DOC022.53.80486

Steam-Assisted Gravity Drainage Water Analysis Handbook

Procedures Manual

03/2021, Edition 3

Table of Contents

Section 1 Introduction

This handbook contains test procedures for the analysis of steam-assisted gravity drainage produced waters.

Test procedures in this document:

Bacteria, APB
Bacteria, HAB
Bacteria, IRB
Bacteria, SLYM
Bacteria, SRB
Chloride, HR, ISE
Chloride, Titration
Chlorine, HR, Free
Chlorine, Total
Conductivity (TDS)
Hardness, Total
Hardness, Ca
Hydrazine
Iron, Ferrous
Iron, Total
Oil & Grease (LLE)
Oil & Grease (SPE)
TOC, LR (Total Organic Carbon)
TOC, HR (Total Organic Carbon)
Oxygen, Dissolved-LR
pH
Salinity
Silica, HR
Silica, LR
Silica, ULR
Sulfate
Sulfide (H_2S)
Sulfite
Suspended Solids, Total (gravimetric)
Suspended Solids, Total (photometric)
Tannins
TPH

Section 2 Sample pretreatment by digestion

Several procedures use sample digestion before the total metal content is found. Digestion uses acid and heat to break organo-metallic bonds and free ions for analysis.

2.1 USEPA-approved digestions

For USEPA reporting, USEPA-approved digestions are necessary. There are two methods for metals analysis: mild and vigorous.

2.1.1 USEPA mild digestion

1. Add concentrated nitric acid to the entire sample at the time of collection. Add 5 mL of acid per liter (or quart) of sample.
2. Move 100 mL of well-mixed sample to a beaker or flask.
3. Add 5 mL of distilled 1:1 hydrochloric acid (HCl).
4. Increase the temperature of the liquid with a steam bath or hot plate until the volume has been reduced to 15–20 mL. Do not boil.
5. Use a filter to remove any insoluble material from the sample.
6. Adjust the pH of the digested sample to pH 4. Add 5.0 N Sodium Hydroxide Standard Solution a drop at a time. Mix thoroughly and examine the pH after each addition.
7. Pour the reduced sample into a 100-mL volumetric flask.
8. Use a small amount of demineralized water to rinse the beaker. Pour the rinse water into the volumetric flask.
9. Repeat the rinse process a few more times to remove all of the reduced sample from the beaker.
10. Add demineralized water to fill the volumetric flask to the 100-mL mark.
11. Use the diluted sample in the test procedure. Record the results.
12. Prepare a blank: Repeat steps 1-11 with demineralized water instead of the sample.
13. Subtract the results of the blank analysis from the results of the sample analysis.

2.1.2 USEPA vigorous digestion

For some samples mild digestion will not be sufficient. Use a vigorous digestion to make sure that all of the organo-metallic bonds are broken.

1. Use redistilled 1:1 Nitric Acid Solution to acidify the entire sample to a pH of less than pH 2. Do not filter the sample before digestion.
2. Move an appropriate sample volume into a beaker and add 3 mL of concentrated redistilled nitric acid. Refer to Table 1.
3. Put the beaker on a hot plate and evaporate to near dryness. Make sure that the sample does not boil.
4. Cool the beaker and add another 3 mL of the concentrated re-distilled nitric acid.
5. Put the cover on the beaker with a watch glass and return it to the hot plate. Increase the temperature of the hot plate so that a gentle reflux occurs. Add additional acid, if necessary, until the digestion is complete (generally shown when the digestate is light in color or does not change color or appearance with continued refluxing).
6. Again, evaporate to near dryness (do not bake) and cool the beaker. If any residue or precipitate results from the evaporation, add redistilled 1:1 hydrochloric acid (5 mL per 100 mL of final volume). Refer to Table 1.
7. Warm the beaker. Adjust the sample to pH 4 by drop-wise addition of 5.0 N Sodium Hydroxide Standard Solution. Mix thoroughly and examine the pH after each addition.
8. Pour the reduced sample into a 100-mL volumetric flask.
9. Use a small amount of demineralized water to rinse the beaker. Pour the rinse water into the volumetric flask.

10. Repeat the rinse process a few more times to remove all of the reduced sample from the beaker.
11. Add demineralized water to fill the volumetric flask to the 100-mL mark.
12. Use the diluted sample in the test procedure. Record the results.
13. Multiply the result by the correction factor in Table 1.
14. Prepare a blank: Repeat steps 1-13 with demineralized water instead of the sample.
15. Subtract the results of the blank analysis from the results of the sample analysis.

Table 1 Vigorous digestion volumes

Expected metal concentration	Suggested sample volume for digestion	Suggested volume of 1:1 HCl	Suggested final volume after digestion	Correction factor
1 mg/L	50 mL	10 mL	200 mL	4
10 mg/L	5 mL	10 mL	200 mL	40
100 mg/L	1 mL	25 mL	500 mL	500

2.2 General Digesdahl digestion

Many samples may be digested with the Digesdahl Digestion Apparatus (2313020). It is designed to digest samples such as oils, wastewater, sludges, feeds, grains, plating baths, food and soils. In this procedure, the sample is oxidized by a mixture of sulfuric acid and hydrogen peroxide. Less than 10 minutes is necessary for the digestion of a dry sample. About 1 minute/mL is necessary for the digestion of liquid samples. The digestion is done in a special flat-bottomed, 100-mL volumetric flask. Aliquots (sample portions) are used for analysis with the colorimetric methods.

Procedures for digestion with the Digesdahl Digestion Apparatus are based on the type and form of the sample. Refer to the Digesdahl Digestion Apparatus Instruction manual supplied with the Digesdahl Digestion Apparatus.

Digesdahl digestion is a process that yields a digest that can be used to find metals, total phosphorus and total Kjeldahl nitrogen (TKN). It is faster than traditional methods, but has comparable accuracy and precision. The digest can be used with colorimetric, turbidimetric or titrimetric tests.

The procedures for the Digesdahl Digestion Apparatus vary with the sample type. Sample types include food products, feeds, grains, wastewater sludges, plating baths, plant tissues, fertilizers, beverages and oils. Most procedures use a two-phase digestion process that uses concentrated sulfuric acid and 50% hydrogen peroxide. Sulfuric acid dehydrates and chars the sample. Hydrogen peroxide is added through the capillary flow funnel to complete the decomposition. The analyst varies the volume of hydrogen peroxide used to control the digestion time (exposure to the hydrogen peroxide).

Some samples are more difficult to digest completely (e.g., resistant or refractory materials, such as nicotinic acid). Several minutes of continued peroxide digestion are necessary after clearing to get 100% nitrogen recovery. To make sure that there is complete sample digestion, think about variables such as sample size, solution temperature and sample contamination. Refer to the Digesdahl Manual (2313018) for complete information.

2.2.1 Frequently asked questions for digestion procedures

This section provides answers to common questions about digestion.

What should be done if the reading on the instrument is over-range?

The concentration range tables found in digestion procedures are only guidelines. Use a smaller analysis volume and repeat the procedure. Record the new analysis volume and use it in the calculation.

Should a reagent blank be prepared each time reagents with the same lot number are used?

To decide, first find the reading of the reagent blank. Set the instrument to zero with deionized or distilled water. If the reagent blank has an insignificant concentration reading and the reagents have the same lot number, a reagent blank does not have to be prepared every time. If the reagent blank shows a reading, analyze it daily or subtract the reading from the sample reading. If a reagent blank is not analyzed daily, set the instrument to zero with deionized water.

Does the exact sample amount and analysis volume given in each procedure need to be used?

The sample amount and the analysis volume for each procedure are only suggested guidelines. Digest any aqueous solution or suspension sample amount up to 40 mL. Less than 0.5 g of anhydrous material is necessary for solid or organic liquid samples—as a routine practice, 0.25 g of sample is used.

How can the initial amount of sample (necessary for digestion) and the analysis volume to be used be refined?

The amount of sample to be digested is a critical aspect of the digestion. The aliquot size of the digest to be used in the analysis is also very important. Tables are provided in each method to find the amount of initial sample to be digested. In order to optimize the specific test to be done, the equations that follow have been developed. Before these equations are used, refer to the manual specifications for the sample type.

To use the equations, find the approximate concentration (in ppm, mg/L or mg/kg). Next, find the range of the colorimetric test to be used (e.g., 0–50 mg/L) and the midpoint of the test range. This midpoint range is optimum but can be lowered to accommodate very low sample concentrations. To find the midpoint of the test range, subtract the lower limit of the range from the higher limit and then divide by 2.

After these determinations are finished, use the equation that follows:

$A = (B \times C \times D) \div (E \times F)$

Where:

A = approximate concentration of sample

B = midpoint of colorimetric test range

C = final volume of digest

D = final volume of analysis

E = sample amount to digest

F = analysis volume of digest

Use algebra to obtain the equations that follow:

Equation 1 is $E = (B \times C \times D) \div (A \times F)$

Equation 2 is $F = (B \times C \times D) \div (A \times E)$

Both equations contain two unknown values, E and F. Some trial and error may be necessary to get the optimum values.

Use equation 1: If the analysis is for copper, use the CuVer™ method with an initial sample that contains approximately 150 ppm Cu. The amount of sample necessary for digestion and the aliquot volume to be used can be found as follows:

Find the test range. In this example, the test range is thought to be 0–5.0 ppm and the midpoint is 2.5. When the Digesdahl system is used, the final volume of digest is 100 mL and the procedure calls for a final analysis volume of 25 mL.

Therefore:

A = 150

B = 2.5

C = 100

D = 25

E = unknown

F = unknown

Substitute values into equation (1) gives:

E = (2.5 × 100 × 25) ÷ (150 × F) or E = 41.7 ÷ F

Since CuVer Copper Reagent is pH sensitive, a small analysis volume (0.5 mL) is necessary so that pH adjustment would not be necessary.

With this in mind, a 0.5-mL analysis volume would give:

E = 41.7 ÷ 0.5 = 83.4 mL digestion sample amount

Because the maximum digestion sample amount is 40 mL for Digesdahl digestions, a 0.5-mL analysis volume is not acceptable for the range. This is where trial and error is necessary. Next, try a 5.0-mL analysis volume and the equation gives:

E = 41.7 ÷ 5.0 = 8.0 mL digestion sample amount

(Round to the nearest whole number for ease of measure.)

From the calculation, an 8.0 mL sample is digested and a 5.0-mL analysis volume is taken. A pH adjustment is necessary before analysis.

Use equation 2: Equation 2 may be used when a minimum sample size is necessary or when a sample has already been digested for one parameter (such as copper) and measurement for another parameter (such as zinc) is necessary. Continue the example for copper, above, a zinc test may also be done. The undigested sample contains approximately 3 ppm zinc and the Zincon method is used. The analysis volume can be found as follows.

In this example, the Zincon method test range is thought to be 0–2.5 ppm so that the midpoint of the range is 1.25. Therefore values are:

A = 3

B =1.25

C = 100

D = 50

E = 8 (as found above)

substitute: F = (1.25 × 100 × 50) ÷ (3 × 8) = 260 mL

This is an extreme example, but it shows the need to compare the values of D and F to make sure that the analysis volume (F) is no more than the final analysis volume (D). If F exceeds D, the analysis cannot be done. A test with a more applicable range is necessary or a larger sample may be digested for this test. Care must also be taken to make sure that the volume of digest taken for analysis (F) is higher than 0.1 mL because accurately pipetting less than 0.1 mL is difficult.

As a comparison, think of the zinc concentration as 75 ppm (A = 75 instead of 3) and substitute again to get:

F = (1.25 × 100 × 50) ÷ (75 × 8) = 10.5 mL

In this case, the aliquot volume is less than the final analysis volume so analysis may be done as specified in the procedure.

Why is the factor in the calculation step 75, 2500 or 5000 (depends on the method used) and where does the factor come from?

In all cases, the factor is a correction for sample dilution. For example, in some tests the factor is 2500. The Digesdahl digestion total volume is 100 mL, the analysis total volume is 25 mL and 100 x 25 = 2500. The mL units are not included with the factor because they cancel out in the formula.

When a slurry is analyzed, how is the total concentration on a dry basis reported?

The sample must be analyzed for moisture content. For necessary apparatus, refer to Table 2 and Table 3.

To find the dry basis weight:

1. Weigh an aluminum dish and record the weight as “A”.
2. Weigh out approximately 2 g of solid sample into the dish. Record the exact weight added as “B.”
3. Put the dish in the oven (103–105 °C, 217–221 °F) for 2 hours.
4. Put in a desiccator and cool to room temperature.
5. Weigh the aluminum dish with the oven-dried sample. Record as “C.”
   Note: *The oven-dried material generally is not meant for additional testing and should be discarded.*
6. Use this formula to calculate the sample on a “dry basis.” Test result (dry basis) = (C – A) ÷ (B – A).
   Note: *Multiply the test result on an “as is” basis, by the factor above, to report as “dry basis".*

Table 2 Necessary apparatus for dry basis weight

Description	Unit	Item no.
Balance, analytical, 120-g	454 g	2936801
Desiccant, Drierite (without indicator)	each	2285901
Desiccator, vacuum (uses ceramic plate)	100/pkg	2088800
Dish, moisture determination, aluminum, 63 x 17.5 mm	each	2164000
Tongs, crucible	each	56900
Oven, laboratory, 120 VAC	each	1428900
or		
Oven, laboratory, 240 VAC	each	1428902

Table 3 Optional apparatus

Description	Unit	Item no.
Desiccator, without stopcock	each	1428500

2.2.2 Adjust the pH

2.2.2.1 For a metals procedure

Note: *If aliquots smaller than 0.5 mL are analyzed, pH adjustment is not necessary.*

1. Find the necessary volume of sample for analysis from the Sample and Analysis Volume Tables after each digestion procedure. Use a pipet to add this volume into a graduated mixing cylinder.
   Note: *To use a pipet to add a volume into a volumetric flask or a regular graduated cylinder is necessary for some methods.*
2. Dilute to about 20 mL with deionized water.
3. Add one drop of 2,4 Dinitrophenol Indicator Solution.
4. Add one drop of 8 N Potassium Hydroxide (KOH) Standard Solution (28232H). Swirl after each addition until the first flash of yellow shows (pH 3). If the sample is analyzed for potassium, use 5 N sodium hydroxide (245026) instead. Do not use a pH meter if the sample is analyzed for potassium or silver.
5. Add one drop of 1 N KOH (2314426). Put the stopper in the cylinder and invert several times to mix. If the sample is analyzed for potassium, use 1 N sodium hydroxide instead.
   Note: *Use pH paper to make sure that the pH is 3. If it is higher than 4, do not adjust again with acid. Start over with a fresh aliquot.*
6. Continue to add 1 N KOH in this manner until the first permanent yellow color shows (pH 3.5–4.0).

7. Look at the cylinder from the top against a white background. Compare the cylinder to a second cylinder filled to the same volume with deionized water.
   Note: *High iron content will cause precipitation (brown cloud) which will co-precipitate other metals. Do this procedure again with a smaller aliquot volume.*
8. Add deionized water to the volume specified in the colorimetric procedure for the parameter under analysis.
9. Continue with the colorimetric procedure.

2.2.2.2 For the Total Kjeldahl Nitrogen colorimetric method

Consult the spectrophotometer or colorimeter procedure to complete the TKN analysis. The procedure that follows is only a guide to use if a procedure is not available.

1. Use a pipet to add an appropriate analysis volume to a graduated mixing cylinder.
2. Add one drop of TKN Indicator (2251900).
3. Add one drop of 8 N KOH Standard Solution (28232H), swirl after each addition until the first flash of pale blue shows (pH 3).
4. Add one drop of 1 N KOH (2314426). Put the stopper in the cylinder and invert several times to mix.
   Note: *Look at the cylinder from the top against a white background. Compare the cylinder to a second cylinder filled to the same volume with deionized water.*
5. Continue to add 1 N KOH in this manner until the first permanent blue color shows.
6. Add deionized water to the volume shown in the colorimetric procedure for the parameter under analysis.
7. Continue with the colorimetric procedure.

Chemical Procedures

Bacteria, Acid-producing

DOC316.53.01328

Visual determination

Semi-quantitative

APB-BART™[1]

Scope and application: For the determination of acid-producing bacteria in brine solutions, produced waters and hydraulic fracturing waters.

[1] APB-BART is a trademark of Droycon Bioconcepts Inc.

Test preparation

Before starting

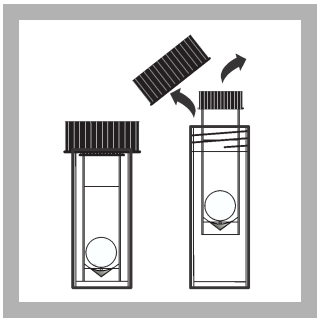
Do not touch the inner surface of the tube or lid. Keep contamination out of the tube and lid. Use the aseptic technique.
Set the caps on a clean surface with the flat surface down.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.
Sterilize the reacted sample before disposal. Refer to Disposal on page 3.

Items to collect

Description	Quantity
BART Test for acid-producing bacteria (APB)	1

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

Test procedure

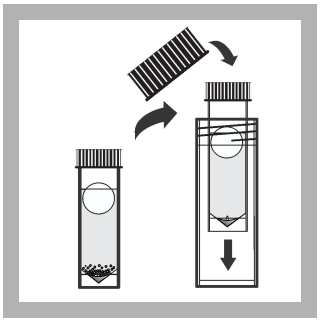


1. Remove the inner tube from the outer tube.

2. Pour at least 20 mL of sample in the outer tube.

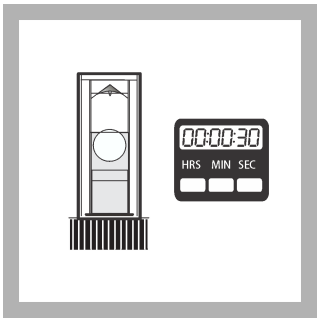
3. Fill the inner tube to the fill line with the sample that is in the outer tube. Tighten the cap on the inner tube.

Discard the unused sample in the outer tube.

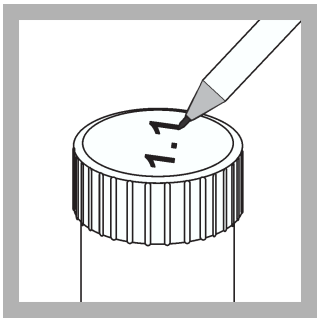


4. Put the inner tube in the empty outer tube. Tighten the cap on the outer tube.

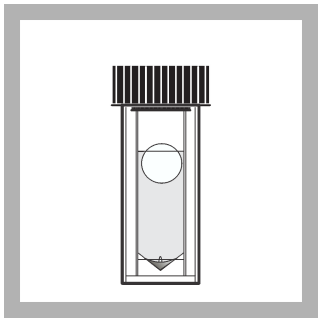
Do not shake or swirl the tubes after the sample is added. Let the ball float to the top with no help.



5. Invert the tube for 30 seconds to dissolve the dye under the cap.

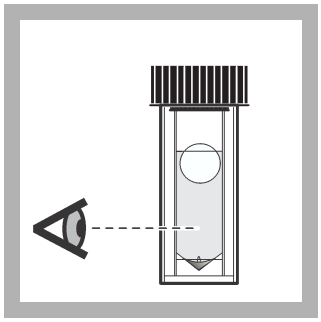


6. Write the date and sample name on the outer tube.



7. Keep the tube at room temperature and away from direct sunlight for 8 days.

Do not move the tube.



8. Examine the tube each day. Record the date when a reaction is first seen. Refer to Test results on page 2.

Interferences

Interfering substance	Interference level
Acidic	Less than pH 6.0. Adjust to pH 6.9 to 7.2 with sterile potassium hydroxide. Subtract 2 days from the Days to reaction in Table 1 on page 2 because the adjustment has a stressful effect on the bacteria.
Salt	More than 6% salt can result in false negatives. Dilute with sterile distilled water until the salt concentration is less than 6%.

Test results

Presence/Absence

When acid-producing bacteria are in the sample, the color of the solution changes from a purple to a yellow-orange color. The solution frequently becomes cloudy.

- Negative (absent/non-aggressive)—The color stays purple.
- Positive (present/aggressive)—The color becomes yellow-orange. The solution can be cloudy.

Make an estimate of the bacteria population

If the test result is positive, make an estimate of the bacteria population and the aggressivity. Refer to Table 1. A faster reaction occurs when the bacteria population is high.

If the acid-producing bacteria (APB) population is highly or moderately aggressive (less than 7 days), a total coliform test is recommended on a fresh sample to identify if there is a hygiene risk.

Table 1 Approximate bacteria population

Days to reaction	Approximate APB population (cfu/mL)	Aggressivity
1	800,000	High
2	70,000	High
3	9000	High
4	1500	Moderate
5	500	Moderate
6	150	Moderate
7	< 100	Low
8	< 100	Low

Advanced test information

If the test result is positive, examine the tubes for dominant bacteria. The dominant bacteria for this test is gRAM-negative fermenting bacteria.

