see *Interferences*) or the concentration of the titrant has changed (see *Standard solution method*).

Standard solution method
Complete the following test to confirm analytical technique and reagent performance.

Procedure for use with the **0.020 N** titrant:

1. Add 25.0 mL of a calcium chloride standard solution, 1000-mg/L as $CaCO_3$, to an Erlenmeyer flask. Dilute to 50 mL with deionized water and mix fully.
2. Add the potassium hydroxide and CalVer 2 indicator. Swirl to mix.
3. Titrate the standard to the end point with the 0.020 N hardness titrant and calculate the result. The titration should use 25 mL of titrant.

Procedure for use with the **0.200 N** titrant:

1. Add 10.0 mL of a Hardness Voluette Ampule Standard Solution, 10,000-mg/L as $CaCO_3$, to an Erlenmeyer flask. Dilute to 50 mL with deionized water and mix fully.
2. Add the potassium hydroxide and CalVer 2 indicator. Swirl to mix.
3. Titrate the standard to the end point with the 0.200 N hardness titrant and calculate the result. The titration should use 10 mL of titrant.

Summary of method

The sample is made alkaline (pH 12 to 13) with potassium hydroxide to precipitate magnesium as magnesium hydroxide. CalVer 2 Calcium Indicator is added as an indicator and combines with any calcium to form a red color. As the TitraVer (EDTA) is added, it will react with all the free calcium ions present. At the end point of the titration, when no free calcium ions are present, the EDTA will remove the calcium complexed with the indicator. The indicator will then change from red to blue.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Hardness (Calcium) Reagent Set (approximately 100 tests), includes:			2447000
CalVer 2 Calcium Indicator Powder Pillows	1	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	Catalog number
Buret, Class A, 25-mL	1	each	2636540
Buret Clamp, double	1	each	32800
Flask, Erlenmeyer, graduated, 250-mL	1	each	50546
Graduated cylinder—select one or more based on range:			
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
Support Stand	1	each	56300

Recommended standards and apparatus

Description	Unit	Catalog number
Calcium Chloride Standard Solution, 1000-mg/L as $CaCO_3$	1 L	12153
Hardness Standard Solution, Voluette ampule, 10,000-mg/L as $CaCO_3$, 10-mL	16/pkg	218710
Pipet, Class A volumetric, 10 mL	each	1451538
Pipet, Class A volumetric, 25 mL	each	1451540
Safety bulb	each	1465100

Optional reagents and apparatus

Description	Unit	Catalog number
CalVer® 2 Calcium Indicator Powder	113 g	28114H
Magnesium Standard Solution, 10-g/L as $CaCO_3$	29 mL	102233
Nitric Acid Solution, ACS	500 mL	15249
Nitric Acid Solution, 1:1	500 mL	254049
Potassium cyanide	125 g	76714
Potassium Hydroxide Standard Solution, 8 N	500 mL	28249
TenSette Pipet, 0.1 to 1.0 mL	each	1970001
Water, deionized	500 mL	27249
Spoon, measuring, 1 g	each	51000
Spoon, measuring, 0.5 g	each	90700
Spoon, measuring, 0.1 g	each	51100
Pipet Tips, for TenSette Pipet 1970001[1]	50/pkg	2185696
Voluette Ampule breaker 10 mL	each	2196800
Pipet, TenSette®, Pipet, 1.0–10.0 mL	each	1970010
Pipet Tips, for TenSette Pipet 1970010[1]	50/pkg	2199796
Sampling Bottle with cap, low density polyethylene, 250 mL	12/pkg	2087076

[1] Other sizes are available

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Hardness, Total

USEPA[1] ManVer 2 Buret Titration Method[2]

Method 8226

0 to 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 the test:

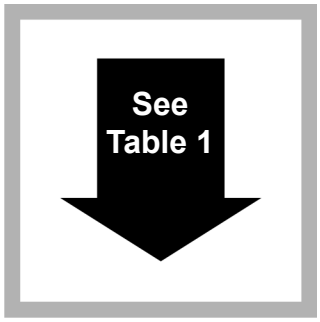
Four drops of Hardness 2 Indicator Solution or a 0.1-g scoop of ManVer 2 Hardness Indicator Powder can be added in place of the ManVer 2 Hardness Indicator Powder Pillow.
Hardness conversions: grains per gallon (gpg) as $CaCO_3$ = mg/L x 0.058; German degrees hardness (Gdh) = mg/L x 0.056

Collect the following items:

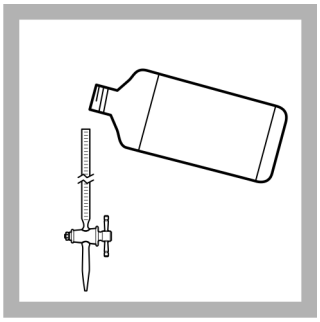
Description	Quantity
ManVer 2 Hardness Indicator Powder Pillow	1
Hardness 1 Buffer Solution	1 mL
TitraVer Hardness Titrant (see *Range-specific information*)	1 bottle
Buret, Class A, 25-mL, with support stand	1
Erlenmeyer flask, 250 mL	1
Graduated cylinder	1

See *Consumables and replacement items* for reorder information.

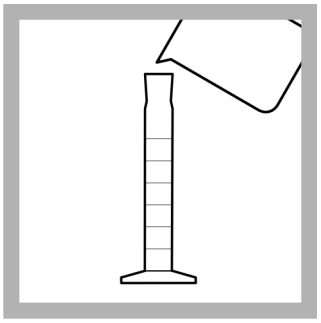
Buret titration



1. Select the sample volume and titrant concentration from *Range-specific information*.



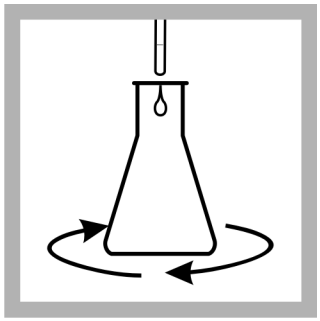
2. Fill a 25-mL buret to the zero mark with the TitraVer Hardness Titrant.



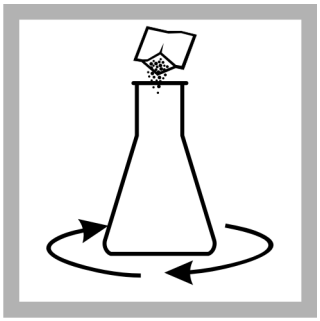
3. Use a graduated cylinder or pipet to measure the sample volume from the *Range-specific information* table.

4. Transfer the sample into a 250-mL Erlenmeyer flask. If the sample volume is less than 50 mL, dilute to approximately 50 mL with deionized water.

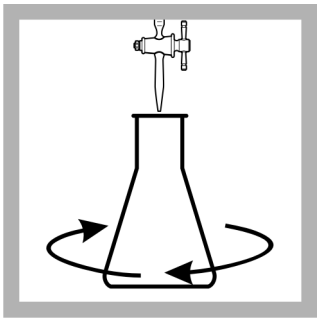
Buret titration (continued)



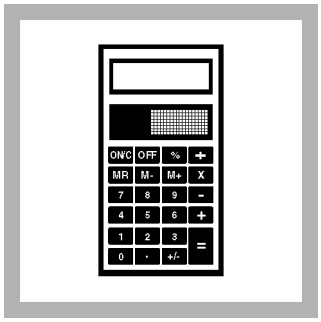
5. Add 1 mL of Hardness 1 Buffer Solution using the 1-mL dropper. Swirl to mix.



6. Add the contents of one ManVer 2 Hardness Indicator Powder Pillow. Swirl to mix.



7. Titrate the sample while swirling the flask until the color changes from red to pure blue.



8. Use the multiplier in the *Range-specific information* to calculate the concentration:

mL titrant used x multiplier = mg/L total hardness as $CaCO_3$

Example: 50 mL of sample was titrated with the 0.020 N titrant and 15 mL of titrant was used to reach the endpoint. The hardness concentration is: 15 x 20 = 300 mg/L as $CaCO_3$

Table 1 Range-specific information

Range (mg/L as $CaCO_3$)	Sample volume (mL)	Hardness titrant concentration	Multiplier
0–500	50	0.020 N	20
400–1000	25	0.020 N	40
1000–2500	10	0.020 N	100
1000–5000	50	0.200 N	200
4000–10,000	25	0.200 N	400
10,000–25,000	10	0.200 N	1000

Interferences

WARNING
Chemical hazard. Potassium cyanide is toxic. Always add it after the buffer solution. Dispose of all cyanide containing wastes according to local regulations

An interfering substance can prevent the color change at the titration end point. A dilution can reduce the interference to a level at which the substance does not interfere. If an interference is suspected, decrease the sample volume, dilute to 50 mL and repeat the test.

Interfering substances lists substances that can interfere with this test.

Table 2 Interfering substances

Interfering substance	Interference level
Acidity	Acidity at 10,000 mg/L as $CaCO_3$ does not interfere.
Alkalinity	Alkalinity at 10,000 mg/L as $CaCO_3$ does not interfere.
Aluminum	Aluminum interferes above 0.20 mg/L aluminum. 0.5 grams of potassium cyanide can be added after the buffer solution to remove interference from up to 1 mg/L aluminum.
Barium	Barium is titrated directly but is seldom found in natural waters in significant amounts.
Chloride	Saturated solutions do not give a distinct end point. The test can be run directly in sea water.
Cobalt	Interferes at all levels and must be absent or masked. 0.5 grams of potassium cyanide can be added after the buffer solution to remove interference from up to 100 mg/L cobalt.
Copper	Copper interferes above 0.10 mg/L copper. 0.5 grams of potassium cyanide can be added after the buffer solution to remove interference from up to 100 mg/L copper.
Iron	Interferes above 15 mg/L by causing an orange-red to green end point. Accurate results can still be obtained up to approximately 30 mg/L iron with this end point. For slightly sharper end points in solutions containing higher levels of iron, HexaVer Hardness Titrant (CDTA) can be used in place of the TitraVer Hardness Titrant (EDTA).
Manganese	Interferes above 20 mg/L. Adding a 0.10-gram scoop of Hydroxylamine Hydrochloride Monohydrate raises this level to 200 mg/L manganese.
Nickel	Interferes at all levels and must be absent or masked. 0.5 grams of potassium cyanide can be added after the buffer solution to remove interference from up to 100 mg/L nickel.
Orthophosphate	Causes a slow end point but does not interfere if the calcium phosphate that forms is allowed to redissolve during the titration.
Polyphosphates	Interfere directly and must be absent.
Polyvalent metal ions	Although less common than calcium and magnesium, other polyvalent metal ions cause the same hardness effects and will be included in the results.
Strontium	Strontium is titrated directly but is seldom found in natural waters in significant amounts.
Zinc	Titrates directly. 0.5 grams of potassium cyanide can be added after the buffer solution to remove interference from up to 100 mg/L zinc.
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents. Adjust the pH before starting the test (see *Sample collection, preservation and storage*).

The addition of one CDTA Magnesium Salt Powder Pillow will remove metals interferences at or below the levels shown in the *Interference level with CDTA pillow* table. If more than one metal is present at or above the concentrations in the *Interference level with CDTA pillow* table, an additional CDTA Magnesium Salt Powder Pillow may be necessary.

Table 3 Interference level with CDTA pillow

Interfering substance	Interference level, mg/L
Aluminum	50
Cobalt	200
Copper	100
Iron	100
Manganese	200
Nickel	400
Zinc	300

The results obtained with CDTA Magnesium Salt will include the hardness contributed by those soluble metal ions present. If the concentration of soluble metal ion is known, a correction can be made to obtain the hardness contributed by calcium and magnesium only. The hardness

contributed per mg/L metal ion is listed in *Hardness equivalence factors* for the individual metals. The mg/L of metal present multiplied by its calcium carbonate hardness equivalent factor should be subtracted for each metal present from the total hardness determined in step 8 of the procedure to obtain the hardness contributed by calcium and magnesium only.

Table 4 Hardness equivalence factors

Interfering substance	Hardness equivalence factors, mg/L as $CaCO_3$
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

Sample collection, preservation and storage

Collect samples in plastic or glass bottles that have been washed with a detergent and rinsed with tap water. Then rinse the bottles in 1:1 nitric acid solution and deionized water.

The following storage instructions are necessary only when immediate analysis is not possible. To preserve the sample, add 1.5 mL of nitric acid per liter (or quart) of sample. Mix. Measure the sample pH to make sure that the pH is 2 or less. Add more nitric acid in 0.5-mL increments if necessary. Mix thoroughly and check the pH after each addition until the pH is 2 or less. Store samples at 4 °C (39 °F) or below. Preserved samples can be stored for at least seven days.

Before starting the test, warm the sample to room temperature and adjust the pH to approximately pH 7 with 5.0 N sodium hydroxide. Mix thoroughly. If a significant amount of nitric acid was added, make a volume correction for the extra acid and hydroxide. Divide the total volume (sample + acid + hydroxide) by the volume of the sample and multiply the result from the test by this value.

Accuracy check

Use the standard additions method to find if the sample has an interference. Use the standard solution method to confirm analytical technique and reagent performance.

Standard additions method (sample spike)
Required for accuracy check:

- Hardness Voluette Ampule Standard Solution, 10,000-mg/L as $CaCO_3$
- Ampule breaker
- TenSette Pipet, 0.1–1.0 mL or 1.0–10.0 mL and Pipet Tips

Procedure for use with the **0.020 N** titrant:

1. Open the standard solution ampule.
2. Use the TenSette Pipet to add 0.1 mL of the standard to the titrated sample. Swirl to mix.
3. Titrate the spiked sample to the end point. Write down the amount of titrant that was used to reach the end point.
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. Write down the amount of titrant that was used to reach the end point.
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. Write down the amount of titrant that was used to reach the end point.
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 (see *Interferences*) or the concentration of the titrant has changed (see *Standard solution method*).

Procedure for use with the **0.200 N** titrant:

1. Open the standard solution ampule.
2. Use the TenSette Pipet to add 1.0 mL of the standard to the titrated sample. Swirl to mix.
3. Titrate the spiked sample to the end point. Write down the amount of titrant that was used to reach the end point.
4. Use the TenSette Pipet to add 2.0 mL of standard to the titrated sample. Swirl to mix.
5. Titrate the spiked sample to the end point. Write down the amount of titrant that was used to reach the end point.
6. Use the TenSette Pipet to add 3.0 mL of standard to the titrated sample. Swirl to mix.
7. Titrate the spiked sample to the end point. Write down the amount of titrant that was used to reach the end point.
8. Each 1.0 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 (see *Interferences*) or the concentration of the titrant has changed (see *Standard solution method*).

Standard solution method
Complete the following test to confirm the analytical technique and reagent performance.

Procedure for use with the **0.020 N** titrant:

1. Add 25.0 mL of a calcium chloride standard solution, 1000-mg/L as $CaCO_3$, to an Erlenmeyer flask. Dilute to 50 mL with deionized water and mix fully.
2. Add the Hardness 1 Buffer Solution and ManVer 2 indicator. Swirl to mix.
3. Titrate the standard to the end point with the 0.020 N hardness titrant and calculate the result. The titration should use 25 (± 0.3) mL of titrant.

Procedure for use with the **0.200 N** titrant:

1. Add 10.0 mL of a Hardness Voluette Ampule Standard Solution, 10,000-mg/L as $CaCO_3$, to an Erlenmeyer flask. Dilute to 50 mL with deionized water and mix fully.
2. Add the Hardness 1 Buffer Solution and ManVer 2 indicator. Swirl to mix.
3. Titrate the standard to the end point with the 0.200 N hardness titrant and calculate the result. The titration should use 10 (± 0.2) mL of titrant.

Summary of method

In the total hardness test, the water sample is first buffered (using an organic amine and one of its salts) to a pH of 10.1. An organic dye, calmagite, is added as the indicator for the test. This dye reacts with calcium and magnesium ions to give a red-colored complex.

EDTA (ethylenediaminetetraacetic acid) is added as a titrant. The EDTA will react with all free calcium and magnesium ions present in the sample. At the end point of the titration, when free magnesium ions are no longer available, EDTA will remove magnesium ions from the indicator, causing a color change from red to blue.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Hardness (Total) Reagent Set (approximately 100 tests), includes;			2447600
(1) ManVer 2 Hardness Indicator Powder Pillows	1	100/pkg	85199
(1) Buffer Solution, Hardness 1	1 mL	100 mL MDB	42432
(1) TitraVer® Hardness Titrant, 0.020 N	varies	1 L	20553
Hardness (Total) Reagent Set (approximately 100 tests), includes:			2447700
(1) ManVer 2 Hardness Indicator Powder Pillows	1	100/pkg	85199
(1) Buffer Solution, Hardness 1	1 mL	100 mL MDB	42432
(1) TitraVer® Hardness Titrant, 0.200 N	varies	500 mL	102149

Required apparatus

Description	Quantity/Test	Unit	Catalog number
Buret, Class A, 25-mL	1	each	2636540
Buret Clamp, double	1	each	32800
Flask, Erlenmeyer, graduated, 250-mL	1	each	50546
Graduated cylinder—select one or more based on range:			
Cylinder, graduated, 10-mL	1	each	50838
Cylinder, graduated, 25-mL	1	each	50840
Cylinder, graduated, 50-mL	1	each	50841
Support Stand	1	each	56300

Recommended standards and apparatus

Description	Unit	Catalog number
Calcium Chloride Standard Solution, 1000-mg/L as $CaCO_3$	1 L	12153
Hardness Standard Solution, Voluette ampule, 10,000-mg/L as $CaCO_3$, 10-mL	16/pkg	218710
Pipet, Class A volumetric, 10 mL	each	1451538
Pipet, Class A volumetric, 25 mL	each	1451540
Safety bulb	each	1465100

Optional reagents and apparatus

Description	Unit	Catalog number
CDTA Magnesium Salt Powder Pillow	100/pkg	1408099
Magnesium Standard Solution, 10-g/L as $CaCO_3$	29 mL	102233
Hardness 2 Indicator Solution	100 mL	42532
HexaVer Hardness Titrant, 0.020 N	1 L	74053
ManVer 2 Hardness Indicator Powder	113 g	28014
Nitric Acid Solution, ACS	500 mL	15249
Nitric Acid Solution, 1:1	500 mL	254049
Potassium cyanide	125 g	76714
Sodium Hydroxide Standard Solution, 5 N	50 mL	245026
TenSette Pipet, 0.1 to 1.0 mL	each	1970001
Water, deionized	500 mL	27249
Spoon, measuring, 1 g	each	51000
Spoon, measuring, 0.5 g	each	90700
Spoon, measuring, 0.1 g	each	51100
Pipet Tips, for TenSette Pipet 1970001	50/pkg	2185696
Voluette Ampule breaker 10 mL	each	2196800
Pipet, TenSette®, Pipet, 1.0–10.0 mL	each	1970010
Pipet Tips, for TenSette Pipet 1970010[1]	50/pkg	2199796
Sampling Bottle with cap, low density polyethylene, 250 mL	12/pkg	2087076

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	Tap Water - sample volume = 50 mL	
	Ca Hardness	Total Hardness
	Titrate from red to pure blue	
Bench 1	mL titrant used =	mL titrant used =
Bench 2	mL titrant used =	mL titrant used =
Bench 3	mL titrant used =	mL titrant used =
Bench 4	mL titrant used =	mL titrant used =
Bench 5a	mL titrant used =	mL titrant used =
Bench 5b	mL titrant used =	mL titrant used =

Hardness = $\frac{\text{(mL titrant used to reach pH)(1,000)}}{\text{50 mL sample}}$ = mg/L

Ca Hardness = $\frac{\text{(_____ mL)(1,000)}}{\text{50 mL sample}}$ = (_____ mL)(multiplier of 20) = _____mg/L

Total Hardness = $\frac{\text{(_____ mL)(1,000)}}{\text{50 mL sample}}$ = (_____ mL)(multiplier of 20) = _____ mg/L

Solids, Total Filterable (Total Dissolved Solids)

DOC316.53.001246

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 the test:

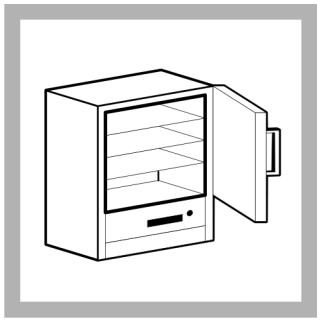
Total Filterable Solids = Total Dissolved Solids (TDS)
Samples with high bicarbonate concentrations may require increased drying at 180 °C to make sure that the conversion of bicarbonate to carbonate is complete.
Limit sample size to no more than 200 mg residue for best results.
When measuring volatile dissolved solids, heat the evaporating dish to 550 °C for 1 hour before beginning the test.
Sample residue from this procedure can be used directly in Method 8277, Solids, Total Volatile and Fixed.

Collect the following items:

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

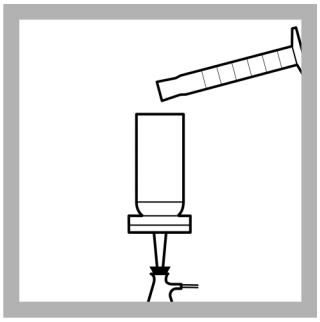
See *Consumables and replacement items* for reorder information.

USEPA Gravimetric Method—Total Filterable Solids, Method 8163

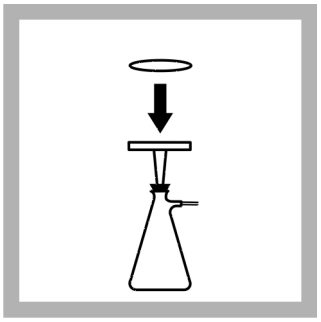


1. Heat a clean evaporating dish in a drying oven at 180 °C for one hour.

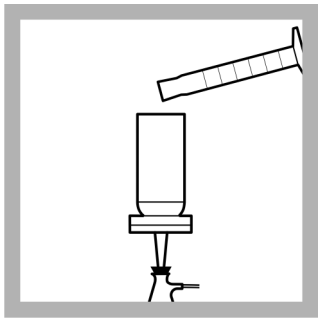
Using metal tongs, remove the evaporating dish from the furnace and place in a desiccator. Cover immediately. Allow the dish to cool slightly before sealing the desiccator as pressure from the heated air inside the desiccator can force the cover off.



2. Assemble the filter holder/flask assembly using a clean filter flask. Before using the flask, remove all residue from the flask by thoroughly cleaning with a dilute solution of ammonium hydroxide and rinsing with deionized water.

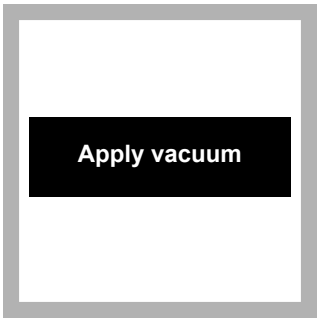


3. Place a 47-mm filter disc in the filter holder. With vacuum applied to the flask, wash the filter with three separate 20-mL volumes of deionized water. Remove all traces of water by continuing vacuum for two to three minutes after the water has passed through the filter. Disconnect the vacuum and discard these washings from the flask.

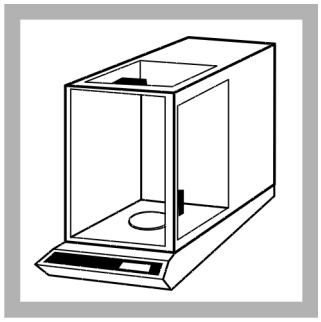


4. Reconnect vacuum to the filter holder/flask assembly. Use a clean 100-mL graduated cylinder to filter 100 mL (or more if solids content is low) of a well-mixed representative water sample.

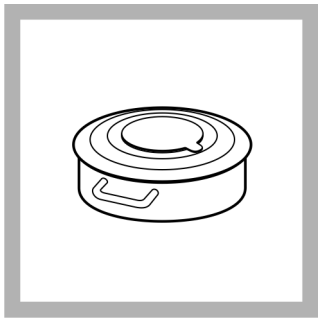
For greatest accuracy, filter as much sample as possible. However, using a sample that contains more than 15 mg of solids will clog the filter prematurely. Adjust the exact volume of the water sample to achieve the optimum condition. Several completed tests will show whether any adjustment is necessary.



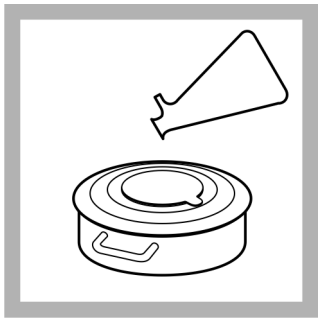
5. Apply vacuum for two to three minutes after the sample has passed through the filter. Disconnect the vacuum.



6. Use tongs to transfer the evaporating dish from the desiccator to the balance. Weigh to the nearest 0.1 mg (0.0001 g) and record this weight as B.



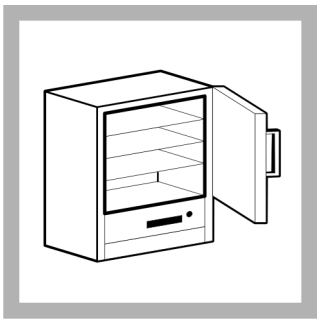
7. Place the steam bath on the hot plate, add water and transfer the evaporating dish from the balance to the steam bath.



8. Pour the 100-mL filtrate sample from the filter flask into the evaporating dish. Evaporate to dryness (this may take up to four hours).

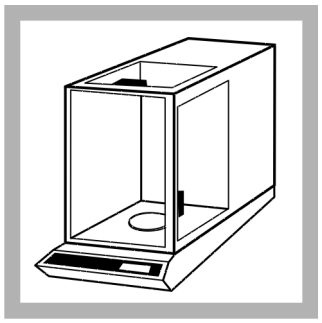
Periodically check the reservoir of the water bath. Add more water if needed.

USEPA Gravimetric Method—Total Filterable Solids, Method 8163 (continued)

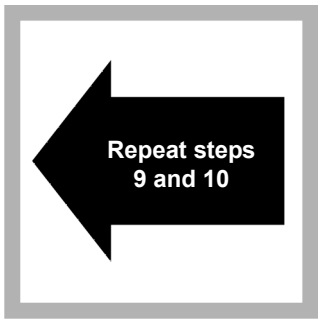


9. Use tongs to transfer the evaporating dish residue to a drying oven and dry at 180 °C for one hour. Transfer to a desiccator and cool.

Allow the dish to cool slightly before sealing the desiccator; pressure from the heated air inside the desiccator can force the cover off.

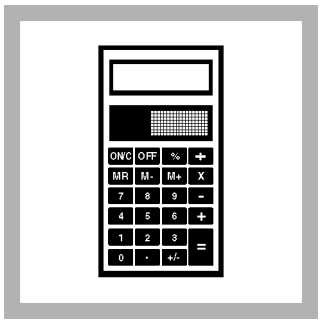


10. Weigh the evaporating dish to the nearest 0.1 mg (0.0001 g) on an analytical balance and record this weight as A.



11. Repeat steps 9 and 10 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.

The solid residue can be used directly in method 8277 to determine Volatile Dissolved Solids.



12. Calculate the Total Filterable Residue (TFR). Refer to *Total filterable residue calculation*.

Total filterable residue calculation

To calculate TFR:

$$\frac{A - B}{\text{Sample volume in liters}} = \text{mg/L TFR}$$

Where:

A = Weight (mg) of residue and dish after drying

B = Weight (mg) of dish Sample Volume = 0.1 L

Example:

A = 20187.3 mg

B = 20140.1 mg

$$\frac{20187.3 - 20140.1}{0.1} = 472 \text{ mg/L TFR}$$

Sample collection, preservation and storage

- Collect samples in clean plastic or glass bottles.
- Samples should be analyzed as soon as possible after collection but can be stored up to seven days by cooling to 4 °C (39 °F).

Summary of method

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

Consumables and replacement items

Required apparatus

Description	Unit	Catalog number
Aspirator, vacuum	each	213100
Balance, Analytical, 115 VAC, 60 Hz	each	2936701
Bottle, wash, 500-mL	each	62011
Cylinder, graduated, 100-mL	each	50842
Desiccant, indicating Drierite	each	2088701
Desiccator, without stopcock	each	1428500
Desiccator Plate, ceramic	each	1428400
Evaporating dish, porcelain, w/lip, 120-mL, 90-mm		
Filter disc, glass fiber, 47-mm	100/pkg	253000
Filter Holder, magnetic	each	1352900
Flask, filtering, 1000-mL	each	54653
Hot plate/stirrer, 7 x 7 inch, 115 VAC	each	2881600
Hot plate/stirrer, 7 x 7 inch, 220–240 VAC	each	2881602
Oven, laboratory, 240 VAC, 50 Hz	each	1428902
Oven, laboratory, 240 VAC, 50 Hz	each	1428902
Oven, laboratory, 120 VAC, 60 Hz	each	1428900
Steam bath, 8-inch diameter		2347900
Stopper, rubber, one-hole, No. 8	6/pkg	211908
Tongs	each	56900
Tubing, rubber, 7.9 x 2.4 mm	3.6 m	56019
Tweezers, plastic	each	1428200
Water, deionized	4 L	27256

Optional reagents and apparatus

Description	Unit	Catalog number
Ammonium Hydroxide, 58% ACS	500 mL	10649
Bottle, w/cap, wide mouth 500 mL poly	12/pkg	2087079
Brush	each	68700
Pump, vacuum, hand-operated	each	1428300
Pump, vacuum, 1.2 CFM, 220 VAC, w/Europeon plug	each	—
Pump, vacuum, 1.2 CFM, 115 VAC, 60 Hz	each	2824800
Rubber policeman for 3/16" rod	each	1430900
Stirring rod, glass	3/pkg	177001

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Conductivity

DOC316.53.01199

USEPA[1] Direct Measurement Method[2]

(0.01 µS/cm to 200.00 mS/cm)

Method 8160

Conductivity Meter

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

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 1 Instrument-specific information

Meter	Standard probe	Rugged probe[1]
HQ40d	CDC40101 CDC40103	CDC40105 CDC40110 CDC40115 CDC40130
HQ30d	CDC40101 CDC40103	CDC40105 CDC40110 CDC40115 CDC40130
HQ14d	CDC40101 CDC40103	CDC40105 CDC40110 CDC40115 CDC40130
sension™ 5	5197500 5197503	—
sension™ 7	5197500 5197503	—

[1] Designed for field use.

Before starting the test:

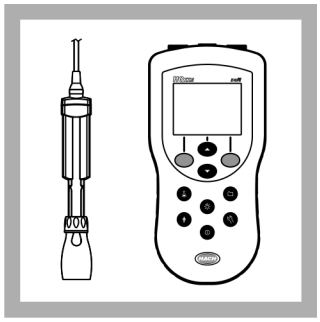
Collect samples in clean plastic or glass bottles.
Analyze samples as soon as possible after collection. However, samples may be stored at least 24 hours by cooling to 4 °C (39 °F) or below (all storage temperatures have changed to 0 to 6 °C as per the EPA MUR, March 2007). When measuring solutions that are not at the reference temperature, the meter automatically adjusts the conductivity value to the reference temperature from 20 or 25 °C.
Water samples containing oils, grease, or fats will coat the electrode and affect the accuracy of the readings. If this occurs, clean the probe with a strong detergent solution, then thoroughly rinse with deionized water.
Mineral build-up on the probe can be removed with a diluted 1:1 Hydrochloric Acid Solution. Refer to the meter user manual.
Calibration instructions are given in the operation section of the meter manual. For most accurate results calibrate before use, or check the accuracy of the meter with a known conductivity standard.
Measurement errors can occur if the appropriate temperature correction value is not chosen. Refer to the *Temperature correction* table for typical correction values.

Collect the following items:

Description	Quantity
One of the following meter/sensor combinations:	1
HQd meter and conductivity IntelliCAL™ probe	
sension meter and conductivity electrode	1
One of the following Hach standards:	
NaCl Standard Solution, 180 ± 10 µS/cm	1
NaCl Standard Solution, 1000 ± 10 µS/cm	1
NaCl Standard Solution, 1990 ± 10 µS/cm	1
NaCl Standard Solution, 18 ± 10 mS/cm	1
Radiometer Analytical Certified Conductivity Standards:	
KCl, 1 Demal, 111.3 mS/cm ± 0.5% at 25 °C	500 mL
KCl, 0.1 Demal, 12.85 mS/cm ± 0.35% at 25 °C	500 mL
KCl, 0.01 Demal, 1408 S/cm ± 0.5% at 25 °C	500 mL
NaCl, 0.05%, 1015 S/cm ± 0.5% at 25 °C	500 mL
KCl Conductivity Standards:	
0.1 Molar KCl, 12.88 mS/cm at 25 °C	500 mL
0.01 Molar KCl, 1413 S/cm at 25 °C	500 mL
0.001 Molar KCl, 148 S/cm at 25 °C	500 mL
Beaker, poly, 100-mL	1

See *Consumables and replacement items* for reorder information.

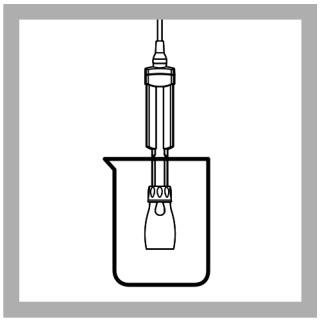
Conductivity



1. Refer to the operation section of the meter manual to prepare the conductivity electrode and meter.

The meter will select the range automatically.

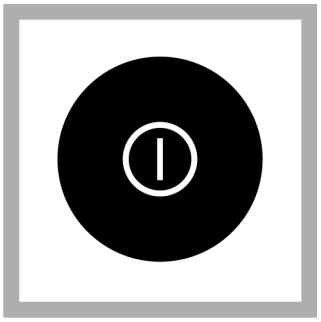
For most accurate results, calibrate the meter before use or check the accuracy of the meter with a known conductivity standard. Refer to the meter user manual for calibration and measurement options.



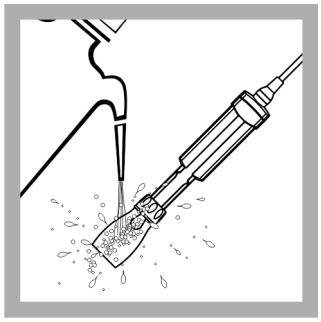
2. Laboratory tests: Immerse the probe in a beaker containing the sample solution. Move the probe up and down and tap it on the beaker to remove bubbles from the electrode.

Field tests: Immerse the probe in the sample solution. Move the probe up and down to remove bubbles from the electrode.

The vent holes should be completely submerged.



3. Turn the meter on. Make sure that the meter is set to measure conductivity.



4. Rinse the probe thoroughly with deionized water after each measurement.

To display other units such as TDS, salinity or resistivity (HQd only), refer to the meter user manual.

Conversions

The *Unit conversion* table provides equations for converting the conductivity readings to other units of measure.

Table 2 Unit conversion

From	To	Use this Equation
mS/cm	mS/cm	mS/cm x 1000
mS/cm	mS/cm	mS/cm x 0.001
mS/cm	mmhos/cm	mS/cm x 1
mS/cm	mmhos/cm	mS/cm x 1
mS/cm	mg/L TDS	mS/cm x 0.5[1]
g/L TDS	mg/L TDS	g/L TDS x 1000
mS/cm	g/L TDS	mS/cm x 0.5
mg/L TDS	g/L TDS	mg/L TDS x 0.001
mg/L TDS	gpg TDS	mg/L TDS x 0.05842
g/L TDS	gpg TDS	g/L TDS x 58.42
mS/cm	ohms cm	1,000,000 ÷ mS/cm
mS/cm	ohms cm	1,000 ÷ mS/cm

[1] TDS is an empirically-derived value from the conductivity measurement. A value of 0.5 is selected here for simplicity and suitability to a wide variety of waters. The *sension* 5 uses a more complex algorithm, based on additional factors, such as temperature, to determine TDS.