Summary of method

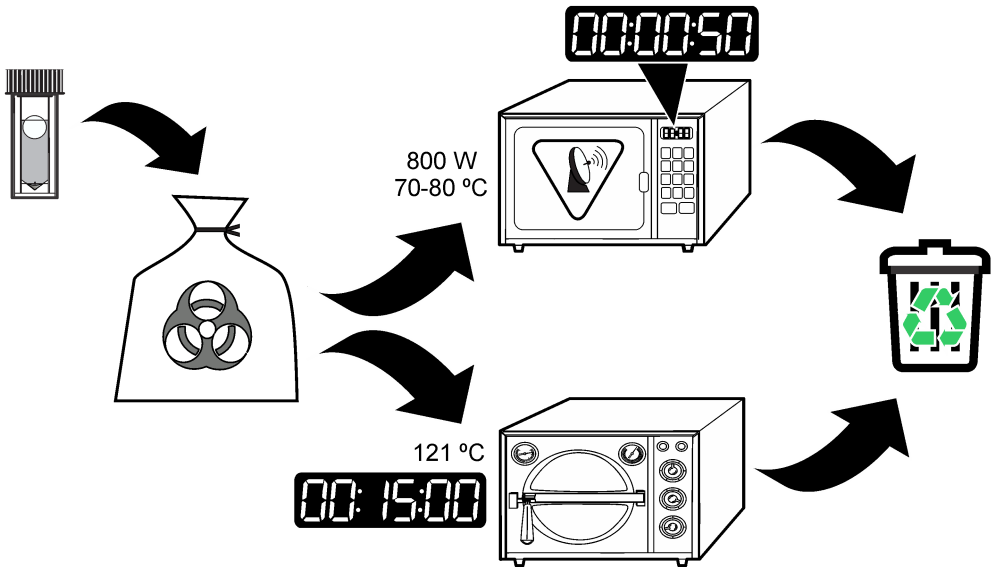
When acid-producing bacteria (APB) are in the sample, the sample becomes acidic (pH 3.5 to 5.5) during incubation. A pH indicator, bromocresol purple, in the APB-BART tube changes from a purple to an orange or yellow color as the pH decreases. This change occurs at a pH of 5.2 to 5.8.

The acid-producing bacteria make acids in very reductive (no oxygen) environments. If oxygen is in the sample, the acid-producing bacteria do not cause acidity in the water, but can cause acidity at the interface between the biofilm and the supporting material (e.g., concrete, steel).

Disposal

Sterilize the reacted sample before disposal. Refer to Figure 1.

Figure 1 Disposal



Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
BART Test for acid-producing bacteria (APB)	1	9/pkg	2831409

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

01/2015, Edition 2

Bacteria, Heterotrophic Aerobic

DOC316.53.01329

Visual determination

Semi-quantitative

HAB-BART™[1]

Scope and application: For the determination of total aerobic bacteria in brine solutions, produced waters and hydraulic fracturing waters.

[1] HAB-BART is a trademark of Droycon Bioconcepts Inc.

Test preparation

Before starting

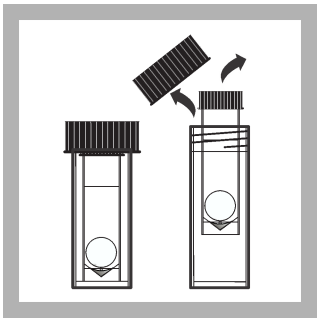
Do not touch the inner surface of the tube or lid. Keep contamination out of the tube and lid. Use the aseptic technique.
Set the caps on a clean surface with the flat surface down.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.
Sterilize the reacted sample before disposal. Refer to Disposal on page 3.

Items to collect

Description	Quantity
BART Test for heterotrophic aerobic bacteria (HAB)	1

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

Test procedure

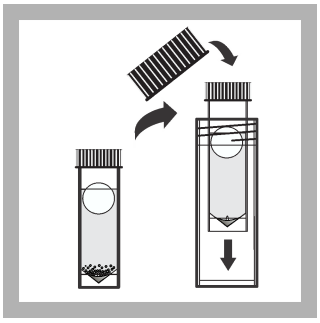


1. Remove the inner tube from the outer tube.

2. Pour at least 20 mL of sample in the outer tube.

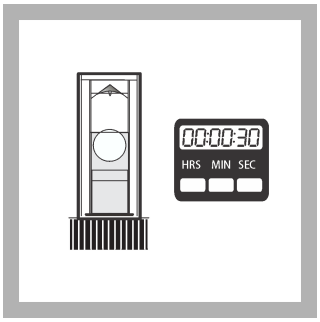
3. Fill the inner tube to the fill line with the sample that is in the outer tube. Tighten the cap on the inner tube.

Discard the unused sample in the outer tube.

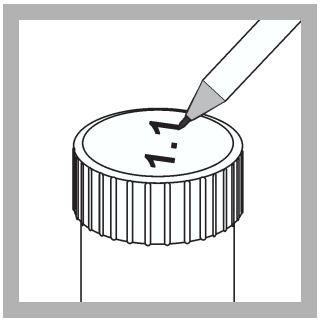


4. Put the inner tube in the empty outer tube. Tighten the cap on the outer tube.

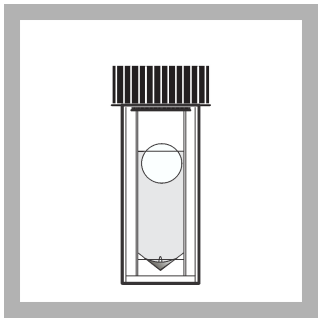
Do not shake or swirl the tubes after the sample is added. Let the ball float to the top with no help.



5. Invert the tube for 30 seconds to dissolve the dye under the cap. For saline waters, invert the tube for 5 minutes.

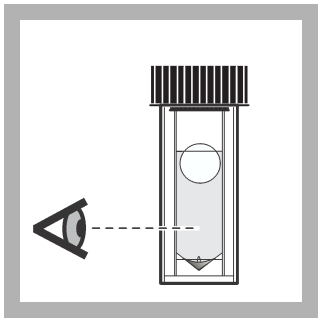


6. Write the date and sample name on the outer tube.



7. Keep the tube at room temperature and away from direct sunlight for 4 days.

Do not move the tube.



8. Examine the tube each day. Record the date when a reaction is first seen. Refer to Test results on page 2.

Test results

Presence/Absence

When heterotrophic aerobic bacteria are in the sample, the color of the solution changes from a blue to a light or medium yellow color. The solution frequently becomes cloudy.

- Negative (absent/non-aggressive)—The color stays blue.
- Positive (present/aggressive)—The color becomes yellow. The solution frequently becomes cloudy.

Make an estimate of the bacteria population

If the test result is positive, make an estimate of the bacteria population and the aggressivity. Refer to Table 1. A faster reaction occurs when the bacteria population is high.

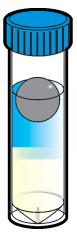
Table 1 Approximate bacteria population

Days to reaction	Approximate HAB population (cfu/mL)	Aggressivity
1	5,400,000	Very high
2	575,000	High
3	61,000	Moderate
4	6500	Moderate to low
5	700	Low
6	Less than 75	Very low

Advanced test information

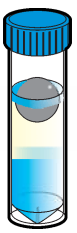
If the test result is positive, examine the tubes for dominant bacteria. Refer to Figure 1.

Figure 1 Dominant bacteria



Aerobic bacteria

The color is bleached from the bottom to the top.



Facultative anaerobic bacteria

The color is bleached from the top to the bottom.

Summary of method

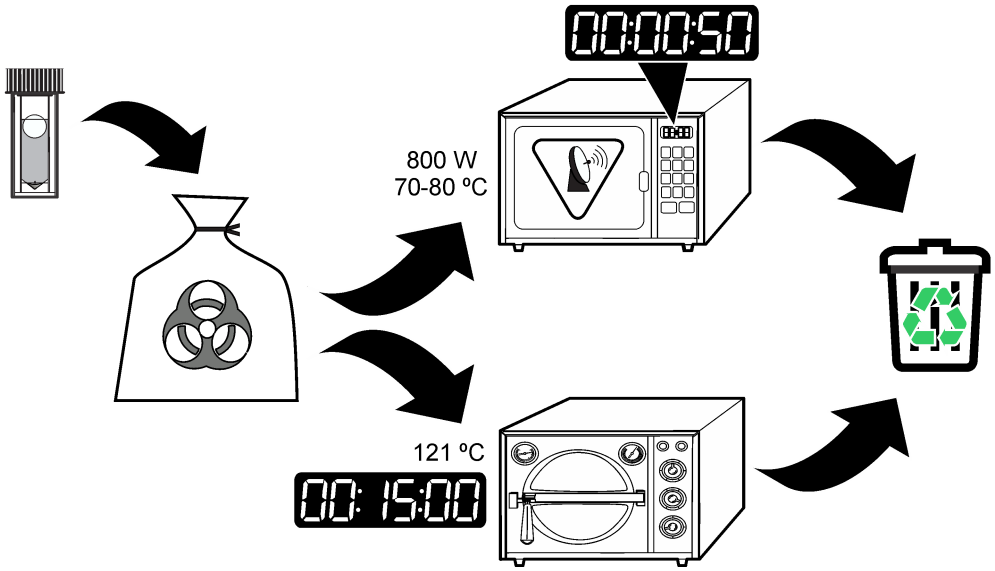
When heterotrophic aerobic bacteria (HAB) are in the sample, the bacteria consume oxygen during incubation. When the oxygen is gone, the bacteria react with the methylene blue dye in the HAB-BART tube and change the dye to the colorless form. The faster the color change, the higher the level of respiration and the larger or more aggressive the bacteria population.

Aerobic bacteria can cause several problems in water (e.g., slime formation, turbidity, taste and odor, corrosion, health risks and hygiene risks). When a problem is found, more tests are recommended to give more information about the microbial problem. This method does not give information about the particular groups of bacteria that can be in the sample.

Disposal

Sterilize the reacted sample before disposal. Refer to Figure 2.

Figure 2 Disposal



Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
BART Test for heterotrophic aerobic bacteria (HAB)	1	9/pkg	2490409
BART Test for heterotrophic aerobic bacteria (HAB)	1	27/pkg	2490427

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01/2016, Edition 3

Bacteria, Iron-related

DOC316.53.01325

Visual determination

Semi-quantitative

IRB-BART™[1]

Scope and application: For the determination of iron-related bacteria in brine solutions, produced waters and hydraulic fracturing waters.

[1] IRB-BART is a trademark of Droycon Bioconcepts Inc.

Test preparation

Before starting

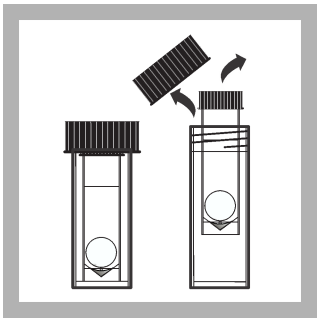
Do not touch the inner surface of the tube or lid. Keep contamination out of the tube and lid. Use the aseptic technique.
Set the caps on a clean surface with the flat surface down.
Iron-related bacteria (IRB) primarily grows on surfaces and not directly in water. Make sure to get a representative sample.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.
Sterilize the reacted sample before disposal. Refer to Disposal on page 3.

Items to collect

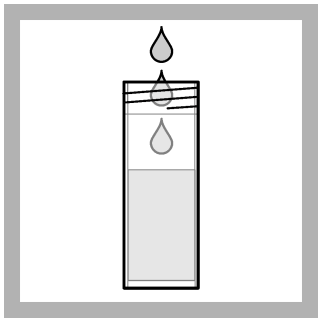
Description	Quantity
BART Test for iron-related bacteria (IRB)	1

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

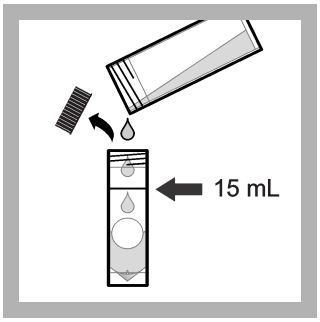
Test procedure



1. Remove the inner tube from the outer tube.

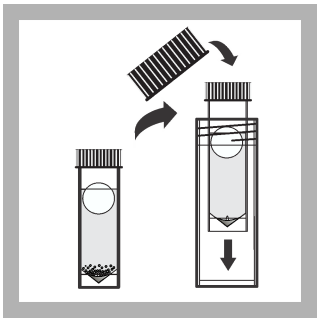


2. Pour at least 20 mL of sample in the outer tube.



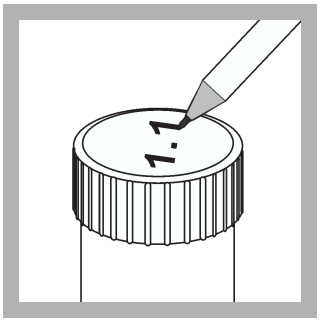
3. Fill the inner tube to the fill line with the sample that is in the outer tube. Tighten the cap on the inner tube.

Discard the unused sample in the outer tube.

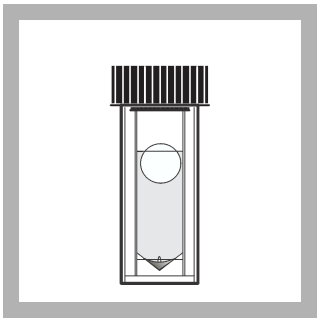


4. Put the inner tube in the empty outer tube. Tighten the cap on the outer tube.

Do not shake or swirl the tubes after the sample is added. Let the ball float to the top with no help.

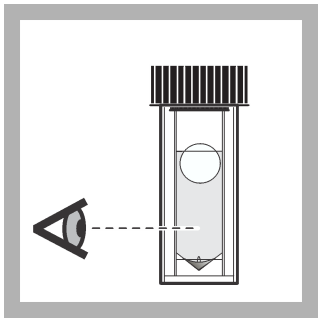


5. Write the date and sample name on the outer tube.



6. Keep the tube at room temperature and away from direct sunlight for 8 days.

Do not move the tube.



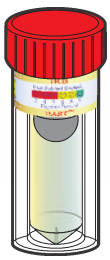
7. Examine the tube each day. Record the date when a reaction is first seen. Refer to Test results on page 2.

Test results

Presence/Absence

When iron-related bacteria are in the sample, a foam or a brown slime ring forms around the ball and/or there is a brown slime growth at the bottom of the tube. Refer to Figure 1.

Figure 1 Negative versus positive test results



Negative (absent/non-aggressive)

The solution has no foam or brown slime.

Positive (present/aggressive)

Foam or a brown slime ring forms around the ball and/or there is a brown slime growth at the bottom of the tube.

Make an estimate of the bacteria population

If the test result is positive, make an estimate of the bacteria population and the aggressivity. Refer to Table 1. A faster reaction occurs when the bacteria population is high.

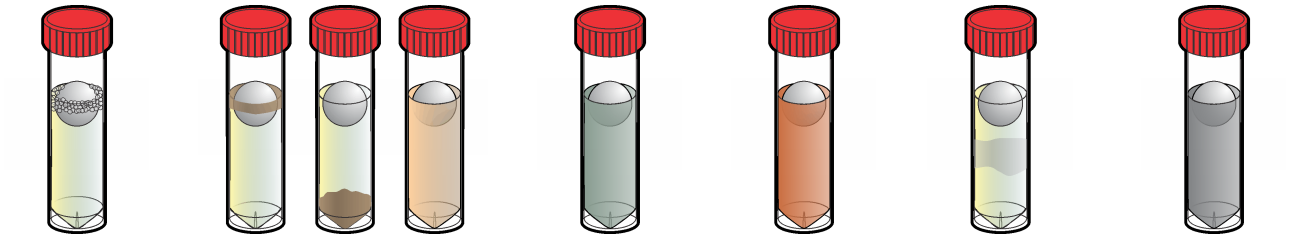
Table 1 Approximate bacteria population

Days to reaction	Approximate IRB population (cfu/mL)	Aggressivity
1	570,000	Very high
2	140,000	High
3	35,000	High
4	9000	Moderate
5	2200	Moderate
6	500	Moderate
7	150	Moderate
8	25	Low

Advanced test information

If the test result is positive, examine the tubes for dominant bacteria. Refer to Figure 2. If the dominant bacteria is enteric or pseudomonads and has a high or very high aggressivity, a fecal coliform test is recommended on a fresh sample to determine if there is a hygiene risk.

Figure 2 Dominant bacteria



Anaerobic bacteria	Iron-related bacteria	Pseudomonads	Enteric bacteria	Heterotrophic bacteria	Pseudomonads and enterics
Foam around ball	Brown rings, gel and/or clouds	Green cloudy	Red cloudy	Cloudy	Black solution

Summary of method

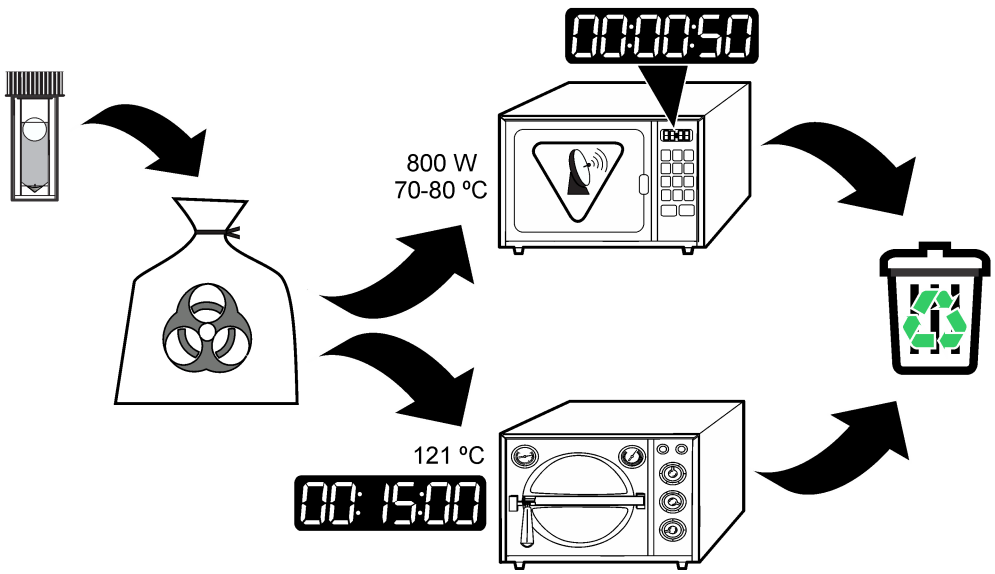
When iron-related bacteria (IRB) are in the sample, a series of reactions occur in the redox and nutrient gradients that develop in the IRB-BART tube during incubation. The iron-related bacteria use the nutrients and ferric iron in the tube to grow. The iron-related bacteria cause foam, clouding, slime and/or color changes.

The bacteria determined in this test include iron oxidizing and reducing bacteria, the sheathed iron bacteria, Gallionella, pseudomonads and enteric bacteria. These organisms can cause biofouling problems such as plugging, corrosion, cloudiness and color.

Disposal

Sterilize the reacted sample before disposal. Refer to Figure 3.

Figure 3 Disposal



Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
BART Test for iron-related bacteria (IRB)	1	9/pkg	2432309
BART Test for iron-related bacteria (IRB)	1	27/pkg	2432327

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07/2016, Edition 3

Bacteria, Slime-forming

DOC316.53.01327

Visual determination

Semi-quantitative

SLYM-BART™[1]

Scope and application: For the determination of slime-forming bacteria in brine solutions, produced waters and hydraulic fracturing waters.

[1] SLYM-BART is a trademark of Droycon Bioconcepts Inc.

Test preparation

Before starting

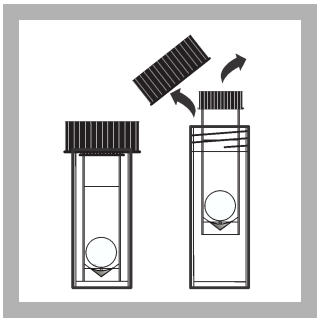
Do not touch the inner surface of the tube or lid. Keep contamination out of the tube and lid. Use the aseptic technique.
Set the caps on a clean surface with the flat surface down.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.
Sterilize the reacted sample before disposal. Refer to Disposal on page 3.

Items to collect

Description	Quantity
BART Test for slime-forming bacteria (SLYM)	1

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

Test procedure

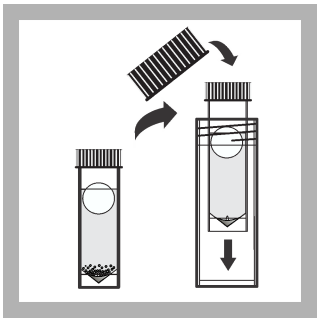


1. Remove the inner tube from the outer tube.

2. Pour at least 20 mL of sample in the outer tube.

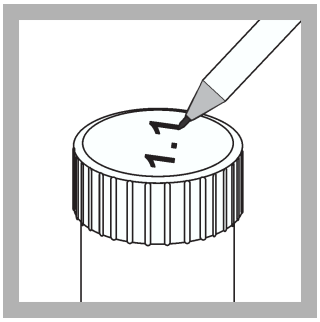
3. Fill the inner tube to the fill line with the sample that is in the outer tube. Tighten the cap on the inner tube.

Discard the unused sample in the outer tube.

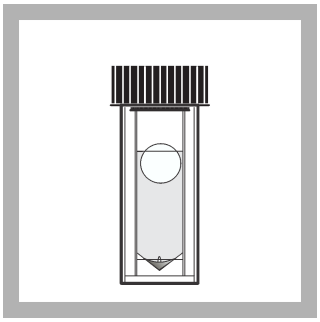


4. Put the inner tube in the empty outer tube. Tighten the cap on the outer tube.

Do not shake or swirl the tubes after the sample is added. Let the ball float to the top with no help.

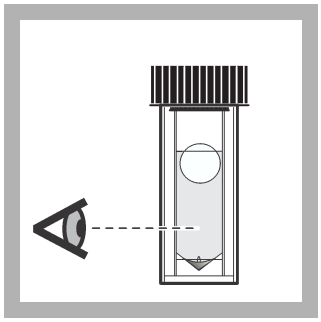


5. Write the date and sample name on the outer tube.



6. Keep the tube at room temperature and away from direct sunlight for 8 days.

Do not move the tube.



7. Examine the tube each day. Record the date when a reaction is first seen. Refer to Test results on page 2.

Test results

Presence/Absence

When slime-forming bacteria are in the sample, the solution becomes cloudy. Refer to Figure 1.

Figure 1 Negative versus positive test results

Negative (absent/non-aggressive)

The solution stays clear with no visible growth or glow under UV light.

Positive (present/aggressive)

The solution is cloudy. A glowing ring is seen under UV light and/or there is slime growth at the bottom of the tube.

Make an estimate of the bacteria population

If the test result is positive, make an estimate of the bacteria population and the aggressivity. Refer to Table 1. A faster reaction occurs when the bacteria population is high.

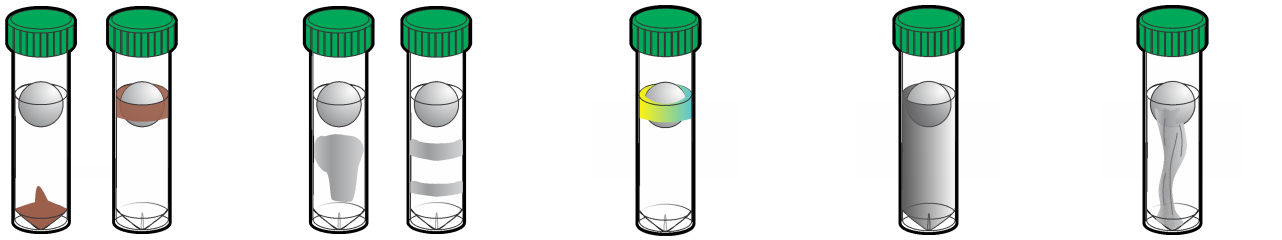
Table 1 Approximate bacteria population

Days to reaction	Approximate slime population (cfu/mL)	Aggressivity
1	1,750,000	Very high
2	440,000	High
3	67,000	High
4	13,000	Moderate
5	2500	Moderate
6	500	Moderate
7	100	Low
8	Less than 20	Low

Advanced test information

If the test result is positive, examine the tubes for dominant bacteria. Refer to Figure 2. If the dominant bacteria is enteric or pseudomonads and has a high or very high aggressivity, a fecal coliform test is recommended on a fresh sample to determine if there is a hygiene risk.

Figure 2 Dominant bacteria



Dense slime bacteria	Slime-forming bacteria	Fluorescing pseudomonads	Pseudomonads and enterics	Tight slime bacteria
Dense slime in bottom or slime ring around ball	Cloudy growth or layered plates	Glows pale blue under UV light	Blackened liquid	Thread-like strands

Summary of method

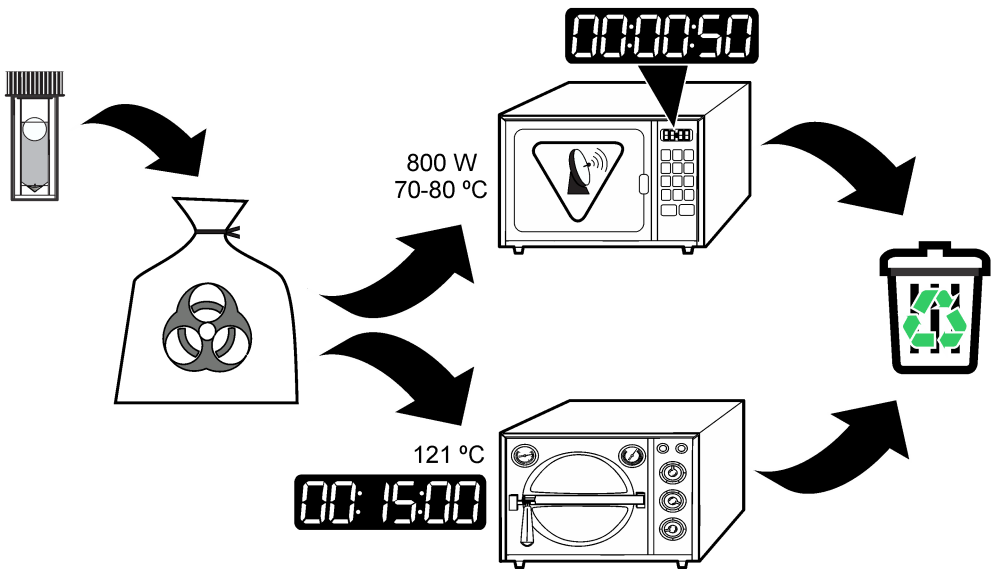
When slime-forming bacteria are in the sample, one or more types of slime grow in the SLYM-BART tube during incubation. The slime is typically seen as a cloudy or gel-like growth, which can be in one location or occur through all the sample. Slime growths are usually white, grey, yellow or beige in color and can darken over time. Slime-forming bacteria typically produce the thickest slime in aerobic (oxidative) conditions, which occur around the floating ball.

Iron-related bacteria also produce slime, but it is typically thinner and various forms of iron accumulate. Slime-forming bacteria can make large amounts of slime without iron.

Disposal

Sterilize the reacted sample before disposal. Refer to Figure 3.

Figure 3 Disposal



Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
BART Test for slime-forming bacteria (SLYM)	1	9/pkg	2432509
BART Test for slime-forming bacteria (SLYM)	1	27/pkg	2432527

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06/2015, Edition 3

Bacteria, Sulfate-reducing

DOC316.53.01326

Visual determination

Semi-quantitative

SRB-BART™[1]

Scope and application: For the determination of sulfate-reducing bacteria in brine solutions, produced waters and hydraulic fracturing waters.

[1] SRB-BART is a trademark of Droycon Bioconcepts Inc.

Test preparation

Before starting

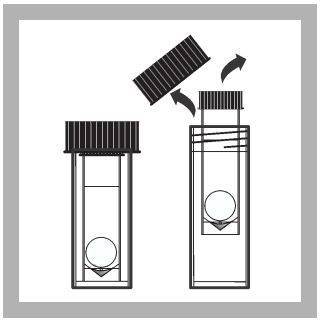
Do not touch the inner surface of the tube or lid. Keep contamination out of the tube and lid. Use the aseptic technique.
Set the caps on a clean surface with the flat surface down.
Sulfate-reducing bacteria (SRB) grow primarily deep within biofilms and not directly in water. Make sure to get a representative sample.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.
Sterilize the reacted sample before disposal. Refer to Disposal on page 3.

Items to collect

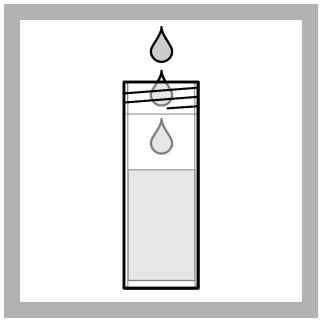
Description	Quantity
BART Test for sulfate-reducing bacteria (SRB)	1

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

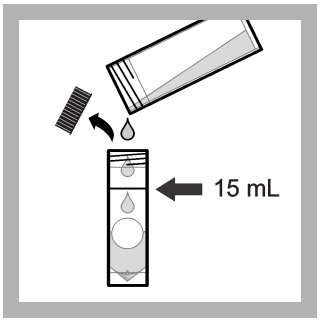
Test procedure



1. Remove the inner tube from the outer tube.

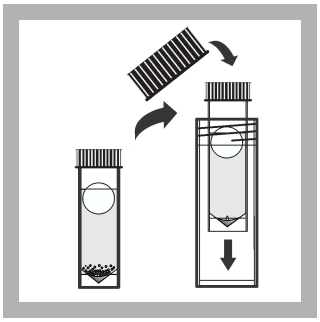


2. Pour at least 20 mL of sample in the outer tube.



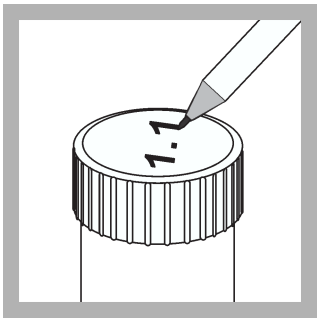
3. Fill the inner tube to the fill line with the sample that is in the outer tube. Tighten the cap on the inner tube.

Discard the unused sample in the outer tube.

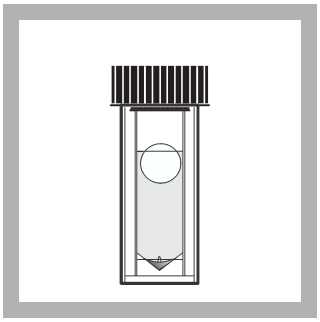


4. Put the inner tube in the empty outer tube. Tighten the cap on the outer tube.

Do not shake or swirl the tubes after the sample is added. Let the ball float to the top with no help.

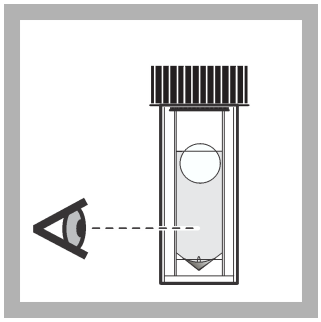


5. Write the date and sample name on the outer tube.



6. Keep the tube at room temperature and away from direct sunlight for 8 days.

Do not move the tube.



7. Examine the tube each day. Record the date when a reaction is first seen. Refer to Test results on page 2.

Interferences

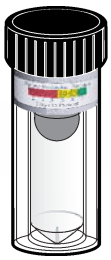
Interfering substance	Interference level
Hydrogen Sulfide (H_2S)	More than 20 ppm can give a false positive. Remove hydrogen gas from the sample as follows: Add 30 mL of sample to the outer tube. Put the outer tube cap on the tube. Shake the tube for 10 seconds. Do not move the tube for 20 seconds. Use this sample in the test procedure.

Test results

Presence/Absence

When sulfate-reducing bacteria are in the sample, a black slime forms in the tube. Refer to Figure 1.

Figure 1 Negative versus positive test results



Negative (absent/non-aggressive)

The solution has no black slime.

Positive (present/aggressive)

A black slime ring forms around the ball and/or there is a black slime growth at the bottom of the tube.

Make an estimate of the bacteria population

If the test result is positive, make an estimate of the bacteria population and the aggressivity. Refer to Table 1. A faster reaction occurs when the bacteria population is high.

Table 1 Approximate bacteria population

Days to reaction	Approximate SRB population (cfu/mL)	Aggressivity
1	2,200,000	Very high
2	500,000	High
3	115,000	High
4	27,000	High

Table 1 Approximate bacteria population (continued)

Days to reaction	Approximate SRB population (cfu/mL)	Aggressivity
5	6000	Moderate
6	1400	Moderate
7	325	Moderate
8	75	Low

Advanced test information

If the test result is positive, examine the tubes for dominant bacteria. Refer to Figure 2.

Figure 2 Dominant bacteria

Dense anaerobic bacteria dominated by Desulfovibrio	Aerobic SRB with aerobic slime forming heterotrophs	Aerobic and anaerobic SRB	Anaerobic bacteria
Black slime on the bottom only	Black slime around the ball only	Black slime on the bottom and around the ball	Cloudy solution

Summary of method

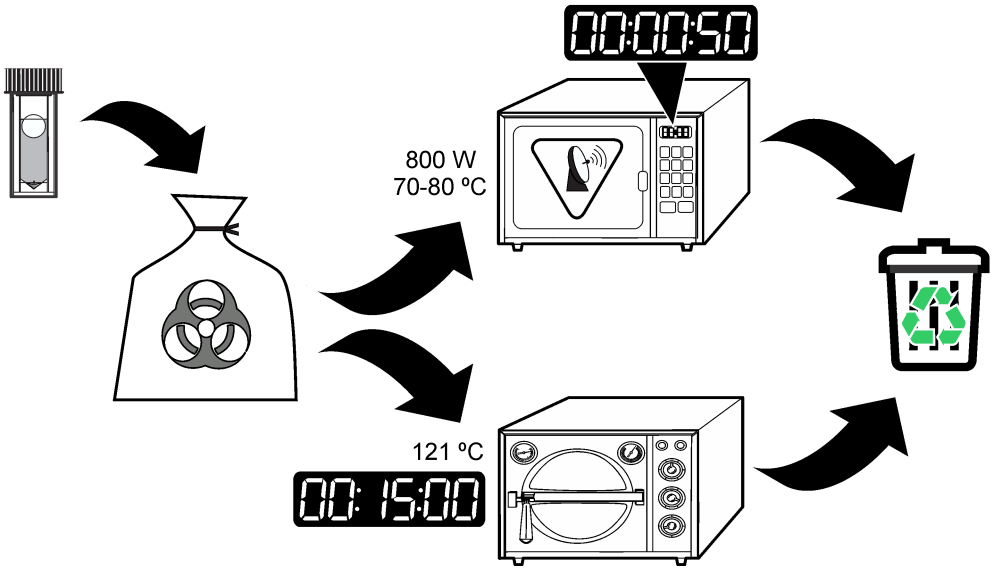
When sulfate-reducing bacteria (SRB) are in the sample, sulfate is reduced to hydrogen sulfide (H_2S) in the SRB-BART tube during incubation. The H_2S reacts with the ferrous iron in the tube to form black iron sulfides. This sulfide commonly forms in the base as a black slime and/or around the ball as an irregular black ring.

Sulfate-reducing bacteria typical grow in anaerobic conditions deep within biofilms (slimes) as a part of a microbial community. Sulfate-reducing bacteria may not be in the free-flowing water over the site of the fouling. Sulfate-reducing bacteria can cause problems such as strong odors, blackening of equipment, slime formations and the start of corrosive processes.

Disposal

Sterilize the reacted sample before disposal. Refer to Figure 3.

Figure 3 Disposal



Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
BART Test for sulfate-reducing bacteria (SRB)	1	9/pkg	2432409
BART Test for sulfate-reducing bacteria (SRB)	1	27/pkg	2432427

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Chloride, HR

DOC316.53.01322

Direct ISE method **Method 10255**

3.55 g/L to 35 g/L Cl^- **Powder Pillow ISA**

Scope and application: For the measurement of high concentrations (1 M) of chloride in brine solutions, produced waters and hydraulic fracturing waters.

Test preparation

Instrument-specific information

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

Table 1 Instrument-specific information

Meter	Probe
HQ4100 and HQ30d portable one input, multi-parameter HQ4200 and HQ40d portable two input, multi-parameter HQ4300 portable three input, multi-parameter HQ430d benchtop one input, multi-parameter HQ440d benchtop two input, multi-parameter	Intellical ISECL181 combination chloride ISE

Before starting

Refer to the meter documentation for meter settings and operation. Refer to probe documentation for probe preparation, maintenance and storage information.
Condition the probe before use. To condition the probe, put the probe in a 3.55 g/L Chloride Standard solution for a minimum of 30 minutes.
Stir the standards and samples at a slow and constant rate to prevent the formation of a vortex.
Air bubbles under the sensor tip can cause slow response or measurement errors. To remove the bubbles, carefully shake the probe.
Calibrate the probe regularly for the best measurement accuracy. Refer to Calibration on page 3.
During calibration, measure the standard solutions from lowest to highest concentration for best results.
Between measurements, rinse the probe with deionized water. Blot dry with a lint-free cloth.
Make sure that the calibration solutions and the samples are at the same temperature (± 2 °C (± 3.6 °F)) for best results.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.
This procedure is specified for the HQ meters and HQd meters. The Sension+ meters can be used, but the menus and navigation will be different.

Items to collect

Description	Quantity
Chloride Ionic Strength Adjustor (ISA) Buffer Powder Pillows	varies
Sodium chloride	11.55 g
Beaker, polypropylene, 50 mL, low form	4

Items to collect (continued)

Description	Quantity
Volumetric flask, 200-mL	3
Water, deionized	varies
Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.)	4
Stirrer, magnetic	1
Wash bottle with deionized water	1
Lint-free cloth	1

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

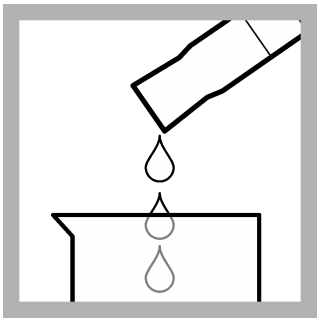
Sample collection

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

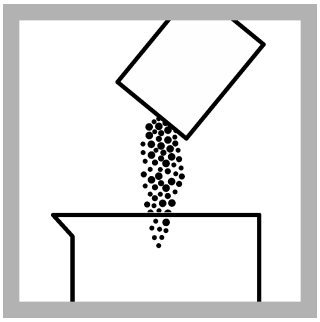
Configure the meter

Make sure that the meter is configured for calibration and measurements in g/L. Refer to the documentation for the applicable meter.

Procedure

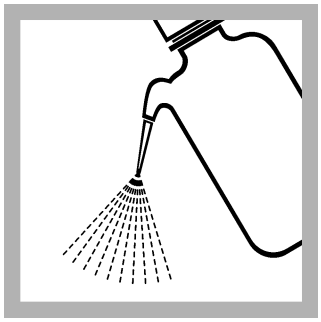


1. Add 25 mL of sample to a beaker.

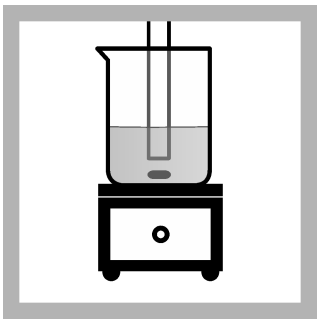


2. Add the contents of one chloride ISA powder pillow.

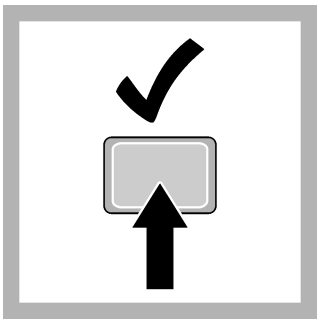
3. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



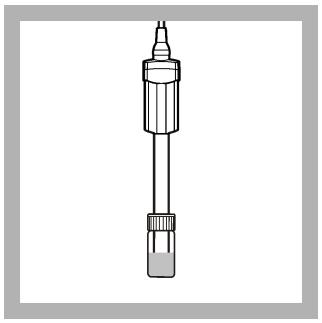
4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



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



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



7. When measurements are done, put the probe in storage. Refer to the probe documentation.

Sample dilution

If the chloride concentration is more than 35 g/L (1 M), dilute the sample to a lower concentration. Complete the steps that follow to make a 1:10 (10-fold) dilution.

1. Measure 2.5 mL of the sample in a 25-mL graduated cylinder.
2. Dilute to the mark with deionized water. Mix well.
3. Pour the diluted sample into a beaker.
4. Use the test procedure to measure the concentration of the sample.
5. Multiply the result by 10 to get the concentration of the sample before dilution.

Calibration

Prepare the standard solutions

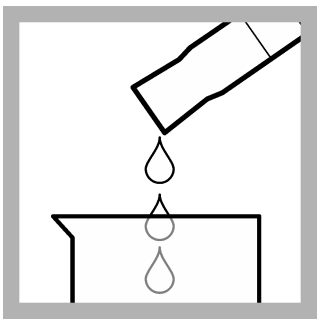
Prepare the standard solutions for calibration as follows.

Items to collect:

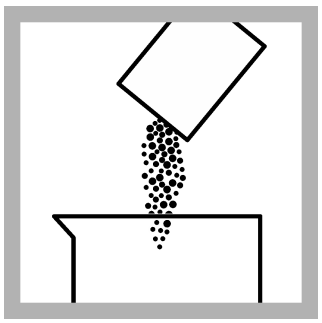
- Sodium chloride (NaCl)
- 200-mL volumetric flasks (3), Class A
- Laboratory balance
- Deionized water

1. Prepare a 35-g/L Chloride Standard Solution as follows:
   a. Weigh 11.5 g of sodium chloride.
   b. Quantitatively move the NaCl into a 200-mL volumetric flask.
   c. Dilute to the mark with deionized water. Mix well.
2. Prepare a 12.5-g/L Chloride Standard Solution as follows:
   a. Move 71.43 mL (or g) of the 35-g/L Chloride Standard Solution into a 200-mL volumetric flask.
   b. Dilute to the mark with deionized water. Mix well.
3. Prepare a 3.55-g/L Chloride Standard Solution as follows:
   a. Move 56.8 mL (or g) of the 12.5-g/L Chloride Standard Solution into a 200-mL volumetric flask.
   b. Dilute to the mark with deionized water. Mix well.

Calibration

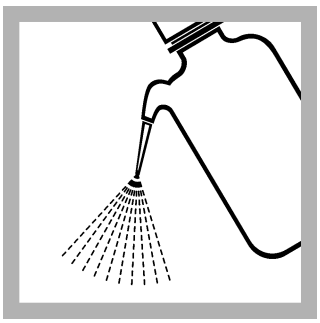


1. Add 25 mL of the lowest concentration standard solution to a beaker.

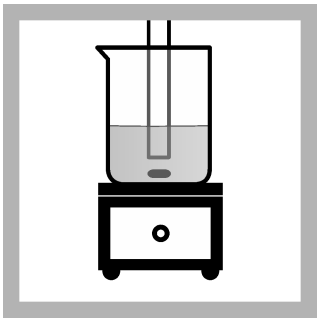


2. Add the contents of one chloride ISA powder pillow.

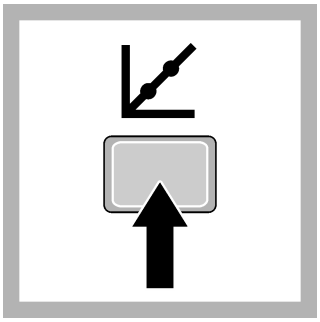
3. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



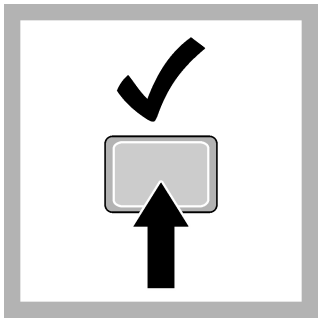
4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



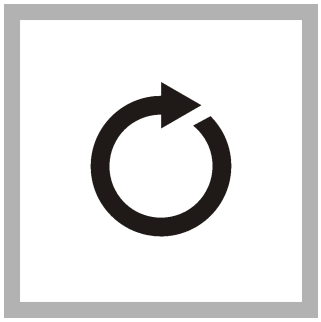
5. Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.