The *Temperature correction* table shows typical temperature correction values for selected solutions using 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

When measuring conductivity, the following items should be considered in order to ensure accurate results:

- If measuring very low levels of conductivity, protect the sample from atmospheric gases (carbon dioxide, ammonia). These gases dissolve readily in water and may cause a rapid change in conductivity. To minimize these effects, boil the sample, then place in a covered container, such as a Low Ionic Strength (LIS) chamber for cooling.
- To remove the conductivity with hydroxide ions, neutralize by adding 4 drops of Phenolphthalein Indicator Solution to 50 mL of sample, then adding Gallic Acid Solution, drop-wise, until the pink color completely disappears.

Accuracy check

Pour a Sodium Chloride Standard Solution (with a conductivity value in the same range as the sample) into a beaker. Perform the conductivity measurements as described above. The conductivity reading should be the same (within accuracy limits) as listed on the Standard Solution label if the meter is calibrated correctly. Calibration can be performed using this solution. Refer to the meter user manual.

Method performance

The accuracy of a conductivity measurement is dependent on many factors associated with the overall system, including the meter, meter settings, choice of electrode and conductivity standards being used during calibration. Refer to the appropriate electrode, meter manual and standard certificate of analysis to help determine system performance.

Summary of method

Electrolytic conductivity is the capacity of ions in a solution to carry electrical current and is the reciprocal of the solution resistivity. Current is carried by inorganic dissolved solids (e.g., chloride, nitrate, sulfate, and phosphate anions) and cations (e.g., sodium, calcium, magnesium, iron, and aluminum). Organic material like oils, phenols, alcohols, and sugars do not carry electrical current well and thus do not have enough conductivity for a useful estimate of concentration.

Measuring conductivity is done by measuring the resistance occurring in an area of the test solution defined by the probe's physical design. Voltage is applied between the two electrodes immersed in the solution, and the voltage drop caused by the resistance of the solution is used to calculate conductivity per centimeter. The basic unit of measure for conductivity is the Siemen (or mho), the reciprocal of the ohm in the resistance measurement. Because ranges normally found in aqueous solutions are small, milliSiemens/cm (10^{-3} S or S/cm) and microSiemens/cm (10^{-6} S or µS/cm) are most commonly used.

Consumables and replacement items

Required apparatus

Description	Quantity	Unit	Catalog number
Select one meter and probe combination:			
HQ40d Meter	1	each	HQ40d53000000
HQ30d Meter	1	each	HQ30d53000000
HQ14d Meter	1	each	HQ14d53000000
IntelliCAL Conductivity Probe, standard, with 1m cable	1	each	CDC40101
IntelliCAL Conductivity Probe, standard, with 3m cable	1	each	CDC40103
IntelliCAL Conductivity Probe, rugged, with 5m cable	1	each	CDC40105
IntelliCAL Conductivity Probe, rugged, with 10m cable	1	each	CDC40110
IntelliCAL Conductivity Probe, rugged, with 15m cable	1	each	CDC40115
IntelliCAL Conductivity Probe, rugged, with 30 m cable	1	each	CDC40130
sens*ion* meters and probes. Select one meter and probe combination:			
*sens**ion*** 5	1	each	5180000
*sens**ion*** 7	1	each	5450000
Conductivity probe, with 1 m cable	1	each	5197500
Conductivity probe, with 3 m cable	1	each	5197503

Recommended standards

Description	Unit	Catalog number
Hach, 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/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
Radiometer Analytical, Certified Conductivity Standards:		
KCl, 1 Demal, 111.3 mS/cm ± 0.5% at 25 °C	500 mL	S51M001
KCl, 0.1 Demal, 12.85 mS/cm ± 0.35% at 25 °C	500 mL	S51M002
KCl, 0.01 Demal, 1408 µS/cm ± 0.5% at 25 °C	500 mL	S51M003
NaCl, 0.05%, 1015 µS/cm ± 0.5% at 25 °C	500 mL	S51M004
KCl Conductivity Standards:		
0.1 Molar KCl, 12.88 mS/cm at 25 °C	500 mL	C20C250
0.01 Molar KCl, 1413 µS/cm at 25 °C	500 mL	C20C270
0.001 Molar KCl, 148 µS/cm at 25 °C	500 mL	C20C280

Optional reagents and apparatus

Description	Unit	Catalog number
Beaker, poly, 100-mL	each	108042
Gallic Acid Solution	50 mL SCDB	1442326
Hydrochloric Acid Solution, 1:1	500 mL	88449
Low Ionic Strength Chamber (LIS)	each	5189900
Phenolphthalein Indicator Solution	15 mL SCDB	16236
Wash Bottle, 125-mL	each	62014
Water, deionized	4 L	27256

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Conductivity/TDS Meter

	Tap Water		Conductivity Standard		Deionized Reagent Water		Distilled Reagent Water	
Bench 1	mg/L	µS/cm	mg/L	µS/cm	mg/L	µS/cm	mg/L	µS/cm
Bench 2	mg/L	µS/cm	mg/L	µS/cm	mg/L	µS/cm	mg/L	µS/cm
Bench 3	mg/L	µS/cm	mg/L	µS/cm	mg/L	µS/cm	mg/L	µS/cm
Bench 4	mg/L	µS/cm	mg/L	µS/cm	mg/L	µS/cm	mg/L	µS/cm
Bench 5a	mg/L	µS/cm	mg/L	µS/cm	mg/L	µS/cm	mg/L	µS/cm
Bench 5b	mg/L	µS/cm	mg/L	µS/cm	mg/L	µS/cm	mg/L	µS/cm

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)
Bench 1		milligrams	mL	milligrams
Bench 2		milligrams	mL	milligrams
Bench 3		milligrams	mL	milligrams
Bench 4		milligrams	mL	milligrams
Bench 5a		milligrams	mL	milligrams
Bench 5b		milligrams	mL	milligrams

$$\text{TDS, mg/L} = \frac{(A - B)(1000)}{\text{sample vol, mL}} = \frac{(_____\ \text{mg} - _____\ \text{mg})(1000)}{100\ \text{mL}} = _____\ \text{mg/L}$$

Section 5
Langelier Index

Stabilization Math

Langelier Index &
Aggressive Index

Langelier Index

- Calculate the Langelier Index using the following lab results:
  - pH = 7.4
  - Temperature = 20°C
  - TDS = 200 mg/L
  - Total Alkalinity = 120 mg/L as $CaCO_3$
  - Ca Hardness = 90 mg/L as $CaCO_3$

Langelier Index

- Langelier Index = pH – pH_s
- pH_s = A + B – log Ca Hardness – log Total Alk
  - Where A = Temperature
  - Where B = TDS

Langelier Index

Values of "A" for various Temperatures, °C	
Temperature, °C	A
0	2.34
5	2.27
10	2.2
15	2.12
20	2.05
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	B
0	9.63
50	9.72
100	9.75
200	9.8
400	9.86
800	9.94
1,600	10.04

Langelier Index

Values of log of Ca or Alkalinity as $CaCO_3$ in mg/L	
mg/L	log_{10}
10	1.00
20	1.30
30	1.48
40	1.60
50	1.70
60	1.78
70	1.84
80	1.90
90	1.95
100	2.00
200	2.30
300	2.48
400	2.60
500	2.70
600	2.78
700	2.84
800	2.90
900	2.95
1,000	3.00

Langelier Index

- There isn't a 120 in the chart for Total Alkalinity ☹
- Use your calculator
  - Take the log of 120
  - Equals 2.07918…
  - Round up to 2.08

Langelier Index

- Langelier Index = pH – pH_s
- pH_s = A + B – log Ca Hardness – log Total Alk
  = 2.05 + 9.80 – 1.95 – 2.08
  = 7.82
- Langelier Index = 7.4 – 7.82
  = -0.42

Langelier Index

- Now determine how aggressive your water is

Corrosivity Characteristics as Addressed by Indices		
Corrosive Characteristics	Langelier Index (LI)	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

Aggressive Index

- Calculate the Aggressive Index using the following lab results:
  - pH = 7.8
  - Total Alkalinity = 100 mg/L as $CaCO_3$
  - Ca Hardness = 200 mg/L as $CaCO_3$

Aggressive Index

- AI = pH + log Ca Hard + log Total Alk

Aggressive Index

Values of log of Ca or Alkalinity as $CaCO_3$ in mg/L	
mg/L	log_{10}
10	1.00
20	1.30
30	1.48
40	1.60
50	1.70
60	1.78
70	1.84
80	1.90
90	1.95
100	2.00
200	2.30
300	2.48
400	2.60
500	2.70
600	2.78
700	2.84
800	2.90
900	2.95
1,000	3.00

Aggressive Index

- AI = pH + log Ca Hard + log Total Alk
  = 7.8 + 2.00 + 2.30
  = 12.10

Aggressive Index

- Now determine how aggressive your water is

Corrosivity Characteristics as Addressed by Indices		
Corrosive Characteristics	Langelier Index (LI)	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**

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How does this work in real life?

- You can determine your pH_s from the Langelier Index and this can be the pH you need leaving your clearwell to be stable
  - That is your water is not corrosive nor scale forming.

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Langelier and Aggressive Indices

Method 8073

Langelier saturation index

The Langelier Saturation Index (LI), a measure of a solution's ability to dissolve or deposit calcium carbonate, is often used as an indicator of the corrosivity of water. The index is not related directly to corrosion, but is related to the deposition of a calcium carbonate film or scale; this covering can insulate pipes, boilers and other components of a system from contact with water. When no protective scale is formed, water is considered to be aggressive and corrosion can occur. Highly corrosive water can cause system failures or result in health problems because of dissolved lead and other heavy metals. An excess of scale can also damage water systems, necessitating repair or replacement.

In developing the LI, Langelier derived an equation for the pH at which water is saturated with calcium carbonate (pH_s). This equation is based on the equilibrium expressions for calcium carbonate solubility and bicarbonate dissociation. To approximate actual conditions more closely, pH_s calculations were modified to include the effects of temperature and ionic strength.

The Langelier Index is defined as the difference between actual pH (measured) and calculated pH_s. The magnitude and sign of the LI value show water's tendency to form or dissolve scale and thus to inhibit or encourage corrosion.

Although information obtained from the LI is not quantitative, it can be useful in estimating water treatment requirements for low pressure boilers, cooling towers and water treatment plants, as well as serving as a general indicator of the corrosivity of water.

Parameter measurement

The Langelier Saturation Index can be calculated easily by using Hach products to determine the pH of calcium carbonate saturation (pH) and the actual pH of a solution. Using a simple formula, the pH is derived from the values for calcium hardness, total alkalinity at pH 4.5, temperature and total filterable residue (total dissolved solids). All of these procedures are included in this manual.

Temperature:
Temperature can be measured in degrees celsius with a laboratory thermometer (Catalog. Number. 566-01). If only a Fahrenheit thermometer is available, conversion to degrees Celsius will be necessary.
[°C = 5/9 x (°F – 32)].

Calculation
After the preceding parameters have been determined, calculate the pH from the following formula:

$$pH_s = A + B - C - D$$

Where:
Constant A takes into account the effect of temperature. It is found by selecting the value from the *Water temperature* table that corresponds to the measured temperature in degrees Celsius.

Constant B is a correction for the ionic strength of the sample. It is determined using the *TDS* table by taking the value that corresponds to the measured total filterable residue or the estimated total dissolved solids (TDS).

Value C is obtained from the *Hardness or alkalinity* table by reading the value corresponding to the calcium hardness (in mg/L $CaCO_3$) of the sample.

Value D is obtained from the *Hardness or alkalinity* table by reading the measured value for total alkalinity (in mg/L $CaCO_3$) of the sample.

The Langelier Saturation Index is the difference between the actual pH of the solution and pH_s calculated above.

$$LI = pH_{actual} - pH_s$$

Interpretation

The LI is a gauge of whether a water will precipitate or dissolve calcium carbonate. If the pH_s is equal to the actual pH, the water is considered “balanced”. This means that calcium carbonate will not be dissolved or precipitated. If the pH_s is less than the actual pH (the LI is a positive number), the water will tend to deposit calcium carbonate and is scale-forming (nonaggressive). If the pH_s is greater than the actual pH (the LI is a negative number), the water is not saturated and will dissolve calcium carbonate (aggressive). In summary:

$pH_S = pH_{actual}$, water is balanced

$pH_S < pH_{actual}$, LI = positive number, water is scale forming (nonaggressive)

$pH_S > pH_{actual}$, LI = negative number, water is not scale forming (aggressive)

It is important to remember that the LI value is not a quantitative measure of calcium carbonate saturation or corrosion.

Because the protective scale formation is dependent on pH, bicarbonate ion, calcium carbonate, dissolved solids and temperature; each may affect the water’s corrosive tendencies independently. Soft, low-alkalinity waters with either low or excessively high pH are corrosive, even though this may not be predicted by the LI. This is because insufficient amounts of calcium carbonate and alkalinity are available to form a protective scale.

Waters with high pH values and sufficient hardness and alkalinity may also be corrosive, even if the LI predicts the opposite. This is the result of calcium and magnesium complexes that cannot actively participate in the scale forming process. Analytical procedures do not distinguish between these complexes and available calcium and magnesium; therefore, the LI value is not accurate in such situations.

Corrosive tendencies may also be exhibited by water containing high concentrations of sulfate, chloride and other ions which interfere with uniform carbonate film formation.

As a result of these and other problems, the LI is useful only for determining the corrosivity of waters containing more than 40 mg/L of alkalinity, sufficient calcium ion concentration and ranging between pH 6.5 and 9.5.

Aggressive index

The Aggressive Index (AI), originally developed for monitoring water in asbestos pipe, is sometimes substituted for the Langelier Index as an indicator of the corrosivity of water. The AI is derived from the actual pH, calcium hardness and total alkalinity. (Use procedures contained in this handbook). Where it is applicable, it is simpler and more convenient than the LI. Because the AI does not include the effects of temperature or dissolved solids, it is less accurate as an analytical tool than the LI.

Calculation

After obtaining the pH, total alkalinity and calcium hardness, use the following formula to calculate the AI:

$$AI = pH_{actual} + C + D$$

Where:
Value C is obtained from the *Hardness or alkalinity* table by reading the value corresponding to the calcium hardness (in mg/L $CaCO_3$) of the sample.

Value D is obtained from the *Hardness or alkalinity* table by reading the measured value for total alkalinity (in mg/L $CaCO_3$) of the sample.

Interpretation

As with LI, the AI is not a quantitative measure of corrosion, but is a general indicator of the tendency for corrosion to occur and as such, should be used with proper reservation. An AI of 12 or above indicates nonaggressive (not corrosive) water. AI values below 10 indicate extremely aggressive (corrosive) conditions. Values of 10–11.9 suggest that the water is moderately aggressive. Corrosivity characteristics of water as indicated by the LI and AI are compared in the *Corrosion characteristics* table.

Table 1 Water temperature

Water temperature, °C	A
0	2.60
4	2.50
8	2.40
12	2.30
16	2.20
20	2.10
25	2.00
30	1.90
40	1.70
50	1.55
60	1.40
70	1.25
80	1.15

Table 2 TDS

TDS, mg/L	B
0	9.70
100	9.77
200	9.83
400	9.86
600	9.89
1000	9.90

Table 3 Hardness or alkalinity

Calcium hardness or total alkalinity in mg/L $CaCO_3$	C[1] or D[2]
10	1.00
20	1.30
30	1.48
40	1.60
50	1.70
60	1.78
70	1.84
80	1.90
100	2.00
200	2.30
300	2.48
400	2.60
500	2.70
600	2.78
700	2.84
800	2.90
900	2.95
1000	3.00

[1] Factor C is the logarithm (base 10) of the calcium hardness expressed in mg/L

[2] Factor D is the logarithm (base 10) of the total alkalinity expressed in mg/L

Table 4 Corrosion characteristics

Corrosive characteristics	Langelier index	Aggressive index
Highly aggressive	< –2.0	< 10.0
Moderately aggressive	–2.0 to 0.0	10.00 to 12.0
Nonaggressive	>0.0	>12.0

References

1. Langelier, W. F., “The Analytical Control of Anticorrosion Water Treatment” Journal of American Water Works Association 1936, 28, 1500.
2. Larson, T.E.; Buswell A. M. “Calcium Carbonate Saturation Index and Alkalinity Interpretations” Journal of American Water Works Association 1942, 34, 1667.
3. Langelier, W. F., “Chemical Equilibria in Water Treatment” Journal of American Water Works Association 1946, 38, 169.
4. Maguire, J. J.; Polsky, J. W. “Simplified Plant Control Test for Boiler Water Dissolved Solids” Combustion 1947, May, 35.
5. Betz Handbook of Industrial Water Conditioning 1962, 6th ed., Betz Laboratories: Trevose, PA.
6. Robinson, R. A.; Stokes, R. H. Electrolyte Solutions 1965, Butterworth & Co. LTD: London.
7. Federal Register 1980, 45 (168), August 27, 1980, p. 57338.