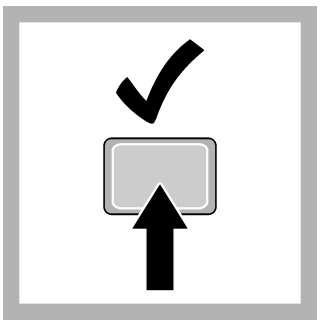
6. Push **Calibrate**. The standard solution value is shown.



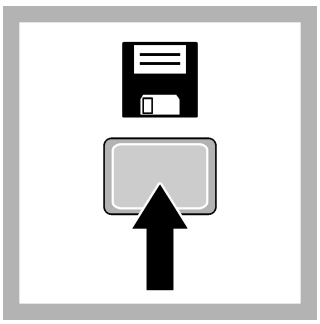
7. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.



8. Measure the remaining standard solutions.



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



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

Interferences

The sensing element reacts to chloride as well as other ions. Typically, probe response to another ion increases the potential, and causes a positive error. If Chloride ISA is added to the standards and samples, the effect of interfering ions is decreased. Refer to Table 2.

Table 2 Interfering substances

Interfering substance	Interference level
Oxidizing agents such as Copper (Cu^{2+}), Iron (Fe^{2+}) and Permanganate (MnO_4^-)	Do not interfere.
Mercury	Interferes at all levels.
Ions that form insoluble salts of silver	Can form a layer of salt on the sensing surface and cause probe errors.
Strong reducing solutions	Can form a surface layer of silver.

Consumables and replacement items

HQ meters, HQd meters and probes

Description	Unit	Item no.
HQ4100 portable one input, multi-parameter meter	each	LEV015.53.4100A
HQ4200 portable two input, multi-parameter meter	each	LEV015.53.4200A

HQ meters, HQd meters and probes (continued)

Description	Unit	Item no.
HQ4300 portable three input, multi-parameter meter	each	LEV015.53.4300A
HQ430d benchtop one input, multi-parameter meter	each	HQ430D
HQ440d benchtop two input, multi-parameter meter	each	HQ440D
Intellical ISECL181 digital combination chloride ISE, 1 meter cable	each	ISECL18101
Intellical ISECL181 digital combination chloride ISE, 3 meter cable	each	ISECL18103

Recommended reagents and standards

Description	Unit	Item no.
Chloride Ionic Strength Adjustor (ISA) Buffer Powder Pillows	100/pkg	2318069
Sodium Chloride, ACS	454 g	18201H

Accessories

Description	Unit	Item no.
Beaker, polypropylene, 50 mL, low form	each	108041
Bottle, wash, 500 mL	each	62011
Graduated cylinder, polypropylene, 25 mL	each	108140
Flask, volumetric, Class A, 200 mL	each	1457445
Water, deionized	4 L	27256
Probe clips, color-coded, for IntelliCAL probes	50/pkg	5818400
Probe holder, 3 probes, for sensION+ benchtop meters	each	LZW9321.99
Probe stand, universal	each	8508850
Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.)	each	4531500
Stirrer, electromagnetic, 120 VAC, with electrode stand	each	4530001
Stirrer, electromagnetic, 230 VAC, with electrode stand	each	4530002

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02/2021, Edition 3

Chloride

DOC316.53.01306

Silver Nitrate Method **Method 10246**

100 to 200,000 mg/L as Cl^- **Digital Titrator**

Scope and application: For oil and gas field waters.

Test preparation

Before starting

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

Items to collect

Description	Quantity
Chloride 2 Indicator Powder Pillows	1
Silver Nitrate Titration Cartridge, 1.128 N	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (size varies with selected sample volume), or TenSette pipet with tips	1
Erlenmeyer flask, 250-mL	1
Water, deionized	varies

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

Sample collection

- Collect samples in clean glass or plastic bottles.
- The sample can be kept for a maximum of 7 days before analysis.

Determine the sample volume

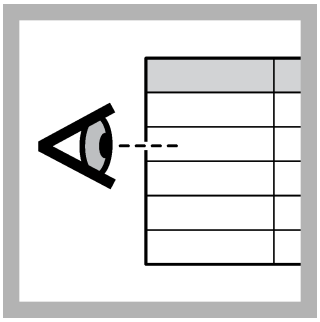
Use the steps that follow to make an estimate of the sample volume to use in the test procedure.

1. Add approximately 75–100 mL of deionized water to a clean titration flask.
2. Use a TenSette pipet to add 0.1 mL of the sample to the titration flask. Swirl to mix.
3. Add the contents of one Chloride 2 Indicator Powder Pillow to the flask. Swirl to mix. The sample color becomes yellow.
4. Titrate the solution quickly with the Silver Nitrate Titration Cartridge until the color changes from yellow to red-brown. Refer to Technique tips on page 3. Record the number of digits on the counter.
5. Find the sample volume to use in the test procedure from Table 1.
6. Rinse the flask fully with deionized water.

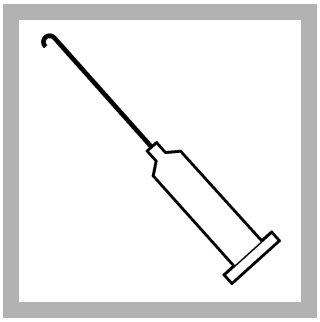
Table 1 Determine the sample volume

Number of digits	Sample volume (mL)
250	0.1
125	0.2
50	0.5
25	1.0
10	2.0
5	5.0
2	20
1	50

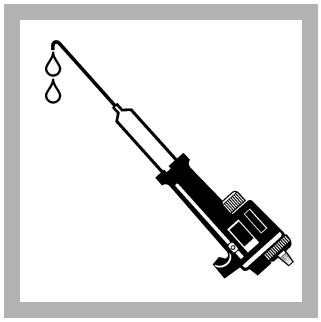
Test procedure



1. Select a sample volume and titration cartridge from Table 2 on page 3.
Refer to Determine the sample volume on page 1.

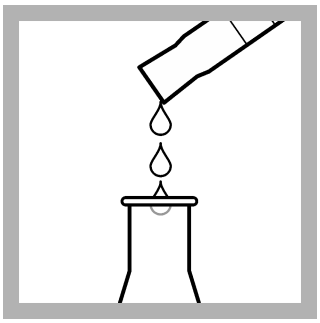


2. Insert a clean delivery tube into the Silver Nitrate Titration Cartridge. Attach the cartridge to the Digital Titrator.
Keep the silver nitrate cartridge in a dark area when not in use.

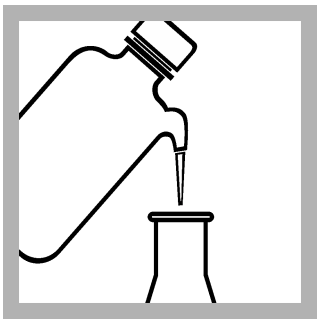


3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.

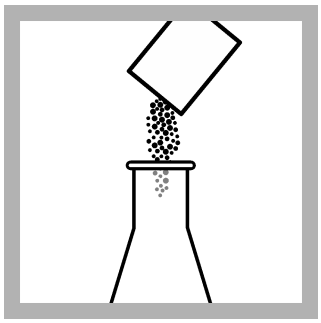
4. Use a graduated cylinder or TenSette pipet to measure the sample volume from Table 2 on page 3.



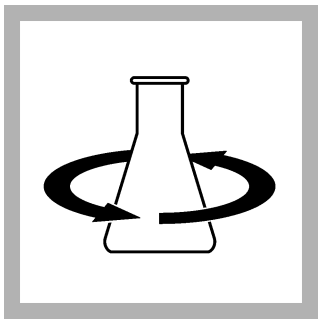
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



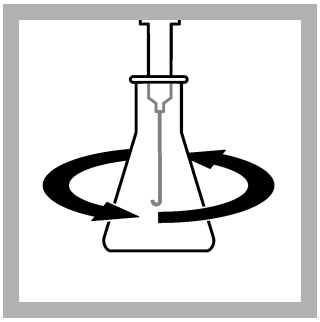
6. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



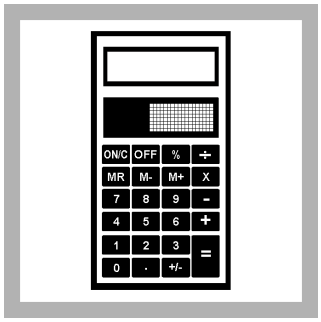
7. Add the contents of one Chloride 2 Indicator Powder Pillow.



8. Swirl to mix.
A small amount of undissolved powder will not have an effect on the results.



9. Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes from yellow to red-brown. Refer to Technique tips on page 3. Record the number of digits on the counter.



10. Use the multiplier in Table 2 on page 3 to calculate the concentration. Digits used × digit multiplier = mg/L Cl^-.

Sample volumes and digit multipliers

Select a range in Table 2, then read across the table row to find the applicable information for this test. Use the digit multiplier to calculate the concentration in the test procedure.

Note: *Refer to* Determine the sample volume *on page 1 to find a sample volume for this test.*

Example: A 50-mL sample was titrated with the 1.128 N Silver Nitrate Titration Cartridge and the counter showed 250 digits at the endpoint. The concentration is 250 digits x 1 = 250 mg/L Cl^-.

Table 2 Sample volumes and digit multipliers

Range (mg/L as Cl^-)	Sample volume (mL)	Digit multiplier
100–400	50	1
250–1000	20	2.5
1000–4000	5	10
2500–10,000	2	25
5000–20,000	1	50
10,000–40,000	0.5	100
25,000–100,000	0.2	250
50,000–200,000	0.1	500

Technique tips

- As an alternative to the deionized water, use demineralized water or other sources of chloride-free water.
- Use the TitraStir Titration Stand to reproducibly stir the sample at a steady rate.
- If the precipitate is red or orange but the solution is yellow, the test result will be low. Do the test again and increase the stir rate during the titration. Complete the steps that follow to prevent the red or orange precipitate formation:

1. Do not add one Chloride 2 Indicator Powder Pillow in step 7 of the test procedure and go directly to step 8.
2. Titrate a fresh sample with the Silver Nitrate Titration Cartridge to approximately 50–75% of the expected endpoint. The solution will have a milky-white precipitate.
3. Add one Chloride 2 Indicator Powder Pillow and swirl to dissolve. The solution becomes yellow. Continue to titrate with the Silver Nitrate Titration Cartridge to the red-brown endpoint.
   If the sample becomes red-brown after the addition of one Chloride 2 Indicator Powder Pillow, too much titrant was added. Repeat the procedure with less titrant.

Conversions

To change the units or chemical form of the test result, multiply the test result by the factor in Table 3.

Table 3 Conversions

mg/L chloride (Cl^-) to...	multiply by...	Example
mg/L sodium chloride (NaCl)	1.65	1000 mg/L chloride x 1.65 = 1650 mg/L NaCl
meq/L chloride (Cl^-)	0.02821	1000 mg/L chloride x 0.02821 = 28.21 meq/L Cl^-

Interferences

Interfering substance	Interference level
Bromide	Interferes directly and is included in the test result.
Cyanide	Interferes directly and is included in the test result.
Iodide	Interferes directly and is included in the test result.
Iron	Concentrations that are more than 20 mg/L prevent the color change at the endpoint.
Orthophosphate	Concentrations that are more than 25 mg/L cause a precipitate to form.
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary. Adjust strongly alkaline or acidic samples to a pH of 2 to 7 with 5.25 N sulfuric acid or 5.0 N sodium hydroxide. Do not use a pH meter directly for the pH adjustment because the pH electrode will contaminate the sample. Collect a separate sample to find the correct quantity of acid or base to add. Then, add the same quantity of acid or base to the sample that is used in the test procedure.
Sulfide	Remove sulfide interference as follows: 1. Add the contents of one Sulfide Inhibitor Reagent Powder Pillow to approximately 125 mL of sample. 2. Mix for 1 minute. 3. Pour the solution through folded filter paper in a funnel. 4. Use the filtered sample in the chloride test procedure.
Sulfite	Concentrations that are more than 10 mg/L interfere with this method. To remove sulfite interference, add 3 drops of 30% Hydrogen Peroxide to the sample, then start the test.

Accuracy check

Standard additions method (sample spike)

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

Items to collect:

- Chloride Voluette Ampule Standard Solution, 12,500-mg/L Cl^-
- Ampule Breaker

- Pipet, TenSette, 0.1–1.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the sample.
2. Use a TenSette pipet to add 0.1 mL of the standard solution to the titrated sample.
3. Titrate the spiked sample to the endpoint. Record the number of digits on the counter.
4. Add one more 0.1-mL addition of the standard solution to the titrated sample.
5. Titrate the spiked sample to the endpoint. Record the number of digits on the counter.
6. Add one more 0.1-mL addition of the standard solution to the titrated sample.
7. Titrate the spiked sample to the endpoint. Record the number of digits on the counter.
8. Compare the actual result to the correct result. The correct result for this titration is 25 digits of the 1.128 N Silver Nitrate Titration Cartridge for each 0.1-mL addition of the standard solution. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

Standard solution method

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

Items to collect:

- Chloride Voluette Ampule Standard Solution, 12,500-mg/L Cl^-
- Ampule Breaker
- Pipet, TenSette, 0.1–1.0 mL and pipet tips

1. Use a TenSette pipet to add 1.0 mL of the standard solution to a 250-mL Erlenmeyer flask.
2. Dilute the standard solution to approximately 100 mL with deionized water.
3. Add one Chloride 2 Indicator Powder Pillow. Swirl to mix.
4. Titrate the prepared standard solution until the color changes from yellow to red-brown. Refer to Technique tips on page 3. The correct number of digits for this titration is 250 (± 25) digits.
5. Compare the actual number of digits that were used in the titration to the correct number of digits. If much more or less titrant was used, there can be a problem with user technique, reagents or apparatus.

Summary of Method

Silver nitrate is used as the titrant and potassium chromate as the indicator. Silver nitrate first reacts selectively with the chloride in the sample to make insoluble white silver chloride. After all the chloride has precipitated, the silver nitrate reacts with the chromate to form an orange or red-brown silver chromate precipitate.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Chloride Reagent Set (approximately 100 tests)	—	each	2288000
Chloride 2 Indicator Powder Pillows (2x)	1	50/pkg	105766
Silver Nitrate Titration Cartridge, 1.128 N	varies	each	1439701
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity/test	Unit	Item no.
Graduated cylinders—Select one or more for the sample volume:			
Cylinder, graduated, 5 mL	1	each	50837
Cylinder, graduated, 10 mL	1	each	50838
Cylinder, graduated, 25 mL	1	each	50840
Cylinder, graduated, 50 mL	1	each	50841
Cylinder, graduated, 100 mL	1	each	50842
Digital Titrator	1	each	1690001
Delivery tube for Digital Titrator, J-hook tip	1	5/pkg	1720500
Flask, Erlenmeyer, 250 mL	1	each	50546
Pipet, TenSette, 0.1–1.0 mL	1	each	1970001
Pipet tips, for TenSette Pipet, 0.1–1.0 mL	1	50/pkg	2185696

Recommended standards

Description	Unit	Item no.
Chloride Standard Solution, 12,500 mg/L as Cl^-, 10-mL Voluette ampules	16/pkg	1425010
Sodium Chloride Standard Solution, 1000-mg/L as Cl^-	500 mL	18349

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette Ampules	each	2196800
Filter paper, folded, 3–5-micron, 12.5 cm	100/pkg	69257
Funnel, poly, 65 mm	each	108367
Hydrogen Peroxide Solution, 30%, ACS	473 mL	14411
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	245032
Stir bar, octagonal	each	2095352
Sulfide Inhibitor Reagent Powder Pillows	100/pkg	241899
Sulfuric Acid Standard Solution, 5.25 N	100 mL	244932
TitraStir Titration Stand, 115 VAC	each	1940000
TitraStir Titration Stand, 230 VAC	each	1940010
Delivery tube for Digital Titrator, 90-degree bend for use with TitraStir Titration Stand	5/pkg	4157800

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12/2014, Edition 2

Chlorine, Free

DOC316.53.01025

DPD Method[1]

Method 10069

0.1 to 10.0 mg/L Cl_2 (HR)

Powder Pillows

Scope and application: For determinations of higher levels of free chlorine (hypochlorous acid and hypochlorite ion) in drinking water, oil and gas, cooling water and industrial process waters. This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

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

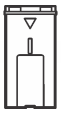
Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows requirements that can change between instruments, such as adapter and sample cell requirements.

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

Table 1 Instrument-specific information

Instrument	Adapter	Sample cell orientation	Sample cell
DR6000	—	The orientation key is toward the arrow on the universal cell adapter.	4864302 
DR5000	A23618	The orientation key is toward the user.	
DR3900	LZV846 (A)	The orientation key is away from the user.	
DR1900	9609900 or 9609800 (C)	The orientation key is toward the arrow on the adapter.	
DR/850, DR/890	—	The orientation key is at the 2 o'clock position.	
DR900	—	The orientation key is toward the user.	
DR3800 DR2800 DR2700	LZV585 (B)	The 1-cm path is aligned with the arrow on the adapter.	5940506 

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
In bright light conditions (e.g., direct sunlight), close the cell compartment, if applicable, with the protective cover during measurements.
If the chlorine concentration is less than 2 mg/L, use Method 8021, program number 80.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

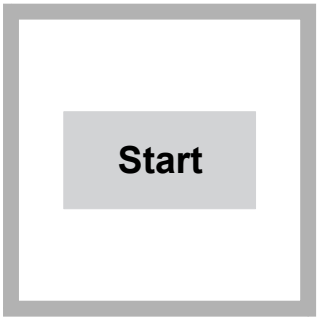
Description	Quantity
DPD Free Chlorine Reagent Powder Pillows, 25-mL	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

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

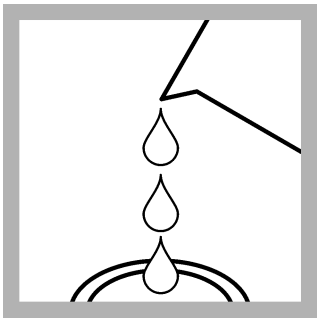
Sample collection

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence the decomposition of chlorine in water.
- Collect samples in clean glass bottles. Do not use plastic containers because these can have a large chlorine demand.
- Pretreat glass sample containers to remove chlorine demand. Soak the containers in a weak bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse fully with deionized or distilled water. If sample containers are rinsed fully with deionized or distilled water after use, only occasional pretreatment is necessary.
- Make sure to get a representative sample. If the sample is taken from a spigot or faucet, let the water flow for at least 5 minutes. Let the container overflow with the sample several times and then put the cap on the sample container so that there is no headspace (air) above the sample.

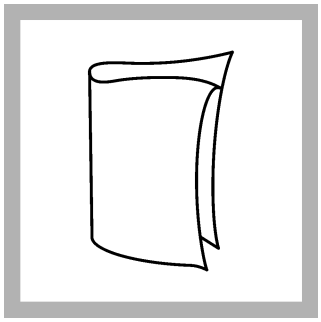
Powder pillow procedure



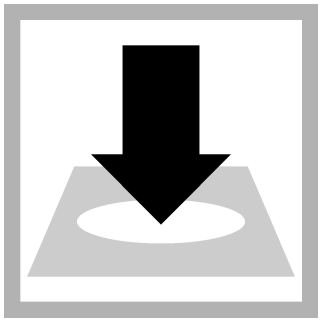
1. Start program **88 Chlorine F&T HR**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



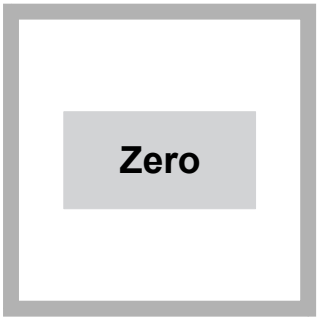
2. Prepare the blank: Fill a sample cell to the 5-mL mark with sample.



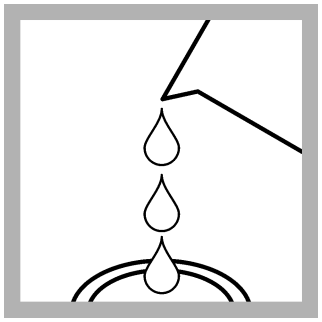
3. Clean the blank sample cell.



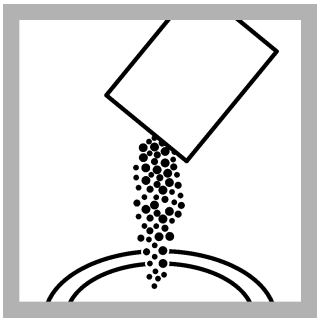
4. Insert the blank into the cell holder.



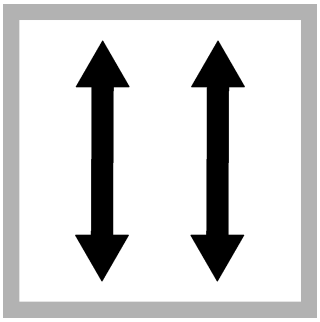
5. Push **ZERO**. The display shows 0.0 mg/L Cl_2.



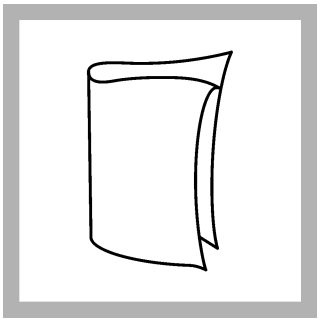
6. Prepare the sample: Fill a second sample cell to the 5-mL mark with sample.