Applied Math for Water

Stabilization Math

Langelier Index – Determine the LI and the corrosive characteristics:

1. Calculate the Langelier Index for the following information:

pH	=	7.65
temperature	=	15°C
TDS	=	200 mg/L
Calcium	=	80 mg/L as $CaCO_3$
Alkalinity	=	100 mg/L as $CaCO_3$

2. Calculate the Langelier Index for the following information:

pH	=	7.4
temperature	=	20°C
TDS	=	200 mg/L
Calcium	=	80 mg/L as $CaCO_3$
Alkalinity	=	100 mg/L as $CaCO_3$

3. Calculate the Langelier Index for the following information:

pH	=	7.4
temperature	=	20°C
TDS	=	400 mg/L
Calcium	=	100 mg/L as $CaCO_3$
Alkalinity	=	100 mg/L as $CaCO_3$

4. Calculate the Langelier Index for the following information:

pH	=	7.0
temperature	=	15°C
TDS	=	200 mg/L
Calcium	=	10 mg/L as $CaCO_3$
Alkalinity	=	10 mg/L as $CaCO_3$

5. Calculate the Langelier Index for the following information:

pH	=	7.6
temperature	=	25°C
TDS	=	400 mg/L
Calcium	=	150 mg/L as $CaCO_3$
Alkalinity	=	170 mg/L as $CaCO_3$

6. Calculate the Langelier Index for the following information:

pH	=	8.6
temperature	=	15°C
TDS	=	200 mg/L
Calcium	=	50 mg/L as $CaCO_3$
Alkalinity	=	100 mg/L as $CaCO_3$

Aggressive Index – Determine the AI and the corrosive characteristics:

7. Calculate the aggressive index for the following information:

Total alkalinity	=	100 mg/L as $CaCO_3$
Calcium	=	70 mg/L as $CaCO_3$
pH	=	7.6

8. Calculate the aggressive index for the following information:

Total alkalinity	=	270 mg/L as $CaCO_3$
Calcium	=	200 mg/L as $CaCO_3$
pH	=	7.3

9. Calculate the aggressive index for the following information:

Total alkalinity	=	100 mg/L as $CaCO_3$
Calcium	=	50 mg/L as $CaCO_3$
pH	=	7.2

10. Calculate the aggressive index for the following information:

Total alkalinity	=	100 mg/L as $CaCO_3$
Calcium	=	70 mg/L as $CaCO_3$
pH	=	7.2

11. Calculate the aggressive index for the following information:

Total alkalinity	=	100 mg/L as $CaCO_3$
Calcium	=	80 mg/L as $CaCO_3$
pH	=	7.1

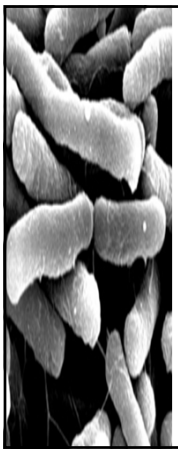
12. Calculate the aggressive index for the following information:

Total alkalinity	=	20 mg/L as $CaCO_3$
Calcium	=	15 mg/L as $CaCO_3$
pH	=	7.0

Answers:

1. – 0.37 MA
2. – 0.55 MA
3. – 0.51 MA
4. – 2.92 HA
5. 0.17 NA
6. 0.38 NA
7. 11.45 MA
8. 12.03 NA
9. 10.9 MA
10. 11.05 MA
11. 11.0 MA
12. 9.48 HA

Section 6
Heterotrophic Plate Count



Heterotrophic Plate Counts

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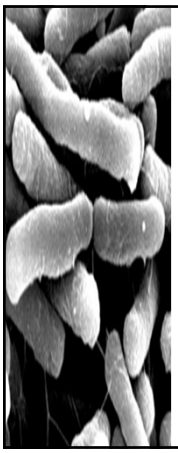
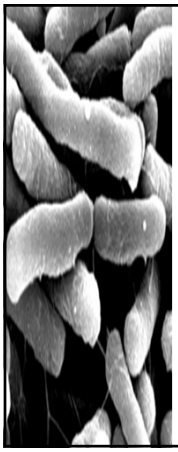


Heterotrophic Plate Count

- 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 2



Heterotrophic Plate Count

- 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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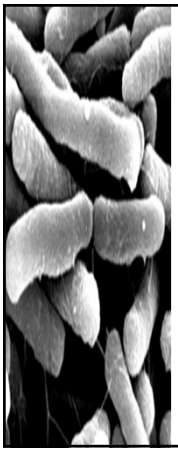

Heterotrophic Plate Count

- 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 (>500cfu/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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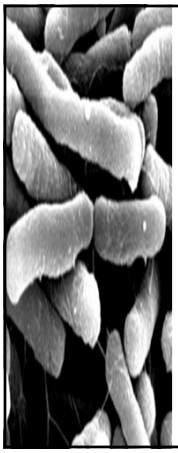

Heterotrophic Plate Count

- 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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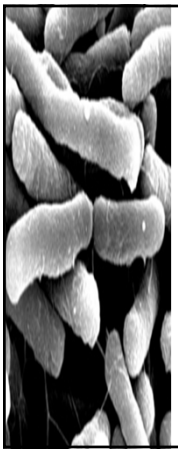

Heterotrophs

- Heterotrophs are organisms that require an external source of organic carbon for growth
  - Bacteria
  - Yeasts
  - Molds

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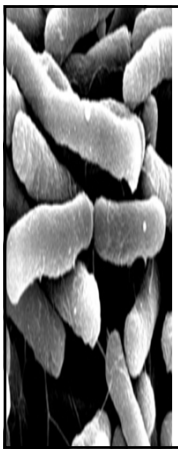

Heterotrophs

- High levels of microbial growth can affect the taste and odor of drinking water
- And may indicate the presence of nutrients and biofilms that could harbor pathogens

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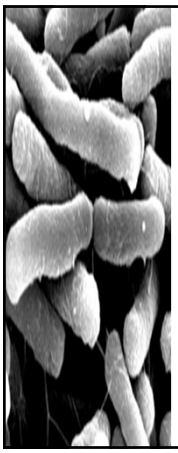

- There is no firm evidence that non-pathogenic bacterial growth as measured by HPC is accompanied by increased risk of illness among customers

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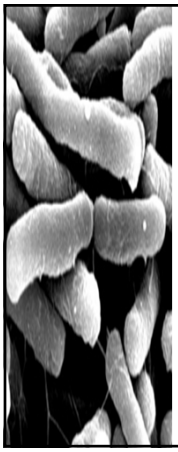

SimPlate for HPC

- IDEXX
  - SimPlate: Video Demonstration

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SimPlate * for HPC Unit Dose

Introduction

SimPlate for HPC method is used for the quantification of heterotrophic plate counts (HPC) in water. It is based on IDEXX's patented Multiple Enzyme Technology*, which detects viable bacteria in water by testing for the presence of key enzymes known to be present in these organisms. It uses multiple enzyme substrates that produce a blue fluorescence when metabolized by waterborne bacteria. The sample and media are added to a SimPlate, incubated, and then examined for fluorescing wells. The number of fluorescing wells corresponds to a Most Probable Number (MPN) of total bacteria in the original sample. The MPN values generated by the SimPlate for HPC method correlate with the Pour Plate method using Total Plate Count Agar incubated at 35°C for 48 hours as described in *Standard Methods for the Examination of Water and Wastewater*[1].

Contents

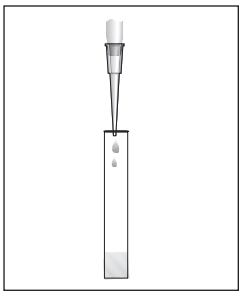
- 25 sterile media tubes for 10 mL samples
- 25 sterile SimPlate plates with lids
- MPN table
- This insert

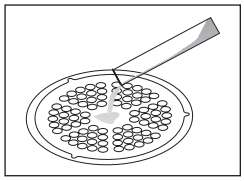
Storage

Store at 2–30°C and away from light. Expiration date is printed on the box of media tubes.

Test Procedure

1. Add 10±0.2 mL of sample to a media tube, re-cap and shake to dissolve. See image #1.
2. Pour the contents of the tube onto the center of the plate base. See image #2.
3. Cover the plate with the lid and gently swirl to distribute the sample into all the wells. See image #3.
   NOTE: Air bubbles in the wells do not interfere with the test.
4. Tip the plate 90°–120° to drain excess sample into the absorbent pad. See image #4.
5. Invert the plate and incubate for 48 hours at 35±0.5°C. See image #5.
6. Count the number of wells showing any fluorescence by holding a 6-watt, 365nm, UV light 5 inches above the plate. Direct light away from your eyes and towards the sample. Alternatively, you may read fluorescent wells through the back of the inverted SimPlate base.
7. Refer to the MPN table provided to determine the Most Probable Number of heterotrophic plate count bacteria in the original sample. The table takes into account the sample/media poured off in step #4 above.

1


2


3

4

5

Procedural Notes

1. Follow aseptic technique.
2. Chlorinated samples should be treated with sodium thiosulfate prior to testing.
3. Results can be read from 45 to 72 hours after start of incubation.
4. Dispose of sample and media in accordance with Good Laboratory Practices.
5. Samples may be diluted before adding to the media as long as the final volume (sample plus sterile diluent) is 10±0.2 mL. Adjust the MPN result to reflect dilutions. For example, if 1 mL of sample and 9 mL of sterile diluent are tested (a 10-fold dilution), multiply the MPN table number by 10 to find the correct MPN/mL.

Quality Control Procedure

The following procedure is recommended for each lot of SimPlate for HPC product:

1. A. Positive Control: IDEXX-QC HPC/TVC[2]: *Enterococcus faecalis.*
   B. Negative Control/Blank: Use 10 mL of rehydrated HPC media.
2. Follow steps 1-7.
3. Negative Control/Blank wells should not fluoresce after incubation.

IDEXX Technical Support:
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China: +86 21 61279528
Japan: +81 422 71 5921
Australia: 1 800 655 978

IDEXX

1. Eaton, AD, Clesceri, LS, Greenberg, AE, Rice, EN. *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, 2005. Washington, DC.
2. IDEXX-QC HPC/TVC, IDEXX Catalog #UN3373-WQC-HPC.

*SimPlate is a trademark or a registered trademark of BioControl Systems, Inc. and is used by IDEXX under license from BioControl Systems, Inc.
*Multiple Enzyme Technology is a trademark of IDEXX Laboratories, Inc. in the United States and/or other countries.
Patent information: idexx.com/patents.
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Unit-Dose
SimPlate For HPC
Most Probable Number (MPN) Table

# 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
15	3.3	2.0	5.4
16	3.5	2.2	5.8
17	3.8	2.3	6.1
18	4.0	2.5	6.4
19	4.3	2.7	6.7
20	4.5	2.9	7.0
21	4.8	3.1	7.4
22	5.1	3.3	7.7
23	5.3	3.5	8.0
24	5.6	3.8	8.4
25	5.9	4.0	8.7
26	6.2	4.2	9.1
27	6.5	4.4	9.4
28	6.8	4.7	9.8
29	7.1	4.9	10.2
30	7.4	5.1	10.6
31	7.7	5.4	10.9
32	8.0	5.6	11.3
33	8.3	5.9	11.7
34	8.6	6.2	12.1
35	9.0	6.4	12.6
36	9.3	6.7	13.0
37	9.7	7.0	13.4
38	10.0	7.3	13.9
39	10.4	7.6	14.3
40	10.8	7.9	14.8
41	11.2	8.2	15.2
42	11.6	8.5	15.7

# Positive Wells	MPN	95% confidence limits lower	upper
43	12.0	8.8	16.2
44	12.4	9.1	16.7
45	12.8	9.5	17.3
46	13.2	9.8	17.8
47	13.7	10.2	18.3
48	14.1	10.6	18.9
49	14.6	10.9	19.5
50	15.1	11.3	20.1
51	15.6	11.7	20.7
52	16.1	12.1	21.3
53	16.6	12.5	22.0
54	17.1	13.0	22.7
55	17.7	13.4	23.4
56	18.3	13.9	24.1
57	18.9	14.4	24.9
58	19.5	14.9	25.7
59	20.2	15.4	26.5
60	20.9	15.9	27.3
61	21.6	16.5	28.2
62	22.3	17.1	29.2
63	23.1	17.7	30.2
64	23.9	18.3	31.2
65	24.8	19.0	32.3
66	25.7	19.7	33.5
67	26.6	20.4	34.7
68	27.6	21.2	36.1
69	28.7	22.0	37.5
70	29.9	22.9	39.0
71	31.1	23.8	40.7
72	32.4	24.8	42.5
73	33.9	25.8	44.4
74	35.5	27.0	46.6
75	37.2	28.2	49.1
76	39.2	29.6	51.9
77	41.4	31.1	55.1
78	44.0	32.8	58.9
79	47.0	34.8	63.6
80	50.7	37.1	69.5
81	55.5	39.8	77.5
82	62.3	43.2	89.9
83	73.8	47.6	114.6
84	>73.8	>47.6	>114.6

MPN is per ml of the 10 ml sample added to the media tube (pour-off is accounted for).

Section 7
Metals and Organic Analysis

Metals and Organic Analysis

Intermediate Water Treatment Laboratory

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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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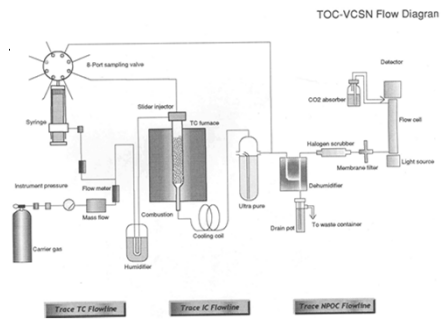
Total Organic Carbon

- 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

7 TDEC - Fleming Traning Center



8 TDEC - Fleming Traning Center

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

9 TDEC - Fleming Traning Center

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

10 TDEC - Fleming Traning Center

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

11 TDEC - Fleming Traning Center

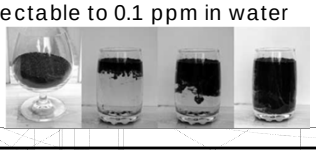
SUVA

- Specific UV Absorbance
- Compares UV-254 to Dissolved Organic Carbon (DOC)
  - There is a relationship between SUVA levels and humic substances

12 TDEC - Fleming Traning Center

Humic Substances

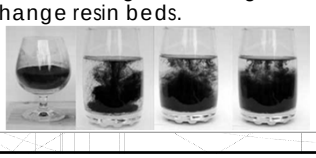
- Humic substances are the organic portion of soil that remains after prolonged microbial decomposition, and that is formed by the decay of leaves, wood, and other vegetable matter.
- They can impart a yellowish-brown to brownish-black color to water; detectable to 0.1 ppm in water



13 TDEC - Fleming Traning Center

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.



14 TDEC - Fleming Traning Center

Color

- sMCL for color is 15 color units

15 TDEC - Fleming Traning Center

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.

16 TDEC - Fleming Traning Center

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.

17 TDEC - Fleming Traning Center

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.

18 TDEC - Fleming Training Center

Color

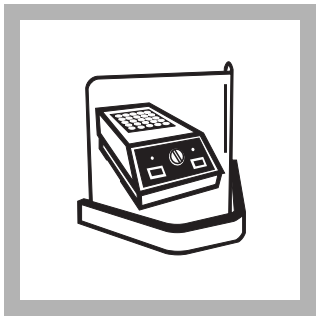
- True color
  - Color of water from which turbidity has been removed
- Apparent color
  - Includes true color and color caused by suspended matter

Method 10140 **THM Reactor Method***

Powder Pillows **(0–200 ppb as Chloroform)**

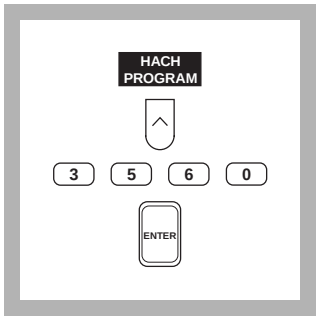
Scope and Application: *For drinking water.*

* 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.

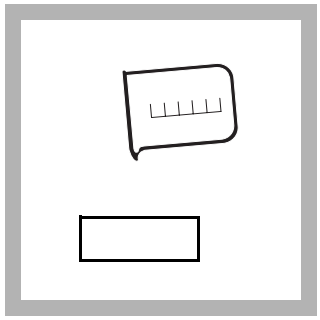
Press **ENTER**.

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

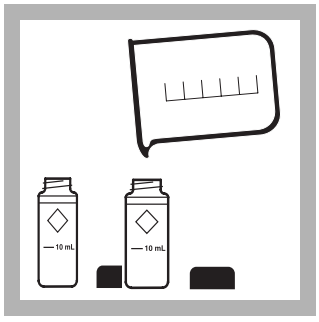
The wavelength (λ), 515 nm, is automatically selected.



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.*

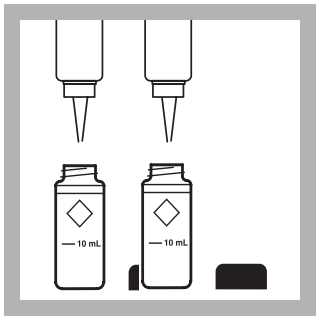
Note: *If analyzing more than four samples, use 450 mL of water.*



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.*

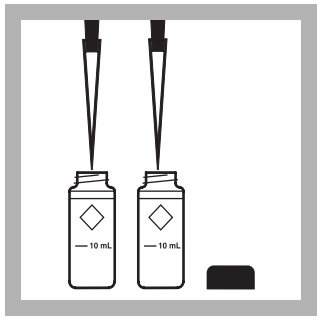
Note: *If dispensing sample with a pipette, the pipette must dispense quickly without causing aeration or back pressure.*



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.*

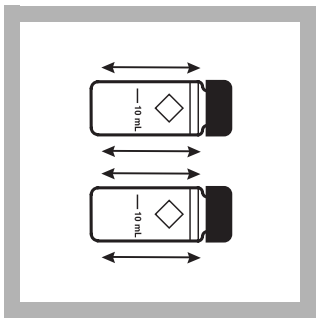


8. Use a TenSette® pipette to add 3 mL of THM Plus Reagent 2 to each cell.

Note: *The liquid is viscous and a small amount may remain in the tip after dispensing. This will not affect the results.*

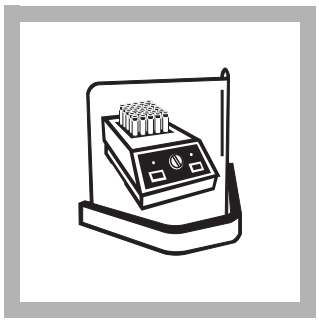
Note: *The THM Plus Reagent 2 must be at room temperature before use.*

THM Plus™ TRIHALOMETHANES, continued

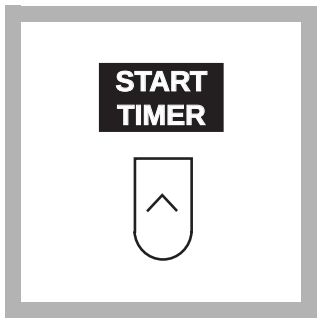


9. Cap tightly and mix by shaking ten times.

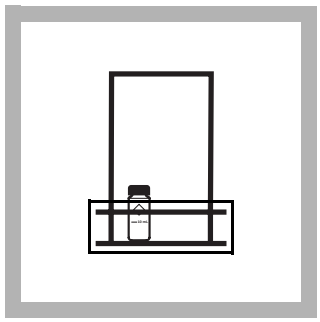
Note: *Thorough mixing ensures that all of the THM goes into the liquid and does not accumulate in the head space.*



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.

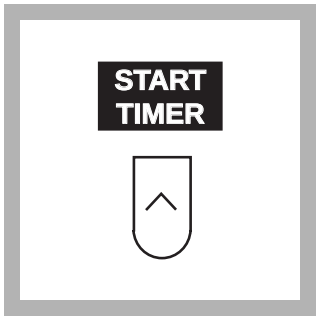


12. At the end of the reaction period, remove the cell from the reactor and place in the cell holder assembly.

Place the assembly in a cooling bath.

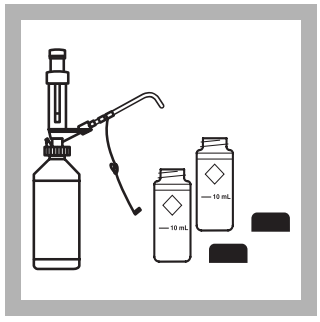
13. Press: ***NEXT TIMER*** twice.

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.

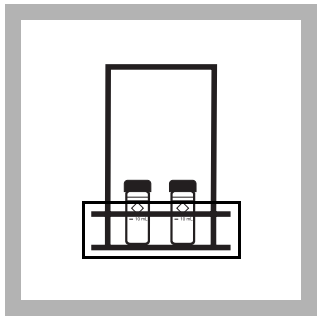
At the end of the cooling period, remove the cell from the cooling bath.



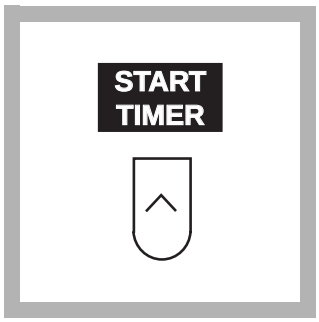
15. Use the Repipet Jr. to add 1 mL of THM Plus Reagent 3 to the sample cell and to the blank. Swirl to mix.

Note: *The sample will become warm*

Note: *The liquid is viscous and may not be entirely dispensed if measured using any other pipetting method.*



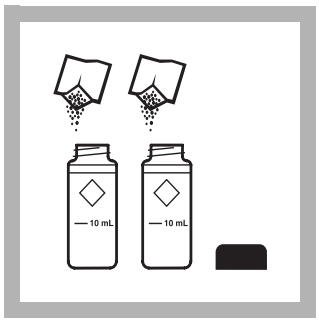
16. Replace the cooling water with fresh, cold tap water. Place the assembly containing the sample and blank cells into the cooling bath.



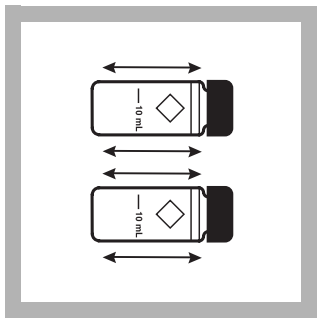
17. Press: ***START TIMER 3*** to begin a three-minute cooling time.

At the end of the cooling period, remove the cells from the cooling bath.

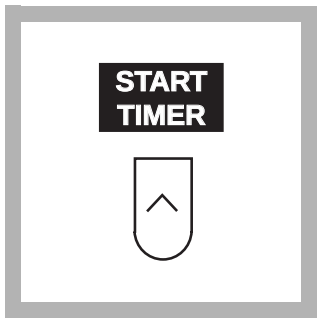
Note: *At the end of the cooling time, the sample temperature should be between 15 and 25 °C.*



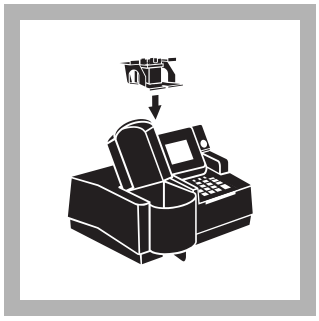
18. Add one THM Plus Reagent 4 Powder Pillow each to the sample cell and to the blank.



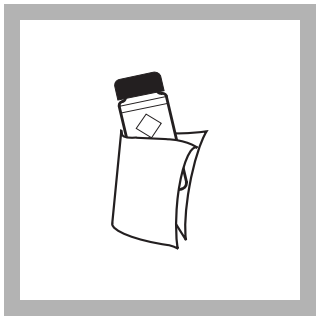
19. Cap each cell tightly and shake to dissolve.



20. Press ***START TIMER 4*** to begin a 15-minute color development time.

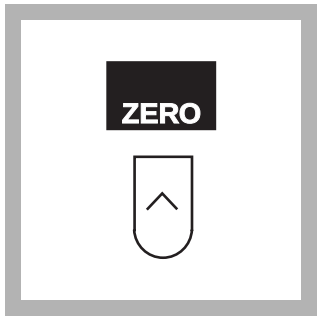


21. While the color is developing, insert the AccuVac® Ampul Adapter into instrument.



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.



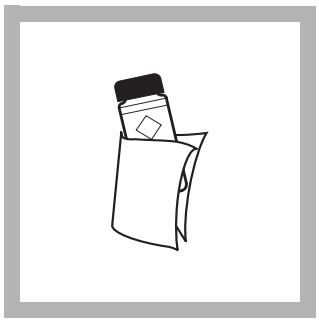
24. Press the soft key under ***ZERO***.

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.*

THM Plus™ TRIHALOMETHANES, continued



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.

THM Plus™ TRIHALOMETHANES, continued

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)

DOC316.53.01092

Direct Reading Method[1] Method 10054

Scope and Application: To indicate the total concentration of UV-absorbing organic compounds in drinking water and drinking water source waters.

[1] Adapted from *Standard Methods for the Examination of Water and Wastewater*, Method 5910.

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 1 Instrument-specific information

Instrument	Sample cell	Cell orientation	Adapter
DR 5000	2624410	Align clear windows facing the user	Multi-cell Adapter, 10-mm faces user

Before starting the test:

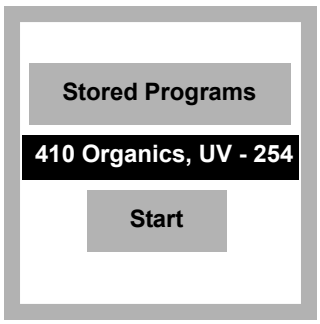
The sample pH should be between 4 and 10. If not, see *Interferences* in this procedure. Samples used for SUVA calculations **must not** be pH adjusted
Any non-plastic filter assembly can be used for this test. Use a 0.45-µm or glass fiber filter of nominal pore size (1–1.5 µm) without organic binder. A 0.45-µm filter must be utilized if the results are to be used for SUVA calculations.
Handle the cell on the frosted sides only.
Use only Organic-Free Reagent Water to zero the instrument.
The Chromic Acid Cleaning Solution is regulated as a hazardous waste for chromium (D007) and corrosivity (D002) when disposed per Federal RCRA. Refer to the current MSDS for safe handling and disposal instructions.

Collect the following items:

Description	Quantity
Organic-free Reagent Water	varies
Filter Assembly	1
Stand, buret	1
Sample Cell (see *Instrument-specific information*)	1

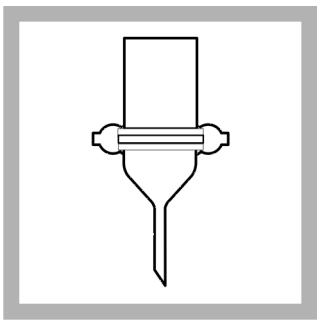
See *Consumables and replacement items* for reorder information.

Organic Constituents

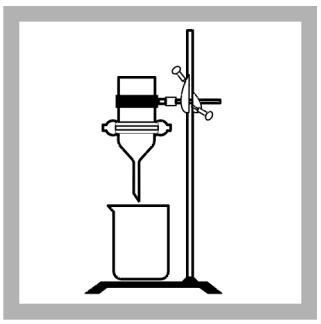


1. Select the test.

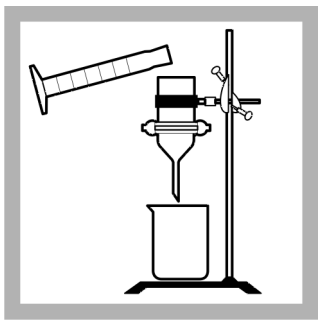
Insert an adapter if required (see *Instrument-specific information*).



2. Assemble the filter apparatus. Be sure to use the white PTFE support plate. Insert the filter with the wrinkled surface upward.

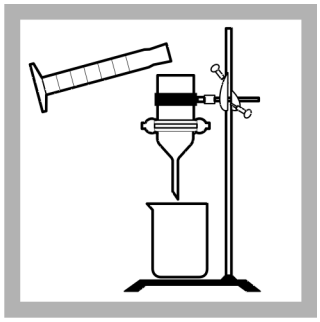


3. Mount the apparatus into a support stand and place a clean glass beaker underneath.

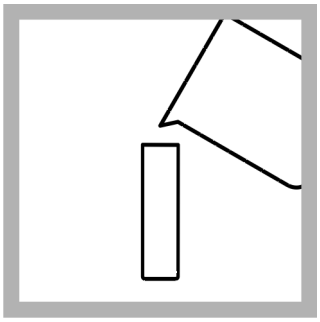


4. Prewash the filter assembly by pouring at least 50 mL of Organic-Free Reagent Water through the filter. Discard the filtered water.

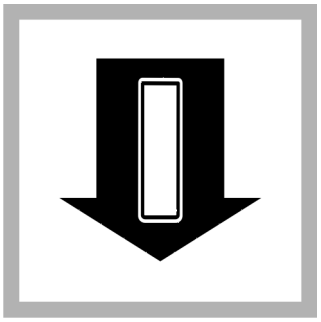
Pre-rinsing removes any soluble impurities from the filter.



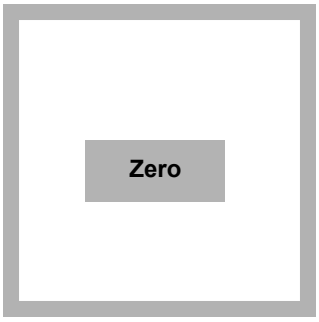
5. Prepared Sample: Pour 50 mL of sample through the filter and collect the filtered sample.



6. Blank Preparation: Rinse a clean 1-cm quartz cell several times with Organic-Free Reagent Water. Fill the cell with Organic-Free Reagent Water. Wipe the cell walls thoroughly.



7. Align the clear windows with the light path. Insert the blank into the cell holder.



8. ZERO the instrument.

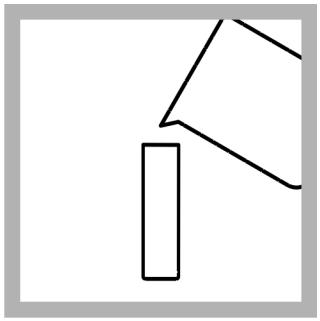
The display will show:

0.000 cm^{-1}

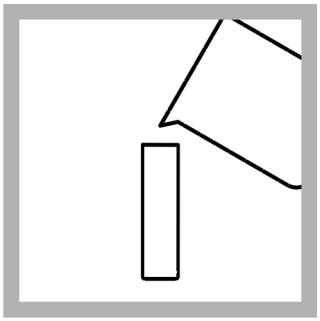
1-cm cell

Lamp Warm Up will be indicated if the UV lamp has not been previously on. This may take 2–3 minutes.

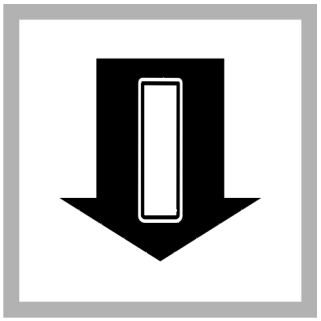
Organic Constituents (continued)



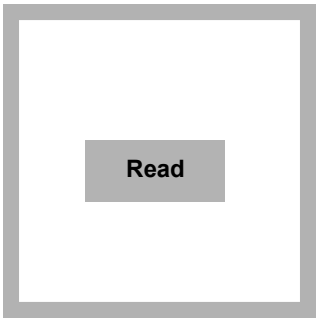
9. Discard the contents of the blank cell and rinse the cell several times with filtered sample.



10. After rinsing, fill the cell with filtered sample. Wipe the cell walls to remove fingerprints.



11. Align the clear windows with the light path. Insert the cell containing the prepared sample into the cell holder.



12. **READ** the results in absorbance per centimeter (cm^{-1}).

For optimum results, the cm^{-1} value should fall between 0.005 and 0.900. If the value is less than 0.005 absorbance using a 1-cm cell, use a 5-cm or 10-cm quartz cell.

To test with the 5-cm or 10-cm cell:

1. Press **OPTIONS>MORE>CHEMICAL FORMS**.
2. Press **5 CM** or **10 CM.** Press **OK>RETURN**.
3. The displayed results (in absorbance per centimeter) will be corrected for the 5-cm or 10-cm cell pathlength selected. If cm^{-1} results are greater than 0.900, accurately dilute the sample with Organic-Free Reagent Water. Correct the test result by the appropriate dilution factor.

Interferences

Table 2 Interfering substances

Interfering substance	Interference level
Sample pH outside 4–10	Add either 1 N Sodium Hydroxide or 1 N Sulfuric Acid to the sample to adjust sample between pH 4-10.
UV-absorbing inorganics (bromide, ferrous iron, nitrate, nitrites)	Follow the UV scanning procedure below.
UV-absorbing Oxidants and reductants (chloramines, chlorates, chlorites, ozone, thiosulfates)	Follow the UV scanning procedure below.

To determine the presence of interferences, a scan of the filtered sample versus Organic-Free Reagent Water is recommended on a regular basis:

1. From the main menu, press **WAVELENGTH SCAN>OPTIONS>**I .
2. Press **200>OK**.
3. Press **400>OK**.
4. Press **1 NM>OK**.

5. Insert the cell containing the Organic-Free Reagent Water (the blank) into the cell compartment.
6. Press **ZERO**. The baseline scan from 200 to 400 nm will begin.

Note: *Lamp Warm Up will be indicated if the UV lamp has not been previously on. This may take 2–3 minutes.*

7. After the baseline scan is recorded, insert the cell containing the filtered sample into the cell compartment. Press **READ** to scan the sample.

If the sample scan shows relatively sharp peaks, interferences may be present. Generally, natural organic matter will show a relatively featureless curve in the UV region with increasing absorption as the wavelength decreases. If the sharp peaks are indicated, an alternate wavelength should be selected and reported.

Sample collection, preservation and storage

- Collect samples in cleaned glass containers. Do not use plastic containers.
- Analyze samples as soon as possible after collection.

Cell cleaning

New or dirty cells should be soaked with Chromic Acid Cleaning Solution to remove trace organic contamination.

1. Allow to soak overnight or up to 12 hours.
2. After soaking, rinse with at least 10 volumes of Organic-Free Reagent Water.

Treatment of cells with chromic acid is required only occasionally if cells are rinsed with Organic-Free Reagent Water after use.

Method performance

Standard: There is no primary standard or calibration for the UV-254 method. Using a Potassium Acid Phthalate solution equivalent to 30-mg/L as carbon, the following reproducibility data was obtained using one instrument. Refer to Standard Methods for the standard preparation.

Program	Precision—95% Confidence Limits of Distribution
410	0.431 - 0.433 cm^{-1}

Summary of method

Filtered sample is measured at 254 nm against organic-free water as a indicator of organic constituents in the sample water. Results are automatically reported in absorbance per centimeter (cm^{-1}). The results can be used in calculating Specific Ultraviolet Absorbance (SUVA).

Estimated detection limit

Because this test is a non-specific measurement for organic constituents, there is no estimated detection limit for program 410.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Organic-Free Reagent Water	varies	500 mL	2641549

Required apparatus

Description	Unit	Catalog number
Beaker, 100-mL	each	50042H
Buret Stand	each	32900
Clamp Holder	each	32600
Clamp, 3-Prong	each	42200
Filter Funnel Assembly, 7-cm	each	2164100
Filter Plate, PTFE, for 21641-00	each	2164200
Filter, glass fiber, 70-mm	100/pkg	253053
Sample Cell, quartz, 1-cm (10 mm)	each	2624410
Sulfuric Acid, 1 N	100 mL MDB	127032

Optional reagents

Description	Unit	Catalog number
Chromic Acid Cleaning Solution	500 mL	123349
Sodium Hydroxide Standard Solution, 1.00 N	100 mL MDB[1]	104532

[1] Larger sizes are available.

Optional apparatus

Description	Unit	Catalog number
Cell Holder for 10-cm (100 mm) sample cells (DR 5000 only)	each	LZY421
Cylinder, graduated, 50-mL	each	50841
Filter, membrane, 47-mm; 0.45-microns, hydrophilic, polyethersulfone SUVA	each	2894700
Filter Holder, glass for vacuum filtration (SUVA)	each	234000
Flask, filtering, glass, 1000-mL (SUVA)	each	54653
pH Paper, pH 1.0 to 11.0	5 rolls/pkg	39133
Tubing, Latex rubber (SUVA)	12 ft	56019
Potassium Acid Phthalate	500 g	31534
Sample Cell, quartz, 1-cm (10 mm), matched pair	pair	4822800
Sample Cell, quartz, 5-cm (50 mm)	each	2624450
Sample Cell, quartz, 10-cm (100 mm)	each	2624401
Standard Methods Book, most current edition	1	2270800
Aspirator (SUVA)	1	213100

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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 form is ferrous iron
  - Fe^{+2} (divalent)
- The insoluble form is ferric iron
  - Fe^{+3} (oxidized)
- The soluble form is converted to insoluble form by a chemical process called oxidation

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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

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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 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

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Iron, Total

DOC316.53.01053

USEPA[1] FerroVer® Method[2] **Method 8008**

0.02 to 3.00 mg/L **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

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 1 Instrument-specific information

Instrument	Powder pillows		AccuVac Ampuls	
	Sample cell	Cell orientation	Sample cell	Adapter
DR 5000	2495402	Fill line faces user	2427606	—
DR 3900	2495402	Fill line faces user	2427606	LZV846 (A)
DR 3800, DR 2800, DR 2700	2495402	Fill line faces right	2122800	LZV584 (C)

Before starting the test:

Digestion is required for determining total iron for EPA reporting purposes. Use the mild or vigorous digestion. Refer to the *Water Analysis Guide* for more information.
For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water in place of the sample. Subtract the reagent blank value from the final results or perform a reagent blank adjust. See the user manual for more information.
Adjust pH of stored samples before analysis.
For turbid samples, treat the blank with one 0.1-g scoop of RoVer Rust Remover. Swirl to mix.