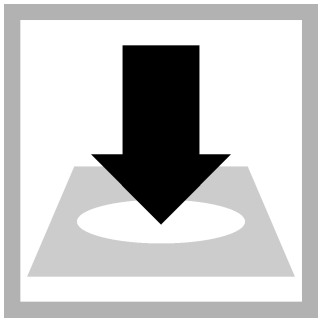
7. Add the contents of one DPD Free Chlorine Powder Pillow for 25-mL samples to the sample.



8. Put the stopper on the sample cell. Shake the sample cell for about 20 seconds to dissolve the reagent. A pink color shows if chlorine is in the sample.



9. Clean the sample cell.



10. Insert the prepared sample into the cell holder.

11. Push **READ**. Results show in mg/L Cl_2.

Interferences

Interfering substance	Interference level
Acidity	More than 150 mg/L $CaCO_3$. The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sodium Hydroxide. Measure the amount to add on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution from the volume addition.
Alkalinity	More than 250 mg/L $CaCO_3$. The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sulfuric Acid. Measure the amount to add on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution from the volume addition.
Bromine, Br_2	Positive interference at all levels
Chlorine Dioxide, ClO_2	Positive interference at all levels
Inorganic chloramines	Positive interference at all levels
Chloramines, organic	May interfere in the result for total chlorine analysis
Hardness	No effect at less than 1000 mg/L as $CaCO_3$
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium, Oxidized (Cr^{6+})	Pre-treat the sample as follows: **1.** Adjust the sample pH to 6–7. **2.** Add 3 drops of Potassium Iodide (30-g/L) to 10 mL of sample. **3.** Mix and wait 1 minute. **4.** Add 3 drops of Sodium Arsenite (5-g/L) and mix. **5.** Use the test procedure to measure the concentration of the treated sample. **6.** Subtract this result from the result without the treatment to obtain the correct chlorine concentration.

Interfering substance	Interference level
Ozone	Positive interference at all levels
Peroxides	May interfere
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary. Adjust to pH 6–7 with acid (Sulfuric Acid, 1.000 N) or base (Sodium Hydroxide, 1.00 N).

Monochloramine interference

For conventional free chlorine disinfection (beyond the breakpoint), typical monochloramine concentrations are very low. If monochloramine is present in the sample, its interference in the free chlorine test depends on the sample temperature, relative amount of monochloramine to free chlorine and the time required to do the analysis. Typical interference levels of monochloramine as mg/L Cl_2 in the free chlorine test are shown in Table 2 (1 minute test time). Measure the monochloramine levels with method 10200 for Chloramine (Mono) and Free Ammonia.

Table 2 Monochloramine interference at different sample temperatures

NH_2Cl (as Cl_2)	5 °C (41 °F)	10 °C (50 °F)	20 °C (68 °F)	30 °C (83 °F)
1.2 mg/L	0.15	0.19	0.30	0.29
2.2 mg/L	0.35	0.38	0.55	0.61
3.2 mg/L	0.38	0.56	0.69	0.73

Accuracy check

Standard additions method (sample spike)

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

Items to collect:

- Chlorine Standard Solution, 2-mL PourRite® Ampule, 50–75 mg/L (use mg/L on label)
- Breaker, PourRite Ampules
- Pipet, TenSette®, 0.1–1.0 mL and tips
- Mixing cylinders, 10-mL (3)

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 5-mL portions of fresh sample. Mix well.
6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
88	5.4 mg/L Cl_2	5.3–5.5 mg/L Cl_2	0.04 mg/L Cl_2

Summary of method

The range of analysis using the DPD method for free chlorine can be extended by adding more indicator in proportion to sample volume. Thus, a larger fill powder pillow of DPD Free Chlorine Reagent is added to a 5-mL sample portion. Chlorine in the sample as hypochlorous acid or hypochlorite ion (free chlorine or free available chlorine) immediately reacts with DPD (N,N-diethyl-p-phenylenediamine) indicator to form a pink color, the intensity of which is proportional to the chlorine concentration. The measurement wavelength is 530 nm for spectrophotometers or 520 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
DPD Free Chlorine Reagent Powder Pillow, 25 mL	1	100/pkg	1407099

Recommended standards and apparatus

Description	Unit	Item no.
Ampule Breaker, 2-mL PourRite Ampules	each	2484600
Ampule Breaker, 10-mL Voluette Ampules	each	2196800
Chlorine Standard Solution, 2-mL PourRite Ampules, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 2-mL PourRite Ampules, 25–30 mg/L	20/pkg	2630020
Chlorine Standard Solution, 10-mL Voluette Ampule, 50–75 mg/L	16/pkg	1426810
SpecCheck Gel Secondary Standard Kit, Chlorine DPD, 0–10 mg/L	4/pkg	2893300

Optional reagents and apparatus

Description	Unit	Item no.
Mixing cylinder, graduated, 25 mL	each	2088640
DPD Free Chlorine Reagent Powder Pillows, 10 mL	1000/pkg	2105528
DPD Free Chlorine Reagent Powder Pillows, 10 mL	300/pkg	2105503
Paper, pH, 0–14 pH range	100/pkg	2601300
Pipet, TenSette, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette Pipet, 0.1–1.0 mL	1000/pkg	2185628
Potassium Iodide, 30-g/L	100 mL	34332
Sodium Arsenite, 5 g/L	100 mL	104732
Sodium Hydroxide Standard Solution, 1.0 N	100 mL MDB	104532
Sulfuric Acid Standard Solution, 1 N	100 mL MDB	127032

Optional reagents and apparatus (continued)

Description	Unit	Item no.
Test tube rack, stainless steel	each	1864100
Thermometer, non-mercury, –10 to +225 °C	each	2635700

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11/2014, Edition 11

Chlorine, Total

DOC316.53.01029

USEPA DPD Method[1] — Method 10070

0.1 to 10.0 mg/L Cl_2 (HR) — Powder Pillows

Scope and application: For testing higher levels of total chlorine (free and combined) in drinking water, cooling water, oil and gas, and industrial process waters.[2] This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

[1] USEPA accepted for reporting drinking water analyses.
[2] Procedure is equivalent to USEPA and Standard Method 4500-Cl G for drinking water and wastewater.

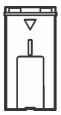
Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows requirements that can change between instruments, such as adapter and sample cell requirements.

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

Table 1 Instrument-specific information

Instrument	Adapter	Sample cell orientation	Sample cell
DR6000	—	The orientation key is toward the arrow on the universal cell adapter.	4864302 
DR5000	A23618	The orientation key is toward the user.	
DR3900	LZV846 (A)	The orientation key is away from the user.	
DR1900	9609900 or 9609800 (C)	The orientation key is toward the arrow on the adapter.	
DR/850, DR/890	—	The orientation key is at the 2 o'clock position.	
DR900	—	The orientation key is toward the user.	
DR3800 DR2800 DR2700	LZV585 (B)	The 1-cm path is aligned with the arrow on the adapter.	5940506 

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
In bright light conditions (e.g., direct sunlight), close the cell compartment, if applicable, with the protective cover during measurements.
If the chlorine concentration is less than 2 mg/L, use Method 8167, program number 80. If the chlorine concentration is less that 500 µg/L, use Method 8370 (for applicable instruments).
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

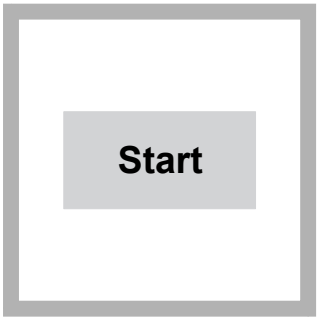
Description	Quantity
DPD Total Chlorine Reagent Powder Pillows, 25-mL	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	1

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

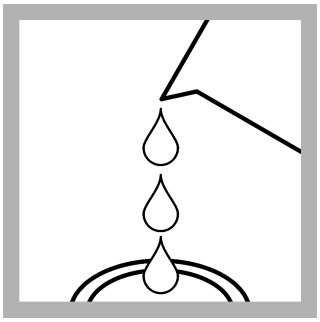
Sample collection

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence the decomposition of chlorine in water.
- Collect samples in clean glass bottles. Do not use plastic containers because these can have a large chlorine demand.
- Pretreat glass sample containers to remove chlorine demand. Soak the containers in a weak bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse fully with deionized or distilled water. If sample containers are rinsed fully with deionized or distilled water after use, only occasional pretreatment is necessary.
- Make sure to get a representative sample. If the sample is taken from a spigot or faucet, let the water flow for at least 5 minutes. Let the container overflow with the sample several times and then put the cap on the sample container so that there is no headspace (air) above the sample.

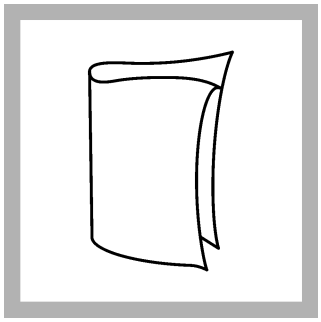
Powder pillow procedure



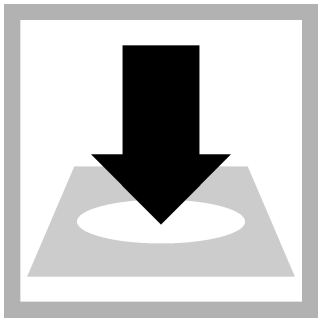
1. Start program **88 Chlorine F&T HR**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



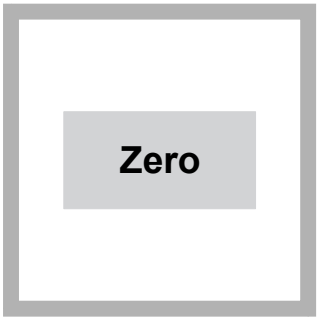
2. Prepare the blank: Fill a sample cell to the 5-mL mark with sample.



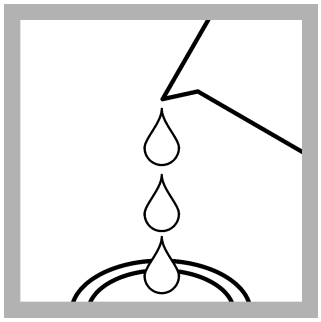
3. Clean the blank sample cell.



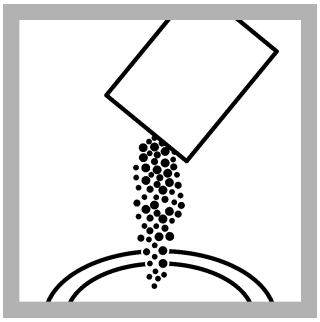
4. Insert the blank into the cell holder.



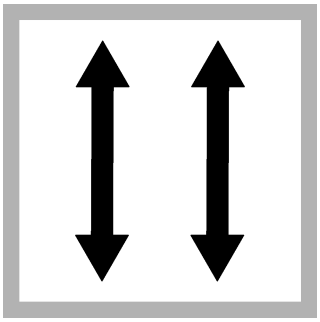
5. Push **ZERO**. The display shows 0.0 mg/L Cl_2.



6. Prepare the sample: Fill a second sample cell to the 5-mL mark with sample.

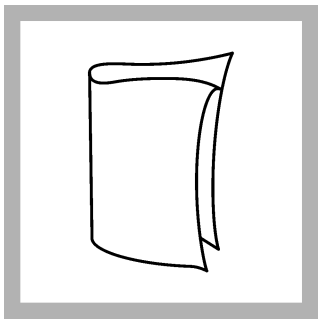


7. Add the contents of one DPD Total Chlorine Powder Pillow for 25-mL samples to the sample.

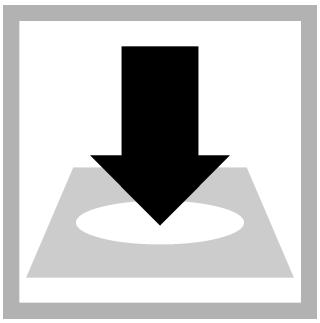


8. Put the stopper on the sample cell. Shake the sample cell about 20 seconds to dissolve the reagent.

9. Start the instrument timer. A 3-minute reaction time starts.



10. Clean the sample cell.



11. When the timer expires, insert the prepared sample into the cell holder.

12. Push **READ**. Results show in mg/L Cl_2.

Interferences

Interfering substance	Interference level
Acidity	More than 150 mg/L $CaCO_3$. The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sodium Hydroxide. Measure the amount to add on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution from the volume addition.
Alkalinity	More than 250 mg/L $CaCO_3$. The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sulfuric Acid. Measure the amount to add on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution from the volume addition.
Bromine, Br_2	Positive interference at all levels
Chlorine Dioxide, ClO_2	Positive interference at all levels
Inorganic chloramines	Positive interference at all levels
Chloramines, organic	May interfere in the result for total chlorine analysis
Hardness	No effect at less than 1000 mg/L as $CaCO_3$
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium, Oxidized (Cr^{6+})	Pre-treat the sample as follows: **1.** Adjust the sample pH to 6–7. **2.** Add 3 drops of Potassium Iodide (30-g/L) to 10 mL of sample. **3.** Mix and wait 1 minute. **4.** Add 3 drops of Sodium Arsenite (5-g/L) and mix. **5.** Use the test procedure to measure the concentration of the treated sample. **6.** Subtract this result from the result without the treatment to obtain the correct chlorine concentration.

Interfering substance	Interference level
Ozone	Positive interference at all levels
Peroxides	May interfere
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary.

Accuracy check

Standard additions method (sample spike)

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

Items to collect:

- Chlorine Standard Solution, 2-mL PourRite® Ampule, 50–75 mg/L (use mg/L on label)
- Ampule breaker
- Pipet, TenSette®, 0.1–1.0 mL and tips

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 5-mL portions of fresh sample. Mix well.
6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
88	5.4 mg/L Cl_2	5.3–5.5 mg/L Cl_2	0.1 mg/L Cl_2

Summary of method

The range of analysis using the DPD method for total chlorine can be extended by adding more indicator in proportion to sample volume. Thus, a larger fill powder pillow of DPD Total Chlorine Reagent is added to a 5-mL sample portion. The combined chlorine oxidizes iodide in the reagent to iodine. The iodine reacts with DPD (N, N-diethyl-p-phenylenediamine) along with free chlorine present in the sample to form a pink color which is proportional to the total chlorine concentration. The measurement wavelength is 530 nm for spectrophotometers or 520 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
DPD Total Chlorine Reagent Powder Pillow, 25 mL	1	100/pkg	1406499

Recommended standards

Description	Unit	Item no.
Chlorine Standard Solution, 2-mL PourRite Ampule, 50-75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette Ampule, 50–75 mg/L	16/pkg	1426810

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette Ampules	each	2196800
PourRite Ampule Breaker, 2 mL	each	2484600
Mixing cylinder, graduated, 25 mL	each	189640
Pipet, TenSette, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette Pipet, 0.1–1.0 mL	1000/pkg	2185628
Paper, pH, 0–14 pH range	100/pkg	2601300
Potassium Iodide, 30-g/L	100 mL	34332
Sodium Arsenite, 5 g/L	100 mL	104732
Sodium Hydroxide Standard Solution, 1.0 N	100 mL MDB	104532
Sulfuric Acid Standard Solution, 1 N	100 mL MDB	127032
Chlorine Standard Solution, 2-mL PourRite Ampules, 25–30 mg/L	20/pkg	2630020
DPD Total Chlorine Reagent Powder Pillows, 25 mL	1000/pkg	1406428

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11/2014, Edition 11

Conductivity

DOC316.53.01324

USEPA direct measurement method[1, 2] **Method 10256**

0.01 µS/cm to 200.0 mS/cm **Conductivity meter**

Scope and application: For brine solutions, produced waters and hydraulic fracturing waters.

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

Test preparation

Instrument-specific information

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

Table 1 Instrument-specific information

Meter	Standard probe	Rugged probe
HQ1140, HQ2100, HQ2200, HQ4100, HQ4200, HQ4300 HQ40d, HQ30d or HQ14d	CDC40101, CDC40103	CDC40105, CDC40110, CDC40115, CDC40130

Before starting

Refer to the meter documentation for meter settings and operation. Refer to probe documentation for probe preparation, maintenance and storage information.
Prepare the probe before initial use. Refer to probe documentation.
When an Intellical probe is connected to an HQ meter or an HQd meter, the meter automatically identifies the measurement parameter and is prepared for use.
Small differences in concentration between samples can increase the stabilization time. Make sure to condition the probe correctly. Try different stir rates to see if the stabilization time decreases.
If solutions are not at the reference temperature, the meter automatically adjusts the conductivity value to the value at the reference temperature.
Measurement errors can occur if the correct temperature correction value is not selected. Refer to Table 2 on page 2 for typical temperature correction values.
Do not touch the tip of the probe.
The cell constant is derived from the calibration standard.
Do not dilute conductivity standards and samples.
For the most accurate results with high conductivity samples, calibrate the cell constant or check the accuracy of the meter with a 111.3 mS/cm (1 Demal) certified conductivity standard.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

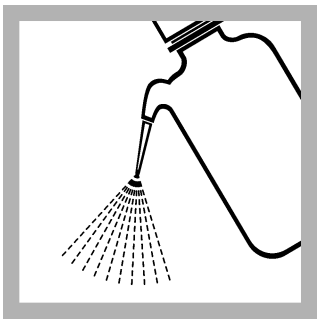
Description	Quantity
Beaker, 100 mL, polypropylene	1
Wash bottle with deionized water	1
Conductivity standard solution (refer to Recommended standards on page 4)	1

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

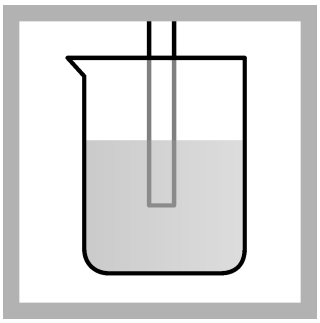
Sample collection and storage

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

Test procedure

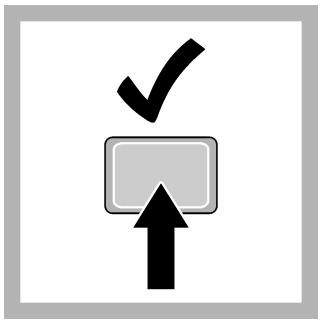


1. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

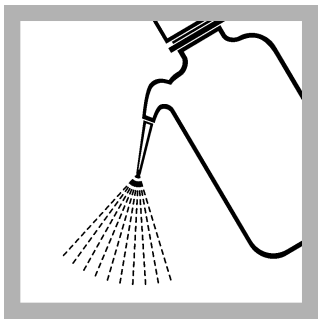


2. Laboratory test: Put the probe in a beaker that contains the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip. Stir the sample at a slow to moderate rate.
Field test: Put the probe in the sample. Move the probe up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

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



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



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

Conversions

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

Table 2 Unit conversion

From	To	Use this equation
mS/cm	µS/cm	mS/cm × 1000
µS/cm	mS/cm	µS/cm × 0.001
µS/cm	µmhos/cm	µS/cm × 1
mS/cm	mmhos/cm	mS/cm × 1

Table 2 Unit conversion (continued)

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

Interferences

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

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

Accuracy check

Standard solution method

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

Items to collect:

- Sodium chloride standard solution with a conductivity value that is close to the value of typical samples.

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

Clean the probe

Clean the probe when:

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

For general contamination, complete the steps that follow.

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

[1] TDS is an empirically-derived value from the conductivity measurement. Select a value of 0.64 for simplicity and suitability to oil and gas field waters.

Method performance

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

Summary of method

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

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

Consumables and replacement items

HQ meters and probes

Description	Unit	Item no.
HQ1140 portable one input, conductivity meter	each	LEV015.53.1140A
HQ2100 portable one input, multi-parameter meter	each	LEV015.53.2100A
HQ2200 portable two input, multi-parameter meter	each	LEV015.53.2200A
HQ4100 portable one input, multi-parameter meter	each	LEV015.53.4100A
HQ4200 portable two input, multi-parameter meter	each	LEV015.53.4200A
HQ4300 portable three input, multi-parameter meter	each	LEV015.53.4300A
Intellical standard conductivity probe, 1 m cable	each	CDC40101
Intellical standard conductivity probe, 3 m cable	each	CDC40103
Intellical rugged conductivity probe, 5 m cable	each	CDC40105
Intellical rugged conductivity probe, 10 m cable	each	CDC40110
Intellical rugged conductivity probe, 15 m cable	each	CDC40115
Intellical rugged conductivity probe, 30 m cable	each	CDC40130

Recommended standards

Description	Unit	Item no.
NaCl conductivity standards:		
Sodium chloride standard solution, 180 ± 10 µS/cm, 90 ± 1 mg/L TDS	100 mL	2307542
Sodium chloride standard solution, 1000 ± 10 µS/cm, 500 ± 5 mg/L TDS	100 mL	1440042
Sodium chloride standard solution, 1990 ± 20 µS/cm, 995 ± 10 mg/L TDS	100 mL	210542
Sodium chloride standard solution, 18,000 ± 50 µS/cm, 9000 ± 25 mg/L TDS	100 mL	2307442
KCl conductivity standards:		
12.88 mS/cm at 25 °C (77 °F), KCl, Singlet one-use packets, 20 mL each	20/pkg	2771520
1413 µS/cm at 25 °C (77 °F), KCl, Singlet one-use packets, 20 mL each	20/pkg	2771420
147 µS/cm at 25 °C (77 °F), KCl, Singlet one-use packets, 20 mL each	20/pkg	2771320

Recommended standards (continued)

Description	Unit	Item no.
KCl, 0.1 M, 12.88 mS/cm at 25 °C (77 °F)	500 mL	C20C250
KCl, 0.01 M, 1413 µS/cm at 25 °C (77 °F)	500 mL	C20C270
KCl, 0.001 M, 148 µS/cm at 25 °C (77 °F)	500 mL	C20C280
Certified conductivity standards:		
KCl, 1 Demal, 111.3 mS/cm ± 0.5% at 25 °C (77 °F)	500 mL	S51M001
KCl, 0.1 Demal, 12.85 mS/cm ± 0.35% at 25 °C (77 °F)	500 mL	S51M002
KCl, 0.01 Demal, 1408 µS/cm ± 0.5% at 25 °C (77 °F)	500 mL	S51M003
NaCl, 0.05%, 1015 µS/cm ± 0.5% at 25 °C (77 °F)	500 mL	S51M004

Optional reagents and accessories

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

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02/2021, Edition 3

Hardness, Total

DOC316.53.01317

EDTA Titration Method

Method 10247

100 to 200,000 mg/L as $CaCO_3$

Digital Titrator

Scope and application: For oil and gas field waters.

Test preparation

Before starting

As an alternative to the ManVer 2 Hardness Indicator Powder Pillow, use 4 drops of Hardness 2 Indicator Solution or a 0.1-g scoop of ManVer 2 Hardness Indicator Powder.
The optional TitraStir Titration Stand can hold the Digital Titrator and stir the sample.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Description	Quantity
ManVer 2 Hardness Indicator Powder Pillow	1
Hardness 1 Buffer Solution	2 mL
0.800 M EDTA titration cartridge	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (use a size that is applicable to the selected sample volume)	1
Erlenmeyer flask, 250 mL	1
Water, deionized	varies

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

Sample collection and storage

- Collect samples in clean glass or plastic bottles that have been cleaned with 1:1 nitric acid and rinsed with deionized water.
- To preserve samples for later analysis, adjust the sample pH to less than 2 with concentrated nitric acid (approximately 2 mL per liter). No acid addition is necessary if the sample is tested immediately.
- Keep the preserved samples at room temperature for a maximum of 6 months.
- Before analysis, adjust the pH to 7 with 5 N sodium hydroxide standard solution.
- Correct the test result for the dilution caused by the volume additions.

Determine the sample volume

Use the steps that follow to make an estimate of the sample volume to use in the test procedure.

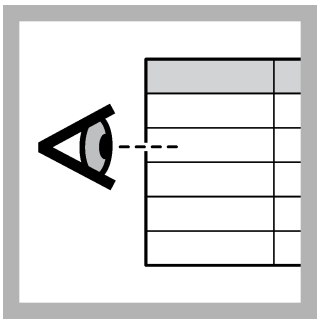
1. Add approximately 75–100 mL of deionized water to a clean titration flask.
2. Use a TenSette pipet to add 0.2 mL of the sample to the titration flask. Swirl to mix.

3. Add 2 mL of Hardness 1 Buffer Solution. Swirl to mix.
4. Add the contents of one ManVer 2 Hardness Indicator Powder Pillow to the flask. Swirl to mix. The sample color becomes red.
5. Titrate the solution quickly with the 0.800 M EDTA Titration Cartridge until the color changes from red to pure blue. Record the number of digits on the counter.
6. Find the sample volume to use in the test procedure from Table 1.
7. Rinse the flask fully with deionized water.

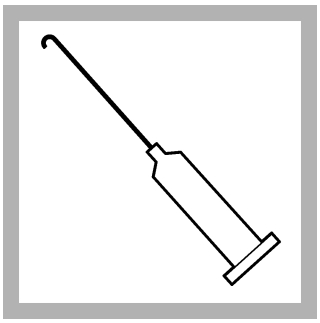
Table 1 Determine the sample volume

Number of digits	Sample volume (mL)
200	0.2
100	0.5
50	1
25	2
10	5
5	10
1	20

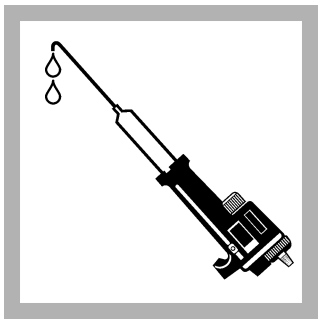
Test procedure



1. Select a sample volume and titration cartridge from Table 2 on page 3. Refer to Determine the sample volume on page 1.

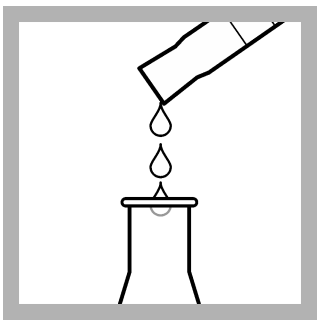


2. Insert a clean delivery tube into the 0.800 M EDTA Titration Cartridge. Attach the cartridge to the Digital Titrator.

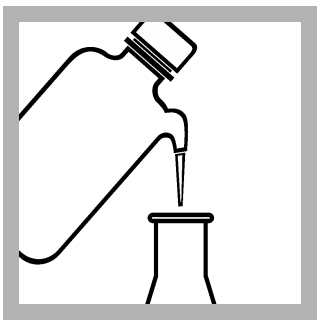


3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.

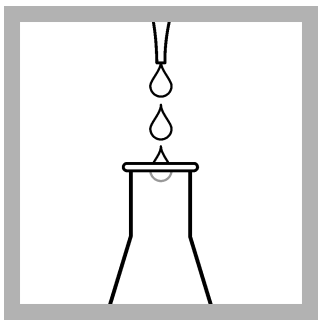
4. Use a graduated cylinder to measure the sample volume from Table 2 on page 3.



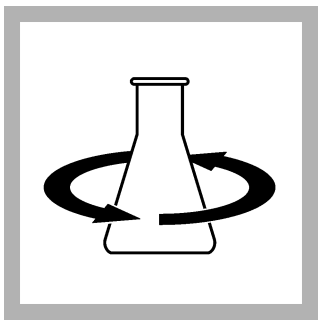
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



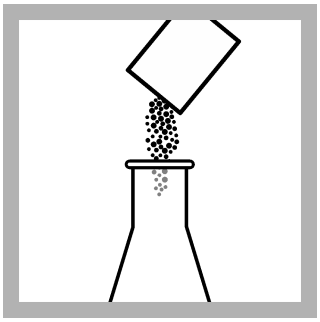
6. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



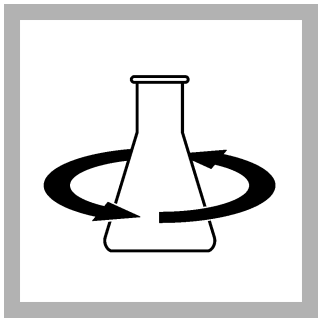
7. Add 1 mL of Hardness 1 Buffer Solution.



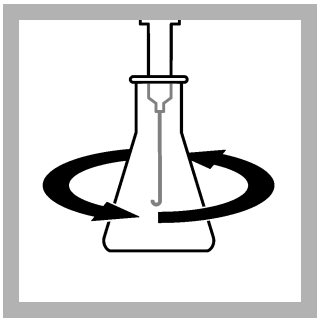
8. Swirl to mix.



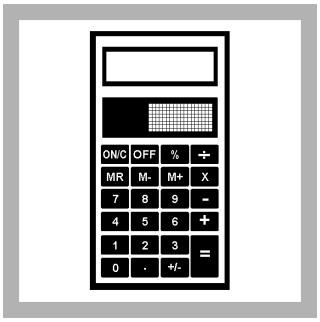
9. Add the contents of one ManVer 2 Hardness Indicator Powder Pillow.



10. Swirl to mix.



11. Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes from red to pure blue. Record the number of digits on the counter.



12. Use the multiplier in Table 2 on page 3 to calculate the concentration. Digits used × digit multiplier = mg/L total hardness as $CaCO_3$.

Sample volumes and digit multipliers

Select a range in Table 2, then read across the table row to find the applicable information for this test. Use the digit multiplier to calculate the concentration in the test procedure.

Example: A 50-mL sample was titrated with the 0.800 M EDTA titration cartridge and the counter showed 250 digits at the endpoint. The concentration is 250 digits x 2 = 500 mg/L total hardness as $CaCO_3$.

Table 2 Sample volumes and digit multipliers

Range (mg/L as $CaCO_3$)	Sample volume (mL)	Digit multiplier
100–400	100	1
200–800	50	2
500–2000	20	5
1000–4000	10	10
2000–8000	5	20
5000–20,000	2	50
10,000–40,000	1	100
20,000–80,000	0.5	200
50,000–200,000	0.2	500

Interferences

⚠ WARNING

Chemical hazard. Potassium cyanide is toxic. Make sure to add potassium cyanide to the sample after the Hardness 1 Buffer Solution has been added. Keep cyanide solutions at more than pH 11 to prevent exposure to hydrogen cyanide gas. Dispose of reacted solutions according to local, state and federal regulations.

An interfering substance can prevent the color change at the titration endpoint. A smaller sample volume can often dilute the interfering substance to a level at which the

substance does not interfere. Table 3 shows the substances that can interfere with this test.

Table 3 Interferences

Interfering substance	Interference level
Acidity	10,000 mg/L acidity as $CaCO_3$ does not interfere.
Alkalinity	10,000 mg/L alkalinity as $CaCO_3$ does not interfere.
Aluminum	Interferes when the sample contains more than 0.20 mg/L aluminum. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 1 mg/L aluminum. As an alternative, add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 5.
Barium	Interferes directly and is included in the test result. Most produced and flowback water samples contain barium at high concentrations. If the barium concentration is known, it can be subtracted from the hardness test result. Multiply the barium concentration as mg/L Ba by 0.729 to get mg/L Ba as $CaCO_3$, then subtract this number from the total hardness as $CaCO_3$ test result.
Chloride	The chloride level in seawater does not interfere. Solutions that are saturated with chloride do not show a sharp endpoint.
Cobalt	Interferes directly and is included in the test result. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 20 mg/L cobalt. As an alternative, add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 5.
Copper	Interferes when the sample contains 0.1 mg/L copper. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 100 mg/L copper. As an alternative, add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 5.
Iron	More than 8 mg/L iron causes an orange-red to green endpoint. Results are accurate to 20 mg/L iron with this endpoint. Most produced and flowback water samples contain iron at very high concentrations. Use a small sample volume to decrease the iron interference when the sample contains more than 100 mg/L iron. If the iron concentration in a small sample volume is more than 100 mg/L, add one CDTA powder pillow to decrease the interference. Refer to Use CDTA to remove metal interferences on page 5.
Manganese	Interferes when the sample contains more than 5 mg/L manganese. As an alternative, add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 5.
Nickel	Interferes when the sample contains 0.5 mg/L nickel. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 200 mg/L nickel. As an alternative, add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 5.
Orthophosphate	Forms calcium phosphate and causes a slow endpoint. If sufficient time is given to let the calcium phosphate dissolve during the titration, the orthophosphate will not interfere with the test.
Polyphosphates	Interfere directly and are included in the test result.
Polyvalent metal ions	Although less common than calcium and magnesium, other polyvalent metal ions are titrated with the calcium and magnesium and are included in the results.
Strontium	Interferes directly and is included in the test result. Most produced and flowback water samples contain strontium at high concentrations. If the strontium concentration is known, it can be subtracted from the hardness test result. Multiply the strontium concentration as mg/L Sr by 1.142 to get mg/L Sr as $CaCO_3$, then subtract this number from the total hardness as $CaCO_3$ test result.

Table 3 Interferences (continued)

Interfering substance	Interference level
Zinc	Interferes at 5 mg/L zinc. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 100 mg/L zinc. As an alternative, add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 5.
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary.

Use CDTA to remove metal interferences

Add one CDTA Magnesium Salt Powder Pillow to remove the interference from metals at or below the levels shown in Table 4. If more than one metal is in the sample at or more than the concentration in Table 4, add an additional CDTA Magnesium Salt Powder Pillow.

The results given with CDTA Magnesium Salt include the hardness from these metals. If the concentration of each metal is known, a correction can be made to get the hardness from calcium and magnesium only. The hardness value from different metal ions is shown in Table 5.

Metal hardness = (mg/L of metal in the sample) x (hardness equivalence factor)

Calcium and magnesium hardness = (total hardness) – (metal hardness)

Table 4 Interference level with one CDTA pillow

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

Table 5 Hardness equivalence factors (mg/L as $CaCO_3$)

Interfering substance	Hardness equivalence factor
Aluminum	3.710
Barium	0.729
Cobalt	1.698
Copper	1.575
Iron	1.792
Manganese	1.822
Nickel	1.705
Strontium	1.142
Zinc	1.531

Accuracy check

Standard additions method (sample spike)

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

Items to collect:

- Hardness Voluette Ampule Standard Solution, 10,000-mg/L as $CaCO_3$
- Ampule Breaker
- Pipet, TenSette, 0.1–1.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the sample.
2. Use a TenSette pipet to add 0.1 mL of the standard solution to the titrated sample.
3. Titrate the spiked sample to the endpoint. Record the number of digits on the counter.
4. Add one more 0.1-mL addition of the standard solution to the titrated sample.
5. Titrate the spiked sample to the endpoint. Record the number of digits on the counter.
6. Add one more 0.1-mL addition of the standard solution to the titrated sample.
7. Titrate the spiked sample to the endpoint. Record the number of digits on the counter.
8. Compare the actual result to the correct result. The correct result for this titration is 10 digits of the 0.800 M EDTA Titration Cartridge for each 0.1-mL addition of the standard solution. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

Standard solution method

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

Items to collect:

- Calcium Chloride Standard Solution, 1000-mg/L as $CaCO_3$

1. Use the test procedure to measure the concentration of the standard solution. Use 20 mL of the prepared standard solution.
2. Compare the actual result to the correct result. If much more or less titrant was used, there can be a problem with user technique, reagents or apparatus.

Summary of method

A buffer solution (an organic amine and one of its salts) is added to the sample to adjust the pH to 10.1. An organic dye, calmagite, is then added as the indicator for the test. The organic dye reacts with calcium and magnesium ions to give a red-colored complex. The EDTA (ethylenediaminetetraacetic acid) titrant is added, which reacts with all of the free calcium, magnesium, barium and strontium ions in the sample. After the EDTA has reacted with all of the free magnesium ions, the EDTA removes the magnesium ions from the indicator. The indicator color then changes from red to blue.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Total Hardness Reagent Set, HR	—	each	2448100
ManVer 2 Hardness Indicator Powder Pillows	1	100/pkg	85199
Buffer Solution, Hardness 1	2 mL	100 mL MDB	42432
EDTA titration cartridge, 0.800 M	varies	each	1439901
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity/test	Unit	Item no.
Graduated cylinders—Select one or more for the sample volume:			
Cylinder, graduated, 5 mL	1	each	50837
Cylinder, graduated, 10 mL	1	each	50838
Cylinder, graduated, 25 mL	1	each	50840
Cylinder, graduated, 50 mL	1	each	50841
Cylinder, graduated, 100 mL	1	each	50842
Digital Titrator	1	each	1690001
Delivery tube for Digital Titrator, J-hook tip	1	5/pkg	1720500
Flask, Erlenmeyer, 250 mL	1	each	50546
Pipet, TenSette, 0.1–1.0 mL	1	each	1970001
Pipet tips, for TenSette Pipet, 0.1–1.0 mL	1	50/pkg	2185696

Recommended standards

Description	Unit	Item no.
Calcium Chloride Standard Solution, 1000-mg/L as $CaCO_3$	1 L	12153
Hardness Standard Solution, 10,000-mg/L as $CaCO_3$, 10-mL Voluette ampule	16/pkg	218710

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette Ampules	each	2196800
CDTA Magnesium Salt Powder Pillow	100/pkg	1408099
Delivery tube for Digital Titrator, 90-degree bend for use with TitraStir Titration Stand	5/pkg	4157800
ManVer Hardness Indicator Solution	100 mL	42532
ManVer 2 Hardness Indicator Powder	113 g	28014
Nitric Acid, concentrated	500 mL	15249
Nitric Acid Solution, 1:1	500 mL	254049
Pipet filler, safety bulb	each	1465100
Pipet, volumetric, Class A, 10 mL	each	1451538
Pipet, volumetric Class A, 20 mL	each	1451520
Pipet, volumetric, Class A, 25 mL	each	1451540
Potassium Cyanide, ACS	100 g	76714
Sampling bottle, with cap, low density polyethylene, 250 mL	12/pkg	2087076
Sodium Hydroxide Solution, 5 N	50 mL	245026
Spoon, measuring, 0.1 g	each	51100
Spoon, measuring, 0.5 g	each	90700
Stir bar, octagonal	each	2095352
TitraStir Titration Stand, 115 VAC	each	1940000
TitraStir Titration Stand, 230 VAC	each	1940010

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12/2014, Edition 2

Hardness, Calcium

DOC316.53.01318

EDTA Titration Method

Method 10253

100 to 200,000 mg/L as $CaCO_3$

Digital Titrator

Scope and application: For oil and gas field waters.

Test preparation

Before starting

Magnesium is not included in the results but must be in the sample for a sharp endpoint. If the sample does not contain magnesium, add 1 to 2 drops of Magnesium Standard Solution, 10-g/L as $CaCO_3$, to the sample before the test is started.
As an alternative to the CalVer 2 Calcium Indicator Power Pillow (85299), use two CalVer 2 Calcium Indicator Power Pillows (94799) or 0.1 g scoop of CalVer 2 Calcium Indicator Powder.
The optional TitraStir Titration Stand can hold the Digital Titrator and stir the sample.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Description	Quantity
CalVer 2 Calcium Indicator Powder Pillow	1
Potassium Hydroxide Standard Solution, 8 N	1 or 2 mL
0.800 M EDTA Titration Cartridge	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (use a size that is applicable to the selected sample volume)	1
Erlenmeyer flask, 250 mL	1
Water, deionized	varies

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

Sample collection and storage

- Collect samples in clean glass or plastic bottles that have been cleaned with 1:1 nitric acid and rinsed with deionized water.
- To preserve samples for later analysis, adjust the sample pH to less than 2 with concentrated nitric acid (approximately 2 mL per liter). No acid addition is necessary if the sample is tested immediately.
- Keep the preserved samples at room temperature for a maximum of 6 months.
- Before analysis, adjust the pH to 7 with potassium hydroxide standard solution.
- Correct the test result for the dilution caused by the volume additions.

Determine the sample volume

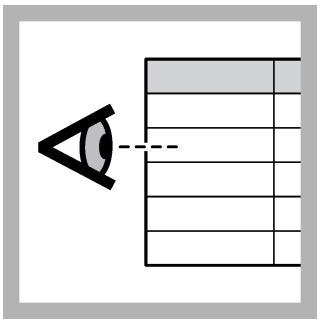
Use the steps that follow to make an estimate of the sample volume to use in the test procedure.

1. Add approximately 75–100 mL of deionized water to a clean titration flask.
2. Use a TenSette pipet to add 0.2 mL of the sample to the titration flask. Swirl to mix.
3. Add 1 mL of 8 N Potassium Hydroxide Standard Solution. Swirl to mix.
4. Add the contents of one CalVer 2 Calcium Indicator Powder Pillow to the flask. Swirl to mix. The sample color becomes red.
5. Titrate the solution quickly with the 0.800 M EDTA Titration Cartridge until the color changes from red to pure blue. Record the number of digits on the counter.
6. Find the sample volume to use in the test procedure from Table 1.
7. Rinse the flask fully with deionized water.

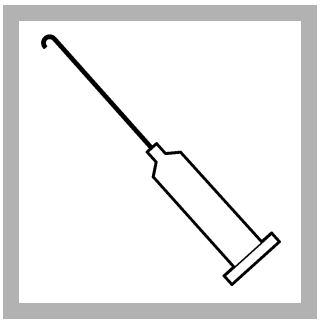
Table 1 Determine the sample volume

Number of digits	Sample volume (mL)
200	0.2
100	0.5
50	1
25	2
10	5
5	10
1	20

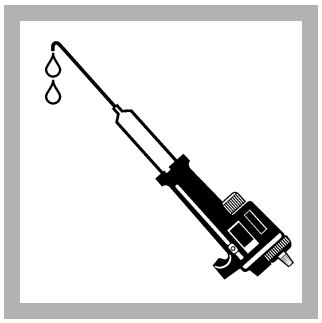
Test procedure



1. Select a sample volume and titration cartridge from Table 2 on page 3. Refer to Determine the sample volume on page 2.

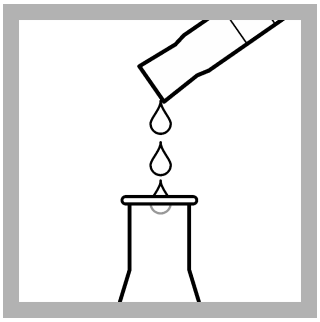


2. Insert a clean delivery tube into the 0.800 M EDTA Titration Cartridge. Attach the cartridge to the Digital Titrator.

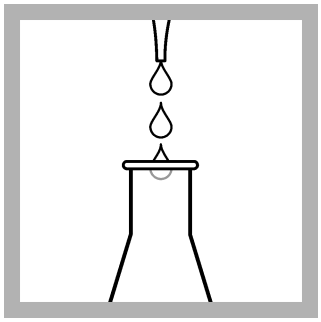


3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.

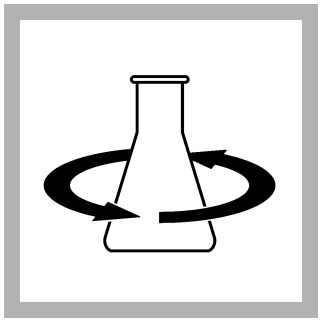
4. Use a graduated cylinder to measure the sample volume from Table 2 on page 3.