Collect the following items:

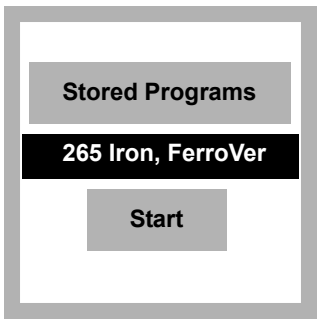
Description	Quantity
Powder Pillow Test:	
FerroVer® Iron Reagent Powder Pillow	1
Sample Cells (see *Instrument-specific information*)	2

Collect the following items: (continued)

Description	Quantity
AccuVac® Ampul test:	
FerroVer® Iron Reagent AccuVac® Ampul	1
Beaker, 50-mL	1
Sample Cells (see *Instrument-specific information*)	1
Stopper of 18 mm tubes	1

See *Consumables and replacement items* for reorder information.

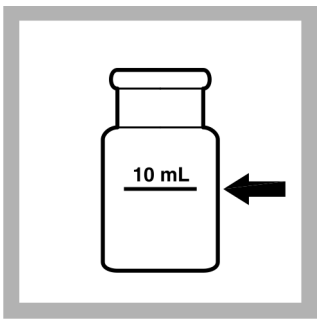
FerroVer method for powder pillows



1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).

Refer to the user manual for orientation.



2. Prepared sample: Fill a clean sample cell with 10 mL of sample

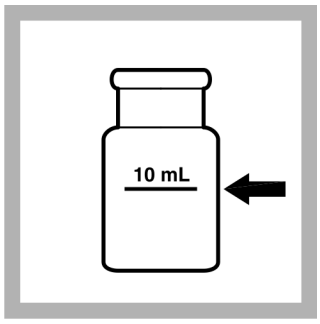
3. Add the contents of one FerroVer Iron Reagent Powder Pillow to the sample cell. Swirl to mix.

Accuracy is not affected by undissolved powder.

4. Start the instrument timer.

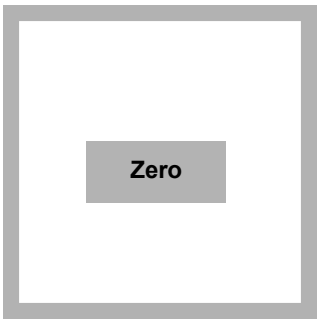
A three-minute reaction period will begin. An orange color will form, if iron is present.

(Allow samples that contain rust to react for at least 5 minutes.)



5. Blank preparation: Fill a second sample cell with 10 mL of sample.

6. When the timer expires, insert the blank into the cell holder.



7. ZERO the instrument.

The display will show:

0.00 mg/L Fe

8. Insert the prepared sample into the cell holder.

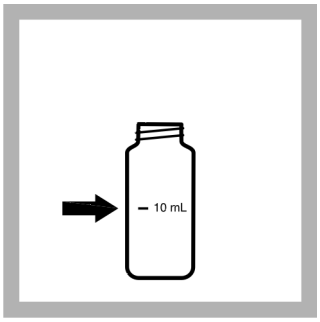
READ the results in mg/L Fe.

FerroVer method for AccuVac® Ampuls

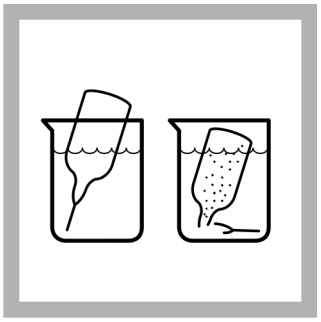
1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).

Refer to the user manual for orientation.



2. Blank Preparation: Fill a round sample cell with 10 mL of sample.



3. Prepared Sample: Collect at least 40 mL of sample in a 50-mL beaker. Fill a FerroVer Iron AccuVac® Ampul with sample from the beaker. Keep the tip immersed while the Ampul fills completely.

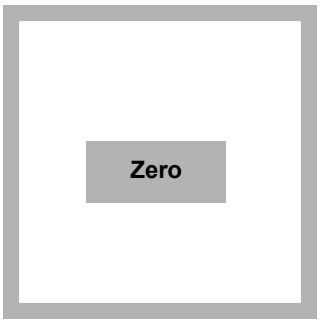
4. Quickly invert the Ampul several times to mix.

Accuracy is not affected by undissolved powder.

5. Start the instrument timer.

A three-minute reaction period will begin. An orange color will develop if iron is present.

6. Wipe the blank and insert it into the cell holder.



7. ZERO the instrument.

The display will show:

0.00 mg/L Fe

8. Wipe the Ampul and insert it into the cell holder.

READ the results in mg/L Fe.

Interferences

Table 2 Interfering substances

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	Requires mild, vigorous or Digesdahl digestion. After digestion, adjust sample to pH 3–5 with sodium hydroxide, then analyze.
Magnesium	No effect at 100,000 mg/L as calcium carbonate.

Table 2 Interfering substances (continued)

Interfering substance	Interference level
Molybdate Molybdenum	No effect at 50 mg/L as Mo.
High Sulfide Levels, S^{2-}	**1.** Treat in fume hood or well-ventilated area. Add 5 mL hydrochloric acid[1], ACS to 100 mL sample in a 250 mL Erlenmeyer flask. Boil 20 minutes. **2.** Cool. Adjust pH to 3–5 with Sodium Hydroxide[1]. Readjust volume to 100 mL with deionized water. **3.** Analyze using *FerroVer method for powder pillows* or *FerroVer method for AccuVac® Ampuls*.
Turbidity	**1.** Add 0.1 g scoop of RoVer® Rust Remover to the blank. Swirl to mix. **2.** Zero the instrument with this blank. **3.** If sample remains turbid, add three 0.2 g scoops of RoVer to a 75 mL sample. Let stand 5 minutes. **4.** Filter through a Glass Membrane Filter and Filter Holder[1]. **5.** Use the filtered sample as the prepared sample and the blank.
Extreme Sample pH	Adjust pH to 3–5.
Highly Buffered Samples	Adjust pH to 3–5.

[1] See *Optional reagents and apparatus*.

Sample collection, preservation and storage

- Collect samples in acid-cleaned glass or plastic containers. No acid addition is necessary if analyzing the sample immediately.
- To preserve samples, adjust the pH to 2 or less with concentrated nitric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature.
- Before analysis, adjust the pH to between 3 and 5 with 5.0 N Sodium Hydroxide Standard Solution.
- Correct the test result for volume additions.
- If only dissolved iron is to be determined, filter the sample before acid addition.

Accuracy check

Standard additions method (sample spike)
Required for accuracy check:

- Iron Voluette® Ampule Standard, 25 mg/L
- Ampule breaker
- TenSette Pipet and Pipet Tips

1. After reading test results, leave the sample cell (unspiked sample) in the instrument.
2. Select Options>More>Standard Additions from the instrument menu.
3. Accept the default values for standard concentration, sample volume and spike volumes. After the values are accepted, the unspiked sample reading will appear in the top row. See the user manual for more information.
4. Open the standard solution ampule.
5. Prepare a 0.1 mL sample spike by adding 0.1 mL of standard to 10 mL of unspiked sample. Start the instrument timer. After the timer expires, read the result.

6. Prepare a 0.2 mL sample spike by adding 0.1 mL of standard to the 0.1 mL sample spike. Start the instrument timer. After the timer expires, read the result.
7. Prepare a 0.3 mL sample spike by adding 0.1 mL of standard to the 0.2 mL sample spike. Start the instrument timer. After the timer expires, read the result.
8. Select **GRAPH** to view the results. Select **IDEAL LINE** (or best-fit) to compare the standard addition results to the theoretical 100% recovery.

Standard additions method for AccuVac Ampuls (sample spike)

1. Fill three mixing cylinders each with 50 mL of sample and spike with 0.2 mL, 0.4 mL and 0.6 mL of standard. Stopper and invert to mix.
2. Transfer 40 mL from each of the three mixing cylinders to three 50 mL beakers.
3. Analyze each standard addition sample as described in the *FerroVer method for AccuVac® Ampuls*.
4. Accept each standard additions reading. Each addition should reflect approximately 100% recovery.

Standard solution method
Note: *Refer to the instrument user manual for specific software navigation instructions.*

Required for accuracy check:

- Iron Standard Solution, 100 mg/L
- 100-mL volumetric flask
- Class A volumetric pipet, 2 mL
- Deionized water
- Pipet filler

1. Prepare a 2.00-mg/L Fe standard solution as follows:
   a. Pipet 2.00 mL of Iron Standard Solution, 100 mg/L, into a 100 mL volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
2. Use the 2.00 mg/L Fe standard solution in place of the sample. Follow the *FerroVer method for powder pillows* test procedure.
3. To adjust the calibration curve using the reading obtained with the Standard Solution, select Options>More>Standard Adjust from the instrument menu.
4. Turn on the Standard Adjust feature and accept the displayed concentration. If an alternate concentration is used, enter the concentration and adjust the curve to that value. Mixed-parameter standards are also available to simulate various matrices.

Method performance

Program	Standard	Precision 95% Confidence Limits of Distribution	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. Test results are measured at 510 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
FerroVer® Iron Reagent Powder Pillows (for 10-mL sample)	1	100/pkg	2105769
OR			
FerroVer® Iron Reagent AccuVac® Ampuls	1	25/pkg	2507025

Required apparatus

Description	Quantity	Unit	Catalog number
Beaker, 50 mL	1	each	50041H
Sample cell, 10 mL round, 25 x 54 mm	1	each	2122800
Sample cell, 10 mL round, 25 x 60 mm	1	6/pkg	2427606
Sample cell, 10 mL square, matched pair	2	2/pkg	2495402
Stopper for 18 mm tube	1	6/pkg	173106

Recommended standards

Description	Unit	Catalog number
Iron Standard Solution, 100 mg/L	100 mL	1417542
Iron Standard Solution, 10 mL Voluette® Ampule, 25 mg/L as 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
Water, deionized	4 L	27256
Pipet, TenSette, 0.1–1.0 mL	each	1970001
Pipet Tips, for TenSette Pipet 1970001	50/pkg	2185696
Pipet Tips, for TenSette Pipet 1970001	1000/pkg	2185628
Flask, volumetric, Class A, 100 mL	each	1457442
Pipet, volumetric, Class A, 2.00 mL	each	1451536
Pipet Filler, safety bulb	each	1465100

Optional reagents and apparatus

Description	Unit	Catalog number
Beaker, 50 mL	each	50041H
Cylinder, mixing, 50 mL	each	189641
Hydrochloric Acid, concentrated	500 mL	13449
Nitric Acid, concentrated	500 mL	15249

Optional reagents and apparatus (continued)

Description	Unit	Catalog number
Sodium Hydroxide Standard Solution, 5.0 N	100 mL	245032
Glass Membrane Filter, 47 mm	100/pkg	253000
Glass Membrane Filter Holder	each	234000
RoVer Rust Remover	454 g	30001
Spoon, measuring, 0.1 g	each	51100

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Section 9
Manganese

Manganese

Water Treatment Lab

TDEC - Fleming Training Center 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

TDEC - Fleming Training Center 2

Manganese

- Concentrations can be much higher in stratified lakes
  - Reducing conditions may occur in the bottom waters causing manganese to be dissolved from the sediment

TDEC - Fleming Training Center 3

MCL

- sMCL = 0.05 mg/L
- High levels of manganese in water can cause staining of plumbing fixtures and laundry

TDEC - Fleming Training Center 4

Manganese

- The soluble 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

TDEC - Fleming Training Center 5

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 MCL

TDEC - Fleming Training Center 6

Manganese

DOC316.53.01057

1-(2-Pyridylazo)-2-Naphthol PAN Method[1]

Method 8149

LR (0.006 to 0.700 mg/L)

Powder Pillows

Scope and Application: For water and wastewater; digestion is required for determining total manganese

[1] Adapted from Goto, K., et al., *Talanta*, 24, 652-3 (1977)

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 1 Instrument-specific information

Instrument	Sample cell	Cell orientation
DR 5000	2495402	Fill line faces user
DR 3900	2495402	Fill line faces user
DR 3800, DR 2800, DR 2700	2495402	Fill line faces right

Before starting the test:

Rinse all glassware with 1:1 Nitric Acid Solution. Rinse again with deionized water.
The alkaline cyanide solution contains cyanide. Cyanide solutions should be collected for disposal as a reactive (D001) waste. Be sure cyanide solutions are stored in a caustic solution with pH >11 to prevent release of hydrogen cyanide gas. Refer to the current MSDS for safe handling and disposal instructions.
Total manganese determination requires a prior digestion. Refer to the *Water Analysis Guide* for more information.

Collect the following items:

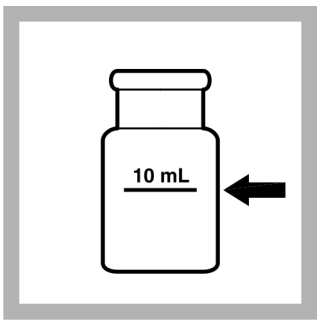
Description	Quantity
Alkaline Cyanide Reagent	12 drops
Ascorbic Acid Powder Pillows	2
PAN Indicator Solution, 0.1%	12 drops
Deionized Water	10 mL
Sample Cells (see *Instrument-specific information*)	2
Stoppers for 18 mm tube	2

See *Consumables and replacement items* for reorder information.

PAN method for powder pillows

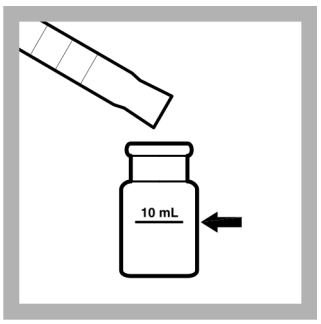
1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).

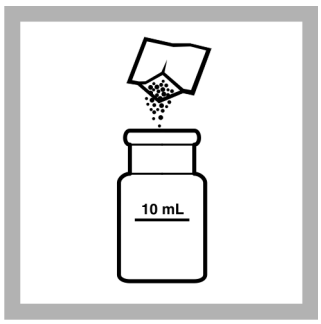


2. Blank Preparation: Pour 10.0 mL of deionized water into a sample cell.

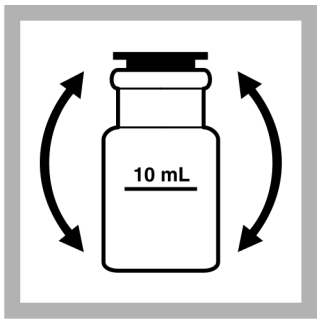
Total manganese determination requires prior digestion.



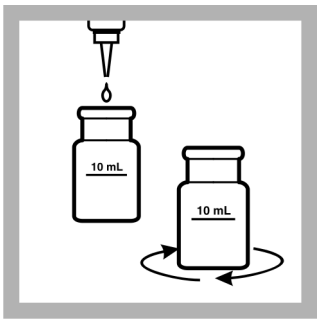
3. Prepared Sample: Pour 10.0 mL of sample into another sample cell.



4. Add the contents of one Ascorbic Acid Powder Pillow to each cell.

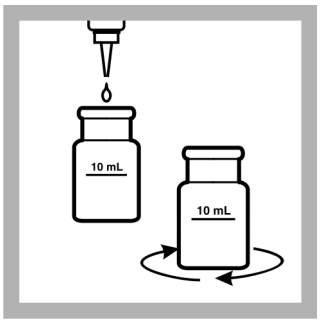


5. Stopper and invert to dissolve the powder.



6. Add 12 drops of Alkaline-Cyanide Reagent Solution to each cell. Swirl gently to mix.

A cloudy solution may form. The turbidity should dissipate after step 7.



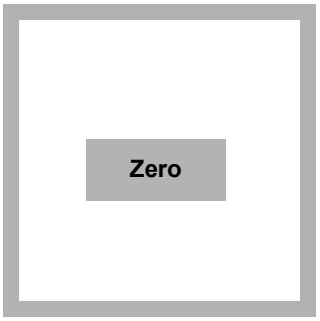
7. Add 12 drops of PAN Indicator Solution, 0.1%, to each sample cell. Swirl gently to mix.

An orange color will develop in the sample if manganese is present.

8. Start the instrument timer.

A two-minute reaction period will begin.

9. When the timer expires, wipe the blank and place it in the cell holder.

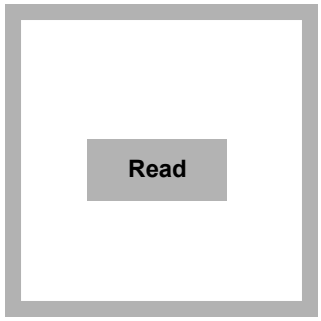


10. ZERO the instrument.

The display will show:

0.000 mg/L Mn

11. Wipe the prepared cell and place it in the holder.



12. READ the results in mg/L Mn.

Interferences

For samples that contain hardness greater than 300 mg/L $CaCO_3$, add 4 drops of Rochelle Salt Solution to the sample **after** adding the Ascorbic Acid Powder Pillow in step 4.

Table 2 Interfering substances

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
Iron	25 mg/L (If sample contains more than 5 mg/L iron, allow a 10-minute reaction period in step 8.)
Lead	0.5 mg/L
Magnesium	300 mg/L as $CaCO_3$
Nickel	40 mg/L
Zinc	15 mg/L

Sample collection, preservation and storage

- Collect samples in a clean plastic container.
- Adjust the pH to 2 or less with Concentrated Nitric Acid* (about 2 mL per liter).
- Preserved samples can be stored up to six months at room temperature.
- Adjust the pH to between 4–5 with 5.0 N Sodium Hydroxide before analysis.
- Correct the test result for volume additions.

Accuracy check

Standard additions method (sample spike)
Required for accuracy check:

- Manganese PourRite® Ampule Standard, 10-mg/L Mn
- Mixing cylinders (3)
- Ampule breaker, PourRite
- TenSette Pipet

1. After reading test results, leave the sample cell (unspiked sample) in the instrument.
2. Select Options>More>Standard additions from the instrument menu.
3. Accept the default values for standard concentration, sample volume and spike volumes. After the values are accepted, the unspiked sample reading will appear in the top row. See the user manual for more information.
4. Open the standard solution ampule.
5. Use the TenSette Pipet to prepare spiked samples: add 0.1 mL, 0.2 mL and 0.3 mL of standard to three 10 mL portions of fresh sample. Mix thoroughly.

6. Follow the *PAN method for powder pillows* test procedure for each of the spiked samples using the powder pillows, starting with the 0.1 mL sample spike. Measure each of the spiked samples in the instrument.
7. Select **GRAPH** to view the results. Select **IDEAL LINE** (or best-fit) to compare the standard addition results to the theoretical 100% recovery.

Standard solution method
Note: *Refer to the instrument user manual for specific software navigation instructions.*

Required for accuracy check:

- Manganese Voluette Standard Solution, 250 mg/L Mn
- 1 L Class A volumetric flask
- Deionized water
- Class A volumetric pipet, 2 mL
- Pipet filler, safety bulb

1. Prepare a 0.5 mg/L manganese standard solution as follows:
   a. Pipet 2.0 mL of Manganese Standard, 250 mg/L as Mn, into a 1000 mL (1 liter) volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
2. Use this solution in place of the sample. Follow the *PAN method for powder pillows* test procedure.
3. To adjust the calibration curve using the reading obtained with the standard solution, select Options>More>Standard Adjust from the instrument menu.
4. Turn on the Standard Adjust feature and accept the displayed concentration. If an alternate concentration is used, enter the concentration and adjust the curve to that value.

Method performance

Program	Standard	Precision 95% Confidence Limits of Distribution	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 for detecting low levels of manganese. An ascorbic acid reagent is used initially to reduce all oxidized forms of manganese to Mn^{2+}. An alkaline-cyanide reagent is added to mask any potential interferences. PAN Indicator is then added to combine with the Mn^{2+} to form an orange-colored complex. Test results are measured at 560 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Manganese Reagent Set, 10 mL (50 tests), includes:	—	—	2651700
Alkaline Cyanide Reagent	12 drops	50 mL SCDB	2122326
Ascorbic Acid Powder Pillows	2 pillows	100/pkg	1457799
PAN Indicator Solution, 0.1%	12 drops	50 mL SCDB	2122426
Water, deionized	10 mL	4 L	27256

Required apparatus

Description	Quantity	Unit	Catalog number
Sample cell, 10 mL square, matched pair	2	2/pkg	2495402
Stoppers for 18 mm Tube	2	6/pkg	173106

Recommended standards

Description	Unit	Catalog number
Manganese Standard Solution, 10-mg/L Mn, 2 mL PourRite® ampule	20/pkg	2605820
Manganese Standard Solution, 250-mg/L Mn, 10-mL Voluette® ampule	16/pkg	1425810
Voluette Ampule breaker 10 mL	each	2196800
PourRite® Ampule breaker 2 mL	each	2484600

Optional reagents and apparatus

Description	Unit	Catalog number
Cylinder, mixing, 25 mL	each	2088640
Nitric Acid, concentrated	500 mL	15249
pH paper, 0-14	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 1970001	50/pkg	2185696
Pipet Tips, for TenSette Pipet 1970001	1000/pkg	2185628
Pipet Tips, for TenSette Pipet 1970010	50/pkg	2199796
Pipet Tips, for TenSette Pipet 1970010	250/pkg	2199725
Rochelle Salt Solution	29 mL	172533
Sodium Hydroxide, 5.0 N	100 mL	245032
Stopper for 18 mm tube	25/pkg	173125
Volumetric flask, Class A, 1000 mL	each	1457453
Volumetric pipet, Class A, 2 mL	each	1451536
PourRite® Ampule breaker 2 mL	each	2484600
Manganese Standard Solution, 2-mL PourRite® Ampule, 25 mg/L	20/pkg	2112820

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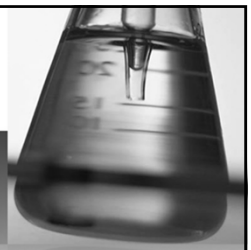
Section 10
Nitrate and Nitrite



Nitrate and Nitrite

Water Treatment Lab

TDEC - Fleming Training Center 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

TDEC - Fleming Training Center 2

Methemoglobinemia

- Blue baby syndrome
- Nitrate that is consumed in drinking water is reduced to nitrite (NO_2^-) in the body
- Blood contains an iron-based compound called hemoglobin, which carries oxygen.
- When nitrite is present, hemoglobin can be converted to methemoglobin, which cannot carry oxygen.

TDEC - Fleming Training Center 3

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

TDEC - Fleming Training Center 4

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

TDEC - Fleming Training Center 5

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

TDEC - Fleming Training Center 6

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

TDEC - Fleming Training Center 7

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

TDEC - Fleming Training Center 8

Nitrite

USEPA[1] Diazotization **Method 8507**

LR (0.002 to 0.300 mg/L NO_2^-–N) **Powder Pillows or AccuVac® Ampuls**

Scope and Application: For water, wastewater and seawater

[1] USEPA approved for wastewater analysis, Federal Register, 44(85), 25505 (May 1, 1979)

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 1 Instrument-specific information

Instrument	Powder pillows		AccuVac Ampuls	
	Sample cell	Cell orientation	Sample cell	Adapter
DR 5000	2495402	Fill line faces user	2427606	—
DR 3900	2495402	Fill line faces user	2427606	LZV846 (A)
DR 3800, DR 2800, DR 2700	2495402	Fill line faces right	2122800	LZV584 (C)

Before starting the test:

For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water instead of the sample.

Collect the following items:

Description	Quantity
Powder Pillow Test:	
NitriVer® 3 Nitrite Reagent Powder Pillows	1
Sample Cells (see *Instrument-specific information*)	2
AccuVac Test:	
NitriVer® 3 Nitrite Reagent AccuVac® Ampul.	1
Beaker, 50-mL	1
Sample Cell (see *Instrument-specific information*)	1

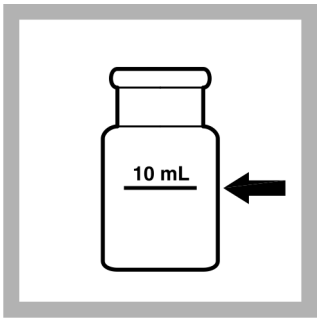
See *Consumables and replacement items* for reorder information.

Diazotization method for powder pillows

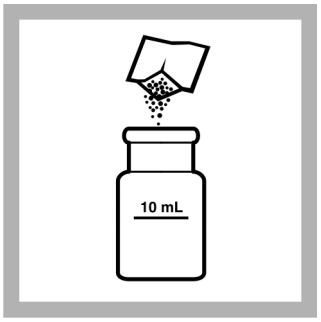
1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).

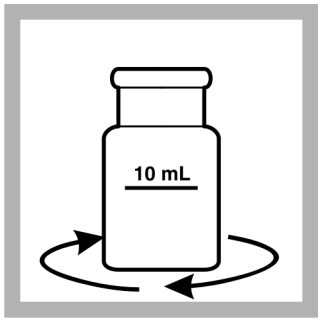
Refer to the user manual for orientation.



2. Fill a sample cell with 10 mL of sample.



3. Prepared Sample: Add the contents of one NitriVer 3 Nitrite Reagent Powder Pillow.

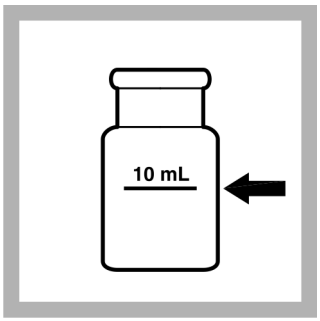


4. Swirl to dissolve.

A pink color will develop if nitrite is present.

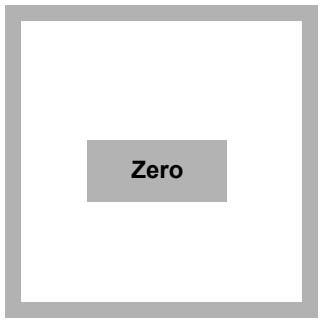
5. Start the instrument timer.

A 20-minute reaction period will begin.



6. Blank Preparation: When the timer expires, fill a second sample cell with 10 mL of sample.

7. Wipe the blank and insert it into the cell holder.

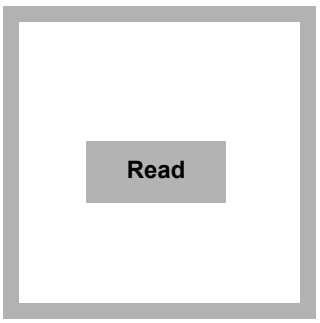


8. ZERO the instrument.

The display will show:

0.000 mg/L NO_2^-–N

9. Wipe the prepared sample and insert it into the cell holder.



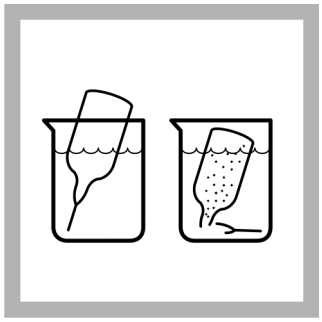
10. READ the results in mg/L NO_2^-–N.

Diazotization method for AccuVac® Ampuls

1. Select the test.

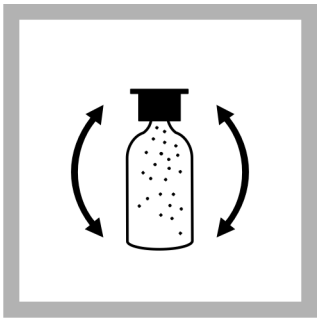
Insert an adapter if required (see *Instrument-specific information*).

Refer to the user manual for orientation.



2. Prepared Sample: Collect at least 40 mL of sample into a 50-mL beaker.

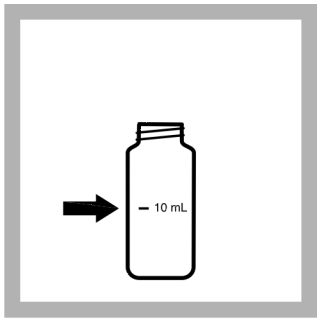
Fill a NitriVer 3 Nitrite AccuVac® Ampul with sample. Keep the tip immersed while the Ampul fills.



3. Invert the Ampul several times to mix. A pink color will develop if nitrite is present.

4. Start the instrument timer.

A 20-minute reaction period will begin.



5. Blank Preparation: When the timer expires, fill a sample cell with 10 mL of sample.

6. Wipe the blank and insert it into the cell holder.

ZERO the instrument.

The display will show: 0.000 mg/L NO_2^-–N.

7. Wipe the Ampul and insert it into the cell holder.

READ the results in mg/L NO_2^-–N.

Interferences

Table 2 Interfering substances

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	Interferes at all levels

Sample collection, preservation and storage

- Collect samples in clean plastic or glass bottles.
- Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 24 to 48 hours.
- Warm to room temperature before running the test.
- Do not use acid preservatives.

Accuracy check

Standard solution method

Note: *Refer to the instrument user manual for specific software navigation instructions.*

1. Preparing nitrite standards is difficult. Use the standard preparation instructions in *Standard Methods for the Examination of Water and Wastewater*, Method 4500—NO_2-B. Prepare a 0.150-mg/L standard.
2. Use the 0.150 mg/L solution in place of the sample. Follow the *Diazotization method for powder pillows* test procedure.
3. To adjust the calibration curve using the reading obtained with the standard solution, select **Options>More>Standard Adjust** from the instrument menu.
4. Turn on the Standard Adjust feature and accept the displayed concentration. If an alternate concentration is used, enter the concentration and adjust the curve to that value.

Method performance

Program	Standard	Precision 95% Confidence Limits of Distribution	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
375	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. Test results are measured at 507 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
NitriVer® 3 Nitrite Reagent Powder Pillows	1	100/pkg	2107169
OR			
NitriVer® 3 Nitrite Reagent AccuVac® Ampul	1	25/pkg	2512025

Required apparatus

Description	Quantity	Unit	Catalog number
Beaker, 50-mL	1	each	50041H
Sample cell, 10 mL round, 25 x 54 mm	1	each	2122800
Sample cell, 10 mL round, 25 x 60 mm	1	6/pkg	2427606
Sample cell, 10 mL square, matched pair	2	2/pkg	2495402

Recommended standards, reagents and apparatus

Description	Unit	Catalog number
Balance, Analytical, 80 g capacity	each	2936701
AccuVac ampules, for blanks	25/pkg	2677925
AccuVac Snapper	each	2405200
AccuVac Drainer	each	4103600
Handbook, Standard Methods for the Examination of Water and Wastewater	each	2270800
Sodium Nitrite, ACS	454 g	245201
Water, deionized	4 L	27256

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Nitrate

Cadmium Reduction Method **Method 8171**

MR (0.1 to 10.0 mg/L NO_3^-–N) **Powder Pillows or AccuVac® Ampuls**

Scope and Application: For water, wastewater and seawater

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 1 Instrument-specific information

Instrument	Powder pillows		AccuVac Ampuls	
	Sample cell	Cell orientation	Sample cell	Adapter
DR 5000	2495402	Fill line faces user	2427606	—
DR 3900	2495402	Fill line faces user	2427606	LZV846 (A)
DR 3800, DR 2800, DR 2700	2495402	Fill line faces right	2122800	LZV584 (C)

Before starting the test:

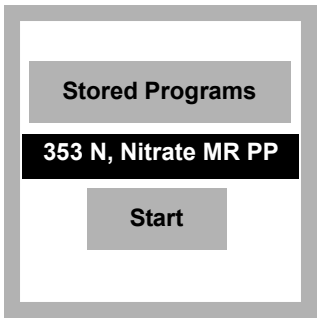
For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water instead of the sample.
A deposit of unoxidized metal will remain at the bottom of the cell after the NitraVer® 5 dissolves. The deposit will not affect results.
This method is technique-sensitive. Shaking time and technique influence color development. For most accurate results, make successive tests on a 10.0-mg/L Nitrate Nitrogen Standard solution. Adjust shaking times to obtain the correct result.
Rinse the sample cell immediately after use to remove all cadmium particles. Retain the used sample for proper hazardous waste disposal for cadmium.
Prepared samples will contain cadmium and must be disposed of according to Federal, State and local hazardous waste regulations. Refer to the current MSDS for safe handling and disposal instructions.

Collect the following items:

Description	Quantity
Powder Pillow Test:	
NitraVer® 5 Nitrate Reagent Powder Pillow	1
Sample Cells (see *Instrument-specific information*)	2
Stopper, Neoprene, #1, solid	2
AccuVac Test:	
NitraVer® 5 Nitrate Reagent AccuVac® Ampul	1
Beaker, 50-mL	1
Sample Cell for blank (see *Instrument-specific information*)	1

See *Consumables and replacement items* for reorder information.

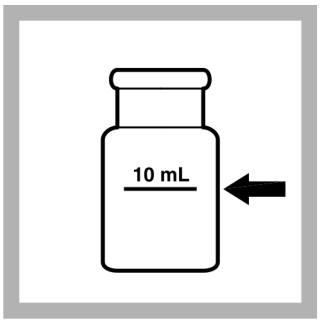
Cadmium reduction method for powder pillows



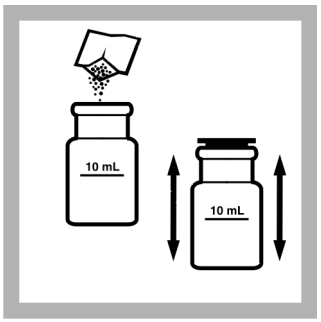
1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).

Refer to the user manual for orientation.



2. Fill a sample cell with 10 mL of sample.



3. Prepared Sample: Add the contents of one NitraVer 5 Nitrate Reagent Powder Pillow. Insert a stopper into the cell.

4. Start the instrument timer.

A one-minute reaction period will begin.

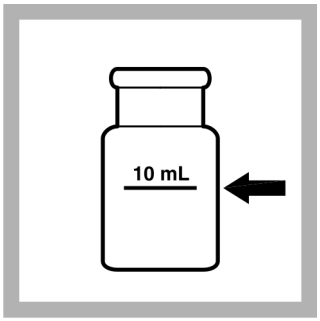
Shake the cell vigorously until the timer expires.
Note: *Some solid material will not dissolve.*

Cadmium reduction method for powder pillows (continued)

5. When the timer expires, start the timer again.

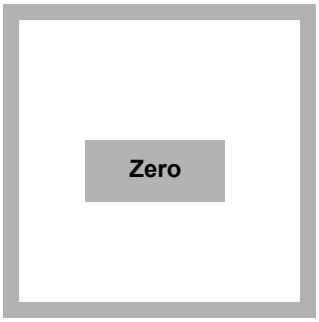
A five-minute reaction period will begin.

An amber color will develop if nitrate is present.



6. Blank Preparation: When the timer expires, fill a second sample cell with 10 mL of sample.

7. Wipe and insert the blank into the cell holder.

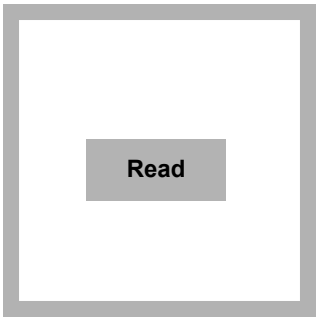


8. ZERO the instrument.

The display will show:

0.0 mg/L NO_3^-–N

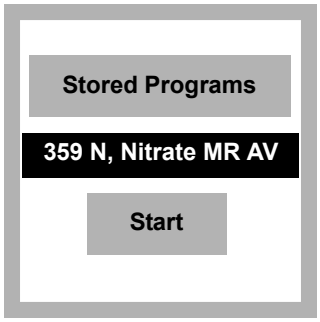
9. Within two minutes after the timer expires, wipe and insert the prepared sample into the cell holder.