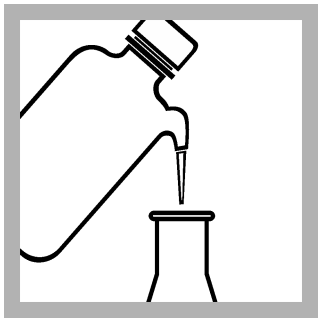
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



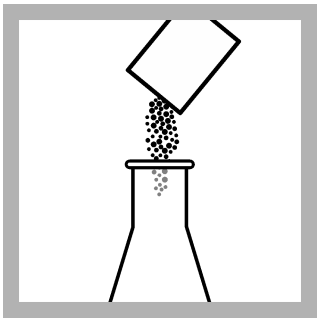
6. If the sample volume is 100 mL, add 2 mL of 8 N Potassium Hydroxide Standard Solution. If the sample volume is 50 mL or less, add 1 mL of 8 N Potassium Hydroxide Standard Solution.



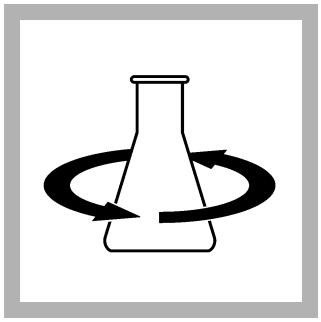
7. Swirl to mix.



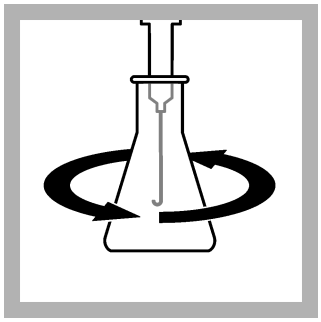
8. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



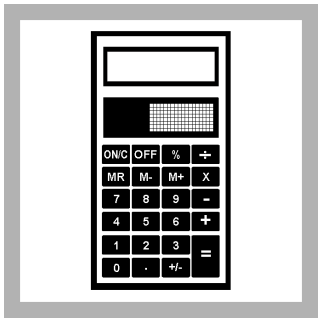
9. Add the contents of one CalVer 2 Calcium Indicator Powder Pillow.



10. Swirl to mix.



11. Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes from red to pure blue. Record the number of digits on the counter.



12. Use the multiplier in Table 2 on page 3 to calculate the concentration. Digits used × digit multiplier = mg/L Ca as $CaCO_3$.

Sample volumes and digit multipliers

Select a range in Table 2, then read across the table row to find the applicable information for this test. Use the digit multiplier to calculate the concentration in the test procedure.

Note: *Refer to* Determine the sample volume *on page 2 to find a sample volume for this test.*

Example: A 50-mL sample was titrated with the 0.800 M EDTA Titration Cartridge and the counter showed 250 digits at the endpoint. The concentration is 250 digits x 2 = 500 mg/L Ca as $CaCO_3$.

Table 2 Sample volumes and digit multipliers

Range (mg/L as $CaCO_3$)	Sample volume (mL)	Digit multiplier
100–400	100	1
200–800	50	2
500–2000	20	5
1000–4000	10	10

Table 2 Sample volumes and digit multipliers (continued)

Range (mg/L as $CaCO_3$)	Sample volume (mL)	Digit multiplier
2000–8000	5	20
5000–20,000	2	50
10,000–40,000	1	100
20,000–80,000	0.5	200
50,000–200,000	0.2	500

Conversion units

To change the units or chemical form of the test result, multiply the test result by the factor in Table 3.

Table 3 Conversions

mg/L Ca as $CaCO_3$ to...	multiply by...	Example
mg/L as Ca	0.40	1000 mg/L as $CaCO_3$ x 0.40 = 400 mg/L Ca
German degrees hardness (Gdh)	0.056	1000 mg/L as $CaCO_3$ × 0.056 = 56 Gdh
Grains per gallon (gpg)	0.058	1000 mg/L as $CaCO_3$ x 0.058 = 58 gpg

Interferences

⚠ WARNING

Chemical hazard. Potassium cyanide is toxic. Make sure to add potassium cyanide to the sample after the 8 N Potassium Hydroxide Standard Solution has been added. Keep cyanide solutions at more than pH 11 to prevent exposure to hydrogen cyanide gas. Dispose of reacted solutions according to local, state and federal regulations.

An interfering substance can prevent the color change at the titration endpoint. A smaller sample volume can often dilute the interfering substance to a level at which the substance does not interfere. Table 4 shows the substances that can interfere with this test.

Table 4 Interferences

Interfering substance	Interference level
Acidity	10,000 mg/L acidity as $CaCO_3$ does not interfere.
Alkalinity	10,000 mg/L alkalinity as $CaCO_3$ does not interfere.
Aluminum	Causes a slow endpoint. The sample can contain a maximum of 200 mg/L aluminum if sufficient time is given for the color change.
Barium	Interferes directly and is included in the test result. Most produced and flowback water samples contain barium at high concentrations. If the barium concentration is known, it can be subtracted from the calcium test result. Multiply the barium concentration as mg/L Ba by 0.729 to get mg/L Ba as $CaCO_3$, then subtract this number from the calcium as $CaCO_3$ test result.
Chloride	The chloride level in seawater does not interfere. Solutions that are saturated with chloride do not show a sharp endpoint.
Cobalt	Interferes directly and is included in the test result. Add 0.5 grams of potassium cyanide after the 8 N Potassium Hydroxide Standard Solution during the test procedure to remove the interference from a maximum of 20 mg/L cobalt.
Copper	Interferes at 0.1 mg/L copper. Add 0.5 grams of potassium cyanide after the 8 N Potassium Hydroxide Standard Solution during the test procedure to remove the interference from a maximum of 100 mg/L copper.

Table 4 Interferences (continued)

Interfering substance	Interference level
Iron	More than 8 mg/L iron causes an orange-red to green endpoint. Results are accurate to 20 mg/L iron with this endpoint. Most produced and flowback water samples contain iron at very high concentrations. Use a small sample volume to decrease the iron interference when the sample contains more than 100 mg/L iron. If the iron concentration in a small sample volume is more than 100 mg/L, add one CDTA powder pillow to decrease the interference.
Magnesium	The formation of magnesium hydroxide at the high test pH prevents interference from 200 mg/L magnesium. Samples with more than 200 mg/L magnesium do not give a distinct endpoint.
Manganese	Interferes at more than 5 mg/L manganese.
Nickel	Interferes at 0.5 mg/L nickel. Add 0.5 grams of potassium cyanide after the 8 N Potassium Hydroxide Standard Solution during the test procedure to remove the interference from a maximum of 200 mg/L nickel.
Orthophosphate	Forms calcium phosphate and causes a slow endpoint. If sufficient time is given to let the calcium phosphate dissolve during the titration, the orthophosphate will not interfere with the test.
Polyphosphates	Interfere directly and are included in the test result.
Strontium	Interferes directly and is included in the test result. Most produced and flowback water samples contain strontium at high concentrations. If the strontium concentration is known, it can be subtracted from the calcium test result. Multiply the strontium concentration as mg/L Sr by 1.142 to get mg/L Sr as $CaCO_3$, then subtract this number from the calcium as $CaCO_3$ test result.
Temperature	Samples at 20 °C (68 °F) or colder should be titrated slowly near the endpoint to give sufficient time for the color change.
Zinc	Interferes at 5 mg/L zinc. Add 0.5 grams of potassium cyanide after the 8 N Potassium Hydroxide Standard Solution during the test procedure to remove the interference from a maximum of 100 mg/L zinc.
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary.

Accuracy check

Standard additions method (sample spike)

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

Items to collect:

- Calcium Hardness Voluette Ampule Standard Solution, 10,000-mg/L as $CaCO_3$
- Ampule Breaker
- Pipet, TenSette, 0.1–1.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the sample.
2. Use a TenSette pipet to add 0.1 mL of the standard solution to the titrated sample.
3. Titrate the spiked sample to the endpoint. Record the number of digits on the counter.
4. Add one more 0.1-mL addition of the standard solution to the titrated sample.
5. Titrate the spiked sample to the endpoint. Record the number of digits on the counter.
6. Add one more 0.1-mL addition of the standard solution to the titrated sample.
7. Titrate the spiked sample to the endpoint. Record the number of digits on the counter.
8. Compare the actual result to the correct result. The correct result for this titration is 10 digits of the 0.800 M EDTA Titration Cartridge for each 0.1-mL addition of the standard solution. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

Summary of method

Potassium hydroxide is added to the sample to adjust the pH to 12 to 13, which causes a magnesium hydroxide precipitate to form. CalVer 2 Calcium Indicator is then added, which reacts with calcium to give a red color. The EDTA titrant is added, which reacts with all the free calcium, barium (as long as both strontium and calcium are present) and strontium in the sample. After the EDTA has reacted with all of the free calcium ions, the EDTA removes the calcium from the indicator. The indicator color then changes from red to blue.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Calcium Hardness Reagent Set, HR, includes:	—	each	2447500
CalVer 2 Calcium Indicator Powder Pillows	1	100/pkg	85299
Potassium Hydroxide Standard Solution, 8 N	1–2 mL	100 mL MDB	28232H
EDTA titration cartridge, 0.800 M	varies	each	1439901
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity/test	Unit	Item no.
Graduated cylinders—Select one or more for the sample volume:			
Cylinder, graduated, 5 mL	1	each	50837
Cylinder, graduated, 10 mL	1	each	50838
Cylinder, graduated, 25 mL	1	each	50840
Cylinder, graduated, 50 mL	1	each	50841
Cylinder, graduated, 100 mL	1	each	50842
Digital Titrator	1	each	1690001
Delivery tube for Digital Titrator, J-hook tip	1	5/pkg	1720500
Flask, Erlenmeyer, 250 mL	1	each	50546
Pipet, TenSette, 0.1–1.0 mL	1	each	1970001
Pipet tips, for TenSette Pipet, 0.1–1.0 mL	1	50/pkg	2185696

Recommended standards

Description	Unit	Item no.
Calcium Hardness Standard Solution, 10,000-mg/L as $CaCO_3$, 10-mL Voluette ampule	16/pkg	218710
Hardness Quality Control Standard, high range	500 mL	2833349

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette Ampules	each	2196800
CalVer® 2 Calcium Indicator Powder	113 g	28114H
CDTA Magnesium Salt Powder Pillow	100/pkg	1408099
Delivery tube for Digital Titrator, 90-degree bend for use with TitraStir Titration Stand	5/pkg	4157800

Optional reagents and apparatus (continued)

Description	Unit	Item no.
Magnesium Standard Solution, 10 g/L as $CaCO_3$	29 mL	102233
Nitric Acid, concentrated	500 mL	15249
Nitric Acid Solution, 1:1	500 mL	254049
Pipet filler, safety bulb	each	1465100
Pipet, volumetric, Class A, 10 mL	each	1451538
Pipet, volumetric Class A, 20 mL	each	1451520
Pipet, volumetric, Class A, 25 mL	each	1451540
Potassium Cyanide, ACS	100 g	76714
Potassium Hydroxide, 8 N	500 mL	28249
Sampling bottle with cap, low density polyethylene, 500 mL	12/pkg	2087079
Sampling bottle, with cap, low density polyethylene, 250 mL	12/pkg	2087076
Spoon, measuring, 0.1 g	each	51100
Stir bar, octagonal	each	2095352
TitraStir Titration Stand, 115 VAC	each	1940000
TitraStir Titration Stand, 230 VAC	each	1940010

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11/2019, Edition 3

Hydrazine

DOC316.53.01046

p-Dimethylaminobenzaldehyde Method[1]

Method 8141

4 to 600 µg/L N_2H_4 (spectrophotometers)

Reagent Solution

10 to 500 µg/L N_2H_4 (colorimeters)

Scope and application: For boiler water/feedwater.

[1] Adapted from ASTM Manual of Industrial Water, D1385-78, 376 (1979).

Test preparation

Instrument-specific information

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

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

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR6000 DR3800 DR2800 DR2700 DR1900	The fill line is to the right.	2495402 
DR5000 DR3900	The fill line is toward the user.	
DR900	The orientation mark is toward the user.	2401906 

Before starting

Analyze the samples immediately. The samples cannot be preserved for later analysis.
Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
The sample temperature must be between 21 ± 4 °C (70 ± 7 °F) for accurate results.
The reagent that is used in this test is corrosive. Use protection for eyes and skin and be prepared to flush any spills with running water.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

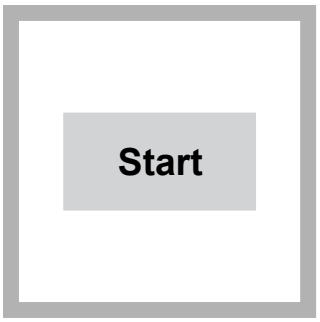
Description	Quantity
HydraVer 2 Reagent Solution	1 mL
Deionized water	10 mL
Graduated cylinder, 25-mL	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

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

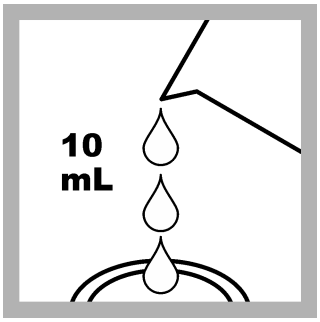
Sample collection

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Collect samples in clean glass or plastic bottles with tight-fitting caps. Completely fill the bottle and immediately tighten the cap.
- Prevent agitation of the sample and exposure to air.

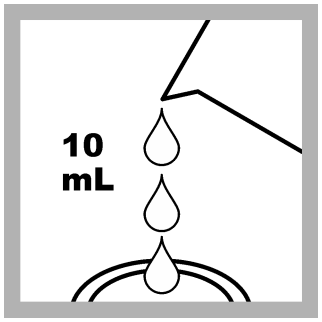
Test procedure



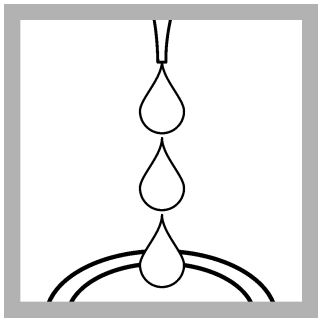
1. Start program **231 Hydrazine**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



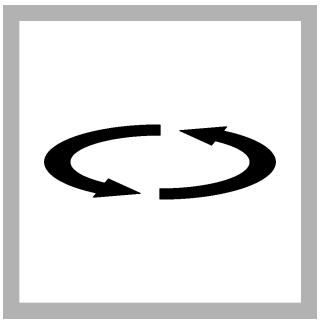
2. Prepare the blank: Use a graduated cylinder to pour 10 mL of deionized water into a sample cell.



3. Prepare the sample: Use a graduated cylinder to pour 10 mL of sample into a second sample cell.



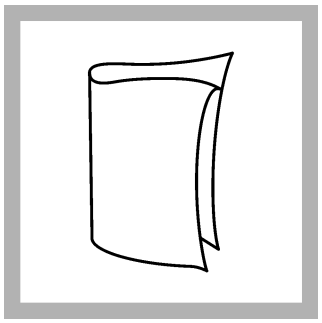
4. Add 0.5 mL of HydraVer 2 Hydrazine Reagent to each sample cell.
A yellow color shows if hydrazine is present in the sample. The blank may also show a light yellow color.



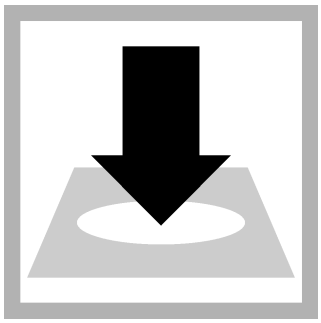
5. Swirl to mix.

6. Start the instrument timer. A 12-minute reaction time starts.

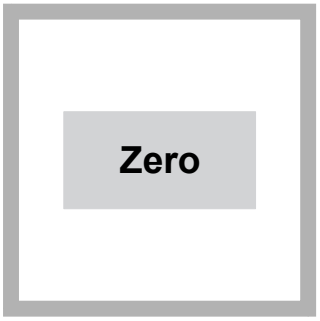
Complete the blank zero steps and insert the prepared sample during the reaction period.



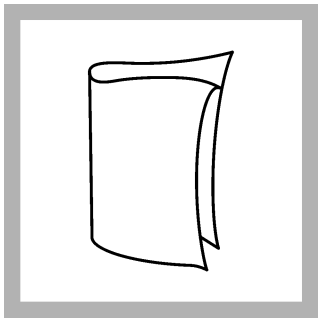
7. Clean the blank sample cell.



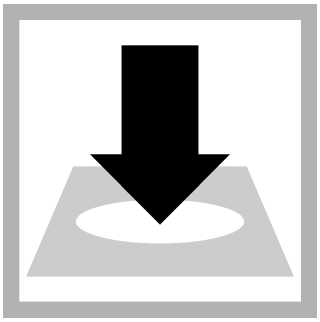
8. Insert the blank into the cell holder.



9. Push **ZERO**. The display shows 0 µg/L N_2H_4.



10. Clean the prepared sample cell.



11. Insert the prepared sample into the cell holder.

12. Immediately after the timer expires, push **READ**. Results show in µg/L N_2H_4.

Interferences

Interfering substance	Interference level
Ammonia	No interference up to 10 mg/L. May cause a positive interference of up to 20% at 20 mg/L.
Highly colored or turbid samples	Prepare a 1:1 mixture of deionized water and household bleach. Add one drop of this mixture to 25 mL of sample in a graduated mixing cylinder and invert to mix. This will destroy any hydrazine in the sample. Use this solution, instead of deionized water, to prepare the blank in the test procedure.
Morpholine	No interference up to 10 mg/L.

Accuracy check

Standard solution method

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

Items to collect:

- Hydrazine sulfate, reagent grade
- 1-L volumetric flask, Class A (2)
- 10-mL volumetric pipet, Class A and pipet filler
- Deionized water, oxygen-free

1. Prepare a 25-mg/L hydrazine stock solution as follows:
   a. Add 0.1016 g of hydrazine sulfate into a 1-L volumetric flask.
   b. Dilute to the mark with oxygen-free deionized water (heat water to boiling and cool). Mix well. Prepare the stock solution each day.
2. Prepare a 0.25-mg/L (250-µg/L) hydrazine standard solution as follows:
   a. Use a pipet to add 10.00 mL of the 25-mg/L hydrazine stock solution into a 1-L volumetric flask.
   b. Dilute to the mark with oxygen-free deionized water. Mix well. Prepare the standard solution immediately before use.
3. Use the test procedure to measure the concentration of the prepared standard solution.
4. Compare the expected result to the actual result.

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

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
231	250 µg/L N_2H_4	247–253 µg/L N_2H_4	4 µg/L N_2H_4

Summary of method

Hydrazine in the sample reacts with the p-dimethylaminobenzaldehyde from the HydraVer 2 Reagent to form a yellow color which is proportional to the hydrazine concentration. The measurement wavelength is 455 nm for spectrophotometers or 420 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Water, deionized	varies	4 L	27256
HydraVer 2 Hydrazine Reagent[1]	1 mL	100 mL MDB	179032

Required apparatus

Description	Quantity/test	Unit	Item no.
Cylinder, graduated, 25 mL	1	each	50840

Recommended standards

Description	Unit	Item no.
Hydrazine Sulfate, ACS	100 g	74226

Optional reagents and apparatus

Description	Unit	Item no.
Mixing cylinder, graduated, 25 mL	each	189640
Flask, volumetric, Class A, 1000 mL glass	each	1457453
Pipet, volumetric, Class A, 10 mL	each	1451538
Pipet filler, safety bulb	each	1465100

[1] HydraVer is a registered trademark of Hach Company.

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08/2019, Edition 10

Iron, Ferrous

DOC316.53.01049

1,10-Phenanthroline Method[1]

Method 8146

0.02 to 3.00 mg/L Fe^{2+}

Powder Pillows

Scope and application: For water, wastewater, seawater, brine solutions, produced waters and hydraulic fracturing waters.

[1] Adapted from Standard Methods for the Examination of Water and Wastewater, 15th ed. 201 (1980).

Test preparation

Instrument-specific information

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

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

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR6000 DR3800 DR2800 DR2700 DR1900	The fill line is to the right.	2495402 
DR5000 DR3900	The fill line is toward the user.	
DR900	The orientation mark is toward the user.	2401906 

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
For the best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to determine the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

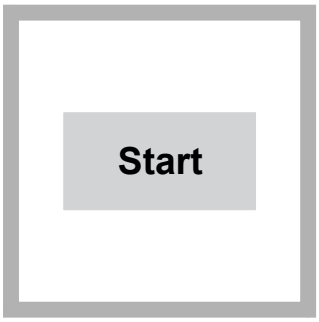
Description	Quantity
Ferrous Iron Reagent Powder Pillows, 25 mL	1
Sample cells. (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

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

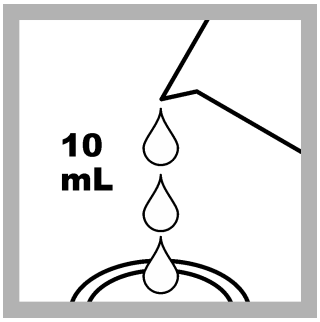
Sample collection

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Collect samples in clean glass or plastic bottles with tight-fitting caps. Completely fill the bottle and immediately tighten the cap.
- Prevent agitation of the sample and exposure to air.