10. READ the results in mg/L NO_3^-–N.

Refer to the user manual to display other chemical forms.

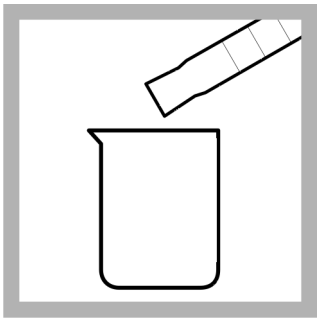
Cadmium reduction method for AccuVac® Ampuls



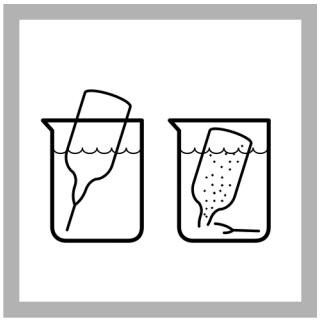
1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).

Refer to the user manual for orientation.



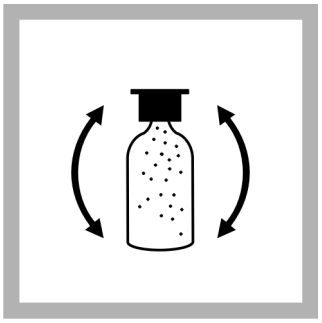
2. Prepared Sample: Collect at least 40 mL of sample in a 50-mL beaker.



3. Fill a NitraVer 5 Nitrate AccuVac® Ampul with sample. Keep the tip immersed while the Ampul fills completely. Place a stopper over the Ampul tip.

4. Start the instrument timer.

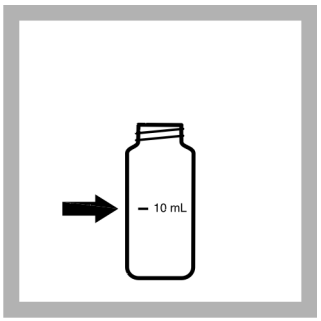
A one-minute reaction period will begin.



5. Invert the Ampul 48–52 times as the timer counts down.

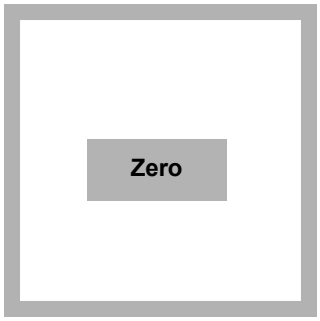
6. When the timer expires, start the timer again.

A five-minute reaction period will begin. An amber color will develop if nitrate is present.



7. Blank Preparation: When the timer expires, fill a round sample cell with 10 mL of sample.

8. Wipe the blank and insert it into the cell holder.

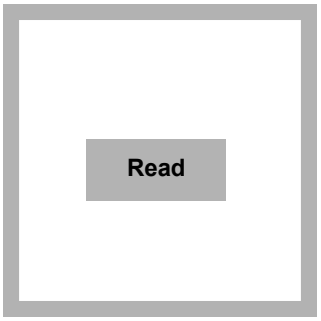


9. ZERO the instrument.

The display will show:

0.0 mg/L NO_3^-–N

10. Within two minutes after the timer expires, wipe the Ampul and insert it into the cell holder.



11. READ the results in mg/L NO_3^-–N.

Interferences

Table 2 Interfering substances

Interfering substance	Interference level
Chloride	Chloride concentrations above 100 mg/L will cause low results. The test may be used at high chloride concentrations (seawater) but a calibration must be done using standards spiked to the same chloride concentration (see *Seawater calibration*).
Ferric iron	Interferes at all levels
Nitrite	Interferes at all levels Compensate for nitrite interference as follows: **1.** Add 30-g/L Bromine Water[1] drop-wise to the sample until a yellow color remains. **2.** Add one drop of 30-g/L Phenol Solution[1] to destroy the color. **3.** Proceed with Step 2 of the test. Report the results as total nitrate and nitrite.
pH	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.
Strong oxidizing and reducing substances	Interfere at all levels

[1] See *Optional reagents and apparatus*.

Seawater calibration

Chloride concentrations above 100 mg/L will cause low results. To perform this test in water with high interference level, calibrate the water using standards spiked to the same chloride concentrations as the required samples. To prepare calibration standards containing 1.0, 3.0, 5.0 and 10.0 mg/L nitrate as NO_3–N:

1. Prepare a 1 L volume of chloride water that matches the concentration of the samples, using the following equation:

   a. Add necessary Chloride concentration (g/L) x (1.6485) = g of ACS grade NaCl to 1 L of deionized water.

   Note: *18.8 g/L is a typical seawater chloride concentration.*

   b. Mix this solution thoroughly to make sure that it is a homogeneous solution. Use this water as the dilution water instead of the deionized water when preparing the nitrate standards.

2. Use Class A glassware or a Tensette Pipet to pipet 1.0, 3.0, 5.0, and 10.0 mL of the 100 mg/L Nitrogen-Nitrate as NO_3^-–N (NIST) Standard Solution (Catalog Number 194749) into four different 100 mL Class A volumetric flasks.

3. Dilute to the mark with the prepared chloride water. Mix thoroughly.

4. Use the prepared chloride water for the 0-mg/L nitrate as NO_3–N standard.

Sample collection, preservation and storage

- Most reliable results are obtained when samples are analyzed as soon as possible after collection. If prompt analysis is impossible, store samples in clean plastic or glass bottles for up to 24 hours at 4 °C. To preserve samples for longer periods, add 2 mL of Concentrated Sulfuric Acid (H_2SO_4)* per liter and store at 4 °C. The results are reported as total nitrate and nitrite.
- Before analysis, warm the sample to room temperature and adjust the pH to 7 with 5.0 N Sodium Hydroxide Standard Solution*. Do not use mercury compounds as preservatives.

* See *Optional reagents and apparatus*.

- Correct the test result for volume additions by dividing the total volume (acid + base + sample) by the original sample volume and multiplying the test result by this factor.

Accuracy check

Standard additions method (sample spike)
Required for accuracy check:

- Nitrate Nitrogen Standard,100-mg/L NO_3^-–N
- TenSette Pipet and Pipet Tips

1. After reading test results, leave the sample cell (unspiked sample) in the instrument.
2. Select **Options>More>Standard Additions** from the instrument menu.
3. Accept the default values for standard concentration, sample volume and spike volumes. After the values are accepted, the unspiked sample reading will appear in the top row. See the user manual for more information.
4. Open the standard solution bottle.
5. Use the TenSette Pipet to prepare spiked samples: add 0.1 mL, 0.2 mL and 0.3 mL of standard to three 10-mL portions of fresh sample.
6. Follow the *Cadmium reduction method for powder pillows* test procedure for each of the spiked samples, starting with the 0.1 mL sample spike. Measure each of the spiked samples in the instrument.
7. Select **GRAPH** to view the results. Select **IDEAL LINE** (or best-fit) to compare the standard addition results to the theoretical 100% recovery.

Standard additions method for AccuVac Ampuls (sample spike)
Required for accuracy check:

- 500 mg/L Nitrate Nitrogen Ampule Standard Solution
- Ampule breaker
- TenSette Pipet and Pipet Tips
- Mixing cylinder, 50-mL (3)

1. Fill three mixing cylinders each with 50-mL of sample and spike with 0.1 mL, 0.2 mL and 0.3 mL of 500 mg/L Nitrate Nitrogen Ampule Standard Solution.
2. Transfer 40 mL from each of the three mixing cylinders to three 50-mL beakers.
3. Analyze each standard addition sample as described in the *Cadmium reduction method for AccuVac® Ampuls*.
4. Accept each standard additions reading. Each addition should reflect approximately 100% recovery. Standard solution method

Note: *Refer to the instrument user manual for specific software navigation instructions.*

Standard Solution Method
Required for accuracy check:

- 5.0-mg/L Nitrate Nitrogen Standard Solution (prepared)
- 100-mg/L Nitrate Nitrogen Standard
- Deionized water
- 100-mL volumetric flask

- 5-mL Volumetric pipet and pipet filler

  OR

- TenSette Pipet and Pipet Tips

1. Prepare a 5.0-mg/L nitrate nitrogen standard solution as follows:
   a. Pipet 5.0 mL of 100-mg/L Nitrate Nitrogen Standard, into a 100-mL volumetric flask.
   b. Dilute to the mark with deionized water. Mix well.
2. Use this 5.0 mg/L nitrate nitrogen standard solution in place of the sample. Follow the *Cadmium reduction method for powder pillows* test procedure.
3. To adjust the calibration curve using the reading obtained with the standard solution, select **Options>More>Standard Adjust** from the instrument menu.
4. Turn on the Standard Adjust feature and accept the displayed concentration. If an alternate concentration is used, enter the concentration and adjust the curve to that value.

Method performance

Program	Standard	Precision 95% Confidence Limits of Distribution	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 nitrates 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. Test results are measured at 400 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
NitraVer® 5 Nitrate Reagent Powder Pillows (for 10 mL sample)	1	100/pkg	2106169
OR			
NitraVer® 5 Nitrate Reagent AccuVac® Ampul	1	25/pkg	2511025

Required apparatus (powder pillows)

Description	Quantity	Unit	Catalog number
Sample cell, 10 mL square, matched pair	2	2/pkg	2495402
Stopper, Neoprene, solid, size #1	2	12/pkg	1480801

Required apparatus (AccuVac)

Description	Quantity	Unit	Catalog number
Beaker, 50-mL	1	each	50041H
Sample cell, 10 mL round, 25 x 54 mm	1	each	2122800
Sample cell, 10 mL round, 25 x 60 mm	1	6/pkg	2427606

Recommended standards

Description	Unit	Catalog number
Mixed Parameter Drinking Water Standard, for F, NO_3–N, PO_4, SO_4	500 mL	2833049
Nitrate Nitrogen Standard Solution, 100-mg/L NO_3^-–N	500 mL	194749
Nitrate Nitrogen Standard Solution, 500 mg/L NO_3–N, 10-mL ampules	16/pkg	1426010
Water, deionized	4 L	27256

Optional reagents and apparatus

Description	Unit	Catalog number
Ampule breaker for 10 mL ampules	each	2196800
Bromine Water, 30-mg/L	29 mL	221120
Cylinder, mixing, 50 mL	each	2088641
Flask, volumetric, 100-mL	each	1457442
Pipet, TenSette, 0.1–1.0 mL	each	1970001
Pipet Tips, for TenSette Pipet 1970001	50/pkg	2185696
Pipet Tips, for TenSette Pipet 1970001	1000/pkg	2185628
Pipet, volumetric, Class A, 5.0 mL	each	1451537
Pipet, volumetric, Class A, 1.0 mL	each	1451535
Pipet, volumetric, Class A, 3.0 mL	each	1451503
Pipet, volumetric, Class A, 10.0 mL	each	1451538
Pipet Filler, safety bulb	each	1465100
Phenol Solution, 30-g/L	29 mL	211220
5.0 N Sodium Hydroxide Standard Solution	1 L	245053
Sulfuric Acid, concentrated	500 mL	97949

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Section 11
Instrument and Probe Maintenance

Instrument and Probe Maintenance

Instruments

- Whenever you have any maintenance done on an instrument, you should keep records on it
  - After maintenance, you should check calibration
- Keep records on calibrations

Instruments

- Good idea to have separate book for each instrument
- Keep instruments clean so they work best
- Always have replacement parts on hand
  - Bulbs for turbidimeters and spectrophotometers

pH Meters

- Good recommendation: water industry should not use gel filled probes
- Calibrate DAILY with fresh buffers
- Three buffers are better than two
  - If you use two buffers, you should use buffers that bracket your normal readings
  - 10 buffer degrades faster than 4 and 7

pH Probes

- Store probes in slightly acidic solution
  - Can be bought premixed
  - pH 4 buffer works also
- Don't store in distilled water or finished water
  - Becomes slow to respond
- pH electrode (glass ball) is porous for H^+ to migrate through
- Can clean with dilute hydrochloric acid (HCl) is slow response for 30-60 seconds then rinse with distilled water for 15-20 minutes
  - Follow manufacturer's recommendation

pH Probes

- Replace annually
  - Good practice to put date on probe
  - Have back up probe at all times
- For fillable probes, if crystals form in reference electrode area
  - Shake out solution
  - Fill with distilled water until crystals dissolve
  - Dump out then refill with correct solution

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

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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

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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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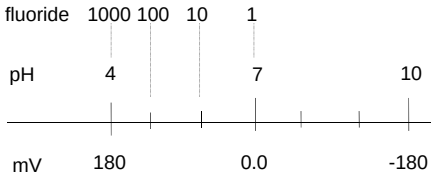
Fluoride Trouble Shooting



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Section 12
Taste and Odor

Taste and Odor

Significance
Sampling
Methods of Determination
Methods of Removing

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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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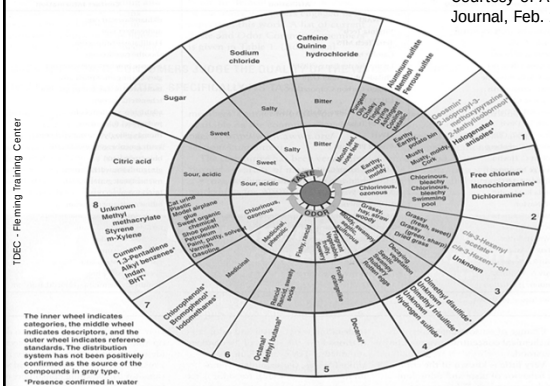
FIGURE 1 Wheel identifying distribution system–generated tastes and odors

Courtesy of AWWA Journal, Feb. 2004



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.

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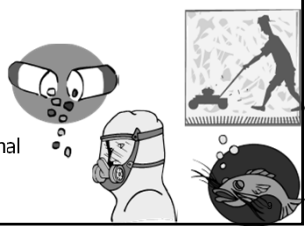
Odors

- Most frequently caused by algae or decaying organic matter
- Intensity and offensiveness vary with the type of organic matter
- Classifications:

•aromatic •fishy
•grassy •musty
•septic •medicinal
•rotten egg



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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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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

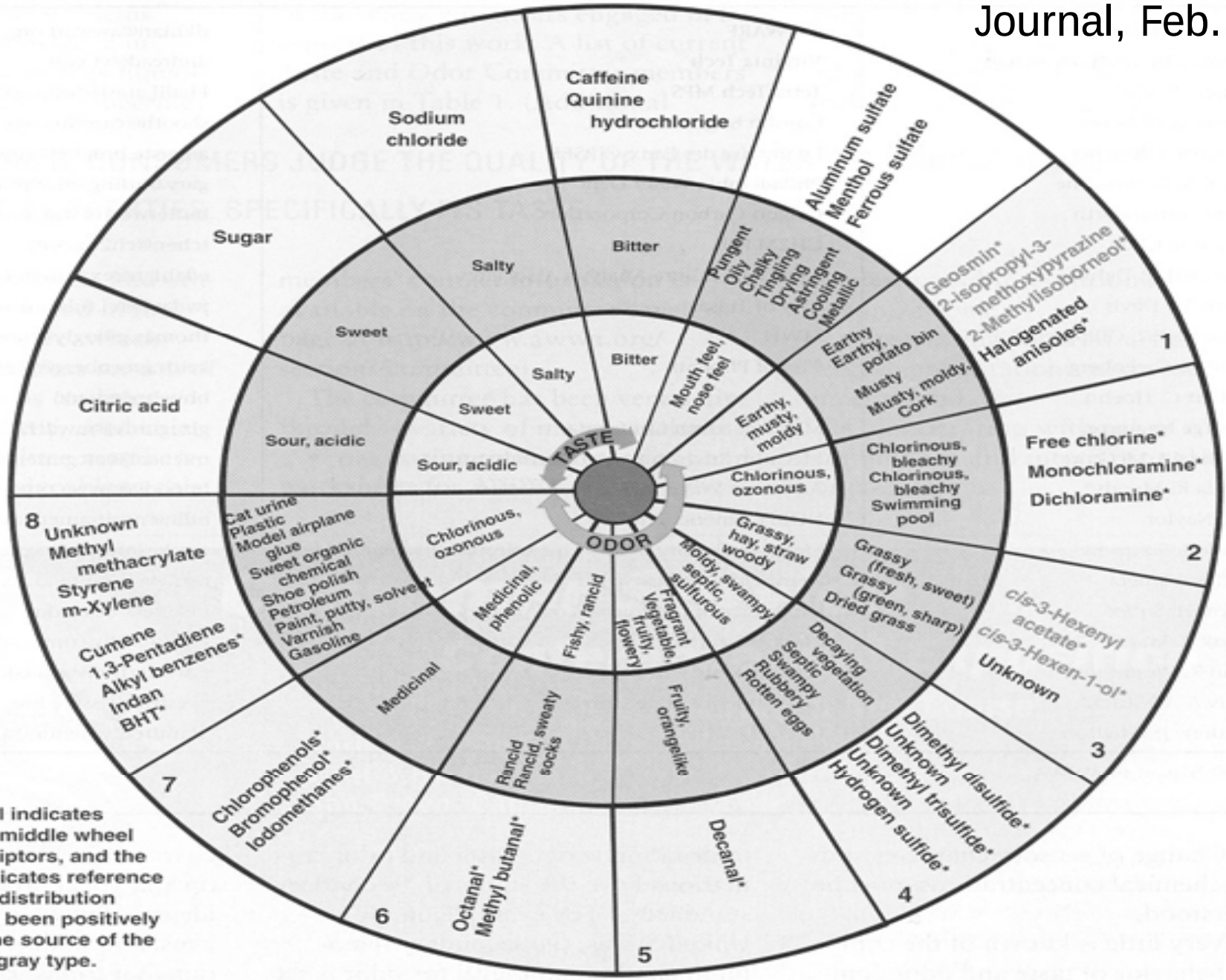
➢ Calculation

- 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.