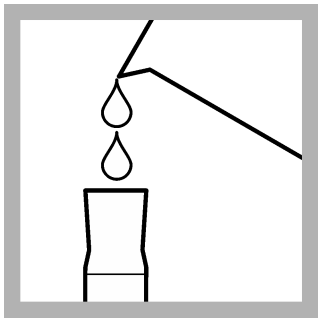
Test procedure



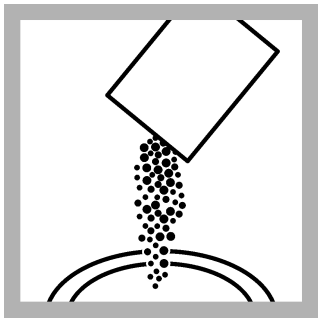
1. Start program **255 Iron, Ferrous**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



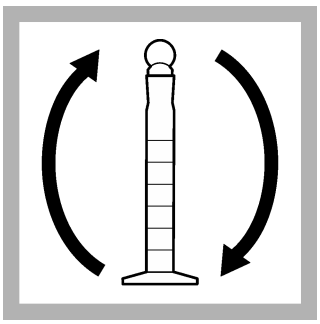
2. Prepare the blank: Fill the sample cell with 10 mL of sample.



3. Prepare the sample: Fill a mixing cylinder to the 25-mL line with sample.

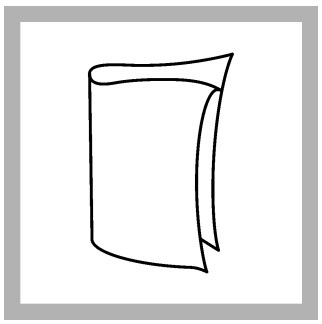


4. Add the contents of one Ferrous Iron Reagent Powder Pillow to the mixing cylinder.
An orange color shows if ferrous iron is present in the sample.

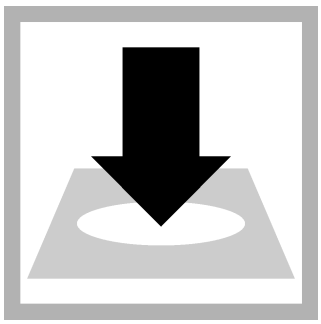


5. Put the stopper on the mixing cylinder. Invert the mixing cylinder several times to mix.
Undissolved powder does not affect accuracy.

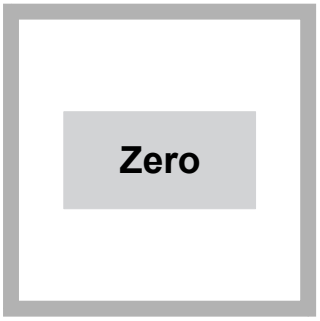
6. Start the instrument timer. A 3-minute reaction time starts.



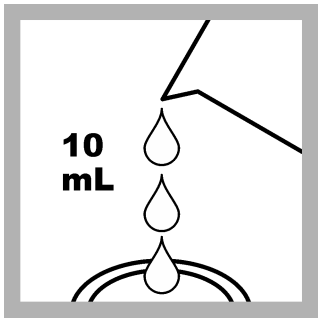
7. When the timer expires, clean the blank sample cell.



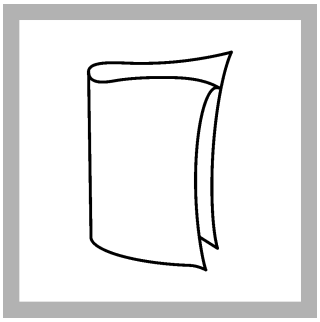
8. Insert the blank into the cell holder.



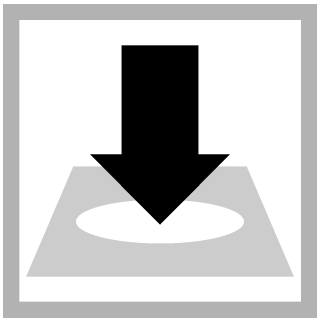
9. Push **ZERO**. The display shows 0.00 mg/L Fe^{2+}.



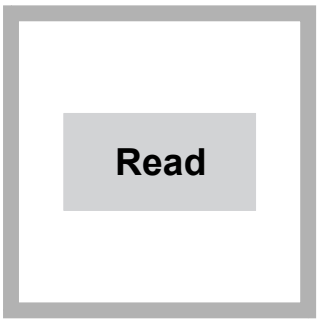
10. Fill a second sample cell with 10 mL of the reacted prepared sample.



11. Clean the prepared sample cell.



12. Insert the prepared sample into the cell holder.



13. Push **READ**. Results show in mg/L Fe^{2+}.

Accuracy check

Standard solution method

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

Items to collect:

- Ferrous Ammonium Sulfate, hexahydrate
- 1-L volumetric flask, Class A
- 100-mL volumetric flask, Class A
- 2-mL volumetric pipet, Class A and pipet filler
- Deionized water

1. Prepare a 100-mg/L Fe^{2+} ferrous iron stock solution as follows:
   a. Add 0.7022 g of ferrous ammonium sulfate, hexahydrate into a 1-L volumetric flask.
   b. Dilute to the mark with deionized water. Mix well.
2. Prepare a 2-mg/L ferrous iron standard solution as follows:
   a. Use a pipet to add 2.00 mL of the 100-mg/L Fe^{2+} ferrous iron stock solution into a 100-mL volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare the standard solution immediately before use.
3. Use the test procedure to measure the concentration of the prepared standard solution.
4. Compare the expected result to the actual result.

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

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
255	2.00 mg/L Fe^{2+}	1.99–2.01 mg/L Fe^{2+}	0.021 mg/L Fe^{2+}

Summary of method

The 1,10-phenanthroline indicator in the Ferrous Iron Reagent reacts with ferrous iron (Fe^{2+}) in the sample to form an orange color in proportion to the iron concentration. Ferric iron (Fe^{3+}) does not react. The ferric iron concentration can be determined by subtracting the ferrous iron concentration from the results of a total iron test. The measurement wavelength is 510 nm for spectrophotometers or 520 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Ferrous Iron Reagent Powder Pillow, 25 mL	1	100/pkg	103769

Recommended standards and apparatus

Description	Unit	Item no.
Balance, analytical, 80 g x 0.1 mg 100–240 VAC	each	2936701
Ferrous Ammonium Sulfate, hexahydrate, ACS	113 g	1125614
Flask, volumetric, Class A, 1000 mL glass	each	1457453
Pipet filler, safety bulb	each	1465100
Pipet, volumetric, Class A, 1.00 mL	each	1451535
Water, deionized	4 L	27256
Wipes, disposable	280/pkg	2097000

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08/2019, Edition 11

Iron, Total

DOC316.53.01314

FerroVer® Method[1]

Method 10249

0.1 to 3.0, 1.0 to 30.0 and 10.0 to 300.0 mg/L Fe

Powder Pillows

Scope and application: For brine solutions, produced waters and hydraulic fracturing waters; digestion is required for total iron determinations.[2]

[1] USEPA approved for reporting wastewater analysis, Federal Register, June 27, 1980; 45 (126:43459).
[2] Adapted from Standard Methods for the Examination of Water and Wastewater.

Test preparation

Instrument-specific information

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

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

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR6000 DR3800 DR2800 DR2700 DR1900	The fill line is to the right.	2495402 
DR5000 DR3900	The fill line is toward the user.	
DR900	The orientation mark is toward the user.	2401906 

Before starting

Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
To make sure that all forms of the metal are measured, digest the sample with heat and acid. Use the mild or vigorous digestion. Refer to the *Water Analysis Guide* for more information.
For the best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to determine the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

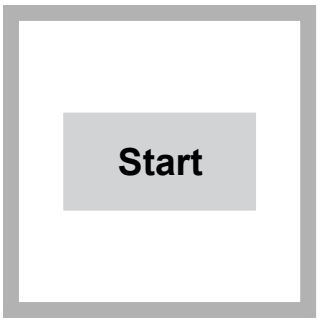
Description	Quantity
FerroVer® Iron Reagent Powder Pillow, 10-mL	1
EDTA solution, 1M	2 drops
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	1

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

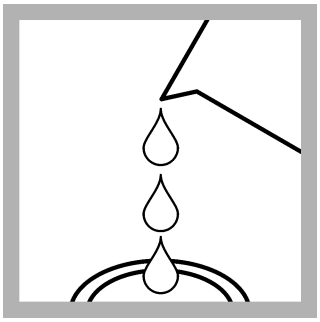
Sample collection and storage

- Collect samples in clean glass or plastic bottles that have been cleaned with 6 N (1:1) hydrochloric acid and rinsed with deionized water.
- To preserve samples for later analysis, adjust the sample pH to less than 2 with concentrated nitric acid (about 2 mL per liter). No acid addition is necessary if the sample is tested immediately.
- To measure only dissolved iron, filter the sample immediately after collection and before acidification.
- Keep the preserved samples at room temperature for a maximum of 6 months.
- Before analysis, adjust the pH to 3–5 with 5.0 N sodium hydroxide standard solution.
- Correct the test result for the dilution caused by the volume additions.

Test procedure



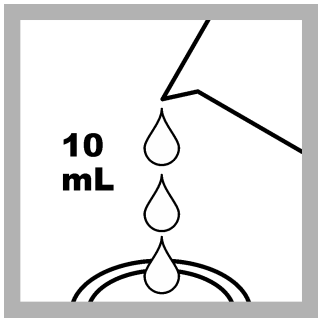
1. Start program **265 Iron, FerroVer**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



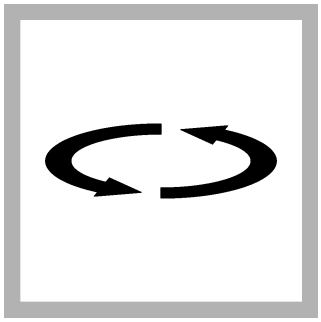
2. Fill a clean sample cell with sample:

- Use 10 mL of sample for the 0.02 to 3.0 mg/L range.
- Use 1.0 mL of sample for the 0.2 to 30.0 mg/L range with a dilution factor of 10.
- Use 0.1 mL of sample for the 2.0 to 300.0 range with a dilution factor of 100.

Note: *Refer to* Set the dilution factor *on page 4.*

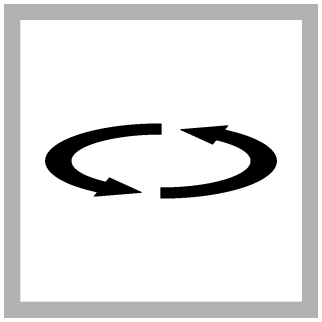


3. If the sample volume is less than 10 mL, add deionized water to the 10-mL line.

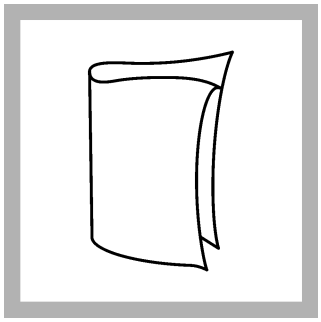


4. Swirl to mix.

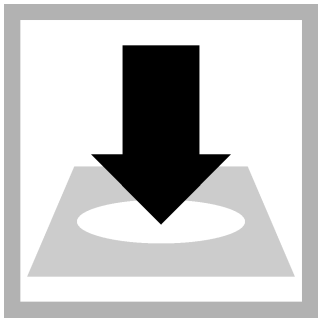
5. Add 2 drops of 1 M EDTA Solution to the sample.



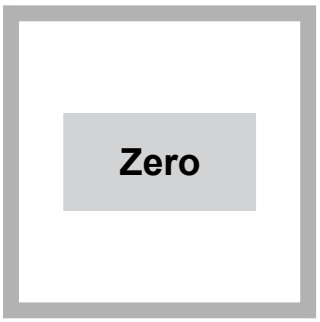
6. Swirl to mix.



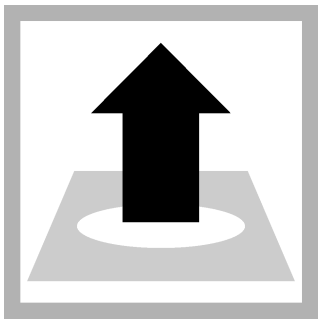
7. Clean the sample cell.



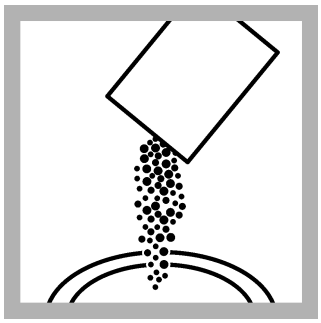
8. Insert the sample cell into the cell holder.



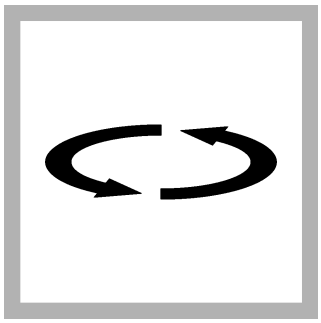
9. Push **ZERO**. The display shows 0.0 mg/L Fe.



10. Remove the sample cell from the cell holder.



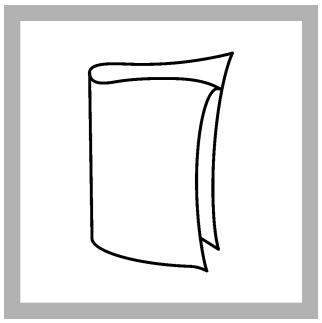
11. Add the contents of one FerroVer Iron Reagent Powder Pillow to the sample cell.



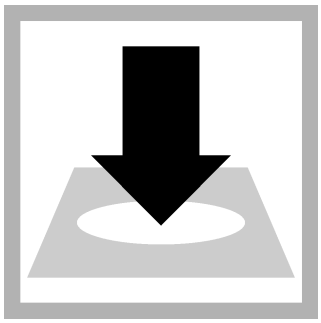
12. Swirl to mix. Accuracy is not affected by undissolved powder.

13. Start the instrument timer. A 3-minute reaction time starts.

If iron is present in the sample, an orange color will show.



14. When the timer expires, clean the sample cell.



15. Insert the sample cell into the cell holder.

16. Push **READ**. Results show in mg/L Fe.

Interferences

Interfering substance	Interference level
Barium, Ba^{2+}	The dilution of samples lowers most barium concentrations below interference levels. No effects are seen on analyzed samples that contain less than 50 mg/L of Ba. No effects are seen when a 1.0 or 0.1 mL sample volume is used in the test procedure. A turbidity may show at higher levels. Use 5 drops of EDTA Solution in the test procedure and allow the sample to react for 5 minutes.
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.

Interfering substance	Interference level
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.
Magnesium	No effect at 100,000 mg/L as $CaCO_3$.
Molybdate molybdenum	No effect at 50 mg/L as Mo.
High sulfide levels, S^{2-}	Pretreat the sample in a fume hood or in an area with sufficient airflow before analysis: **1.** Add 5 mL of 6.0 N (1:1) hydrochloric acid solution to 100 mL of sample in a 250-mL Erlenmeyer flask. **2.** Boil for 20 minutes. **3.** Let the solution cool to room temperature. **4.** Adjust the pH to 3–5 with 5 N sodium hydroxide solution. **5.** Add deionized water until the volume is 100 mL. **6.** Use the treated sample in the test procedure.
Strontium, Sr^{2+}	Strontium by itself does not interfere. Strontium in combination with Barium will cause a precipitate to form. The dilution of samples lowers most strontium concentrations below interference levels. No effects are seen on analyzed samples that contain less than 50 mg/L of combined Ba and Sr. No effects are seen when a 1.0 or 0.1 mL sample volume is used in the test procedure. A turbidity may show at higher levels. Use 5 drops of EDTA Solution in the test procedure and allow the sample to react for 5 minutes.
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary. Adjust the sample pH to 3–5 before the test is started. Correct the test result for the dilution from the volume addition.

Set the dilution factor

Instruments that have a dilution factor option can include the dilution factor in the result and show the concentration of the original, undiluted sample. For example, if the sample is diluted by a factor of 10, the instrument multiplies the result by 10 and shows the calculated result in the instrument display.

1. Select **Options>More>Dilution** factor from the instrument menu.

   Note: *DR1900: Select* ***Options>Advanced Options>Dilution Factors>On****.*

   Note: *Colorimeters include a dilution factor when the chemical form is set. Go to* ***Options>Advanced Options>Chemical Form*** *and select LR, MR or HR.*
2. Enter the dilution factor:
   - 1 mL sample diluted to 10 mL: dilution factor is 10.
   - 0.1 mL sample diluted to 10 mL: dilution factor is 100.
3. Push **OK** to confirm. Push **OK** again.
4. Push **RETURN** to go back to the measurement screen.

Accuracy check

Standard additions method (sample spike)

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

Items to collect:

- Iron Voluette® Ampule Standard, 25 mg/L
- Ampule breaker
- Pipet, TenSette®, 0.1–1.0 mL and tips

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 10-mL portions of fresh sample. Mix well.
6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Standard solution method

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

Items to collect:

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

1. Prepare a 2.00 mg/L iron standard solution as follows:
   a. Use a pipet to add 2.00 mL of 100 mg/L iron standard solution into the volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
2. Use the test procedure to measure the concentration of the prepared standard solution.
3. Compare the expected result to the actual result.

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

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
265	2.00 mg/L Fe	1.99–2.01 mg/L Fe	0.021 mg/L Fe

Summary of method

FerroVer Iron Reagent converts all soluble iron and most insoluble forms of iron in the sample to soluble ferrous iron. The ferrous iron reacts with the 1-10 phenanthroline indicator in the reagent to form an orange color in proportion to the iron concentration. The measurement wavelength is 510 nm for spectrophotometers or 520 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
FerroVer Iron Reagent Powder Pillow[1], 10 mL	1	100/pkg	2105769
EDTA Solution, 1 M	2 drops	50 mL SCDB	2241926

Recommended standards

Description	Unit	Item no.
Iron Standard Solution, 100-mg/L Fe	100 mL	1417542
Iron Standard Solution, 10-mL Voluette Ampule, 25-mg/L Fe	16/pkg	1425310
Water, deionized	4 L	27256
Pipet, TenSette, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette Pipet, 0.1–1.0 mL	1000/pkg	2185628
Flask, volumetric, Class A, 100 mL, glass	each	1457442
Pipet, volumetric, Class A, 2 mL	each	1451536
Pipet filler, safety bulb	each	1465100

Optional reagents and apparatus

Description	Unit	Item no.
Hydrochloric Acid, concentrated	500 mL	13449
Nitric Acid, concentrated	500 mL	15249
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	245032
Filter, glass fiber membrane, 1.5 micron, 47 mm	100/pkg	253000
Filter membrane filter holder, 47 mm	each	234000
RoVer Rust Remover	454 g	30001
Spoon, measuring, 0.1 g	each	51100

[1] FerroVer is a registered trademark of Hach Company

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07/2014, Edition 10

Oil and Grease

DOC316.53.01187

USEPA[1] Hexane Extractable Gravimetric Method — Method 10056

15 to 3000 mg/L HEM and SGT-HEM

Scope and application: For water, wastewater, brine solutions, produced waters and hydraulic fracturing waters.

[1] This procedure is equivalent to USEPA Method 1664. Adapted from *Standard Methods for the Examination of Water and Wastewater*, Section 5520B.

Test preparation

Before starting

Determine a blank value (350 mL of distilled or deionized water) with each new lot of reagents. If the blank result is greater than 5 mg, correct the source of error or remove interferences before analysis.
Use the equivalent quantity of acid to determine the blank and all samples from each sampling source.
Let the sample temperature increase to room temperature before analysis.
Do not use plastic tubing to pour the solvent between containers.
Do not rinse the collecting vessel with sample before analysis.
Anhydrous sodium sulfate is used to remove traces of water from the hexane extraction layer. Dry the sodium sulfate at 200–250 °C for 24 hours for best performance.
Spilled reagent can have a negative effect on the test accuracy. Spilled reagent is hazardous to skin and other materials.
To determine both, the HEM and the SGT-HEM, clean and dry two distillation flasks (one for each procedure) before analysis. • HEM = n-hexane extractable materials • SGT-HEM = Silica Gel Treated n-hexane extractable materials
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Description	Quantity
Hydrochloric Acid Solution, 6.0 N (1:1)	4 mL
Hexane, ACS grade	100–200 mL
pH paper	varies
Silica gel with indicator (for desiccator)	varies
Silica gel, 100–200 mesh	1–30 g
Sodium sulfate, anhydrous	10 g
Adapter, vacuum connector/gas inlet, 28/15	1
Aspirator, vacuum pump	1
Balance, analytical, 115 VAC 60 Hz	1
Boiling chips, silicon carbide	3–10
Clamp, 3-prong	2
Clamp holder	2

Items to collect (continued)

Description	Quantity
Clamp, pinch type, No. 28, F/Glass Joints	2
Condenser, reflux, with ground glass joints, 28/15	1
Cylinder, graduated, 500-mL	1
Cylinder, graduated, 50 mL	1
Desiccator	1
Desiccator plate	1
Filter funnel, 65-mm, short stem	1
Filter paper, 12.5-cm, folded, pore size 8 to 12 µm	1
Flask, Erlenmeyer, 125-mL	1
Flask, Erlenmeyer, 125-mL, with ground glass joint 28/15	2
Funnel, separatory, 500 mL	1
Marker, laboratory	1
Oven, drying, 120 VAC, 50 Hz	1
Pipet filler, safety bulb	1
Pipet, serological, 5 mL	1
Ring support, 4-inch	1
Rod, glass	1
Steam bath, 8-inch, 5-ring	1
Hot plate, 7 inch x 7 inch, digital, 120 VAC	1
Stir bar, 22.2 x 7.9 mm	1
Support, ring stand, 5-inch x 8-inch base	2
Tongs, crucible, 9-inch	1
Tube, connecting, J-shaped, with ground glass joint, 28/15	1
Tubing, rubber, 7.9 mm x 2.4 mm	1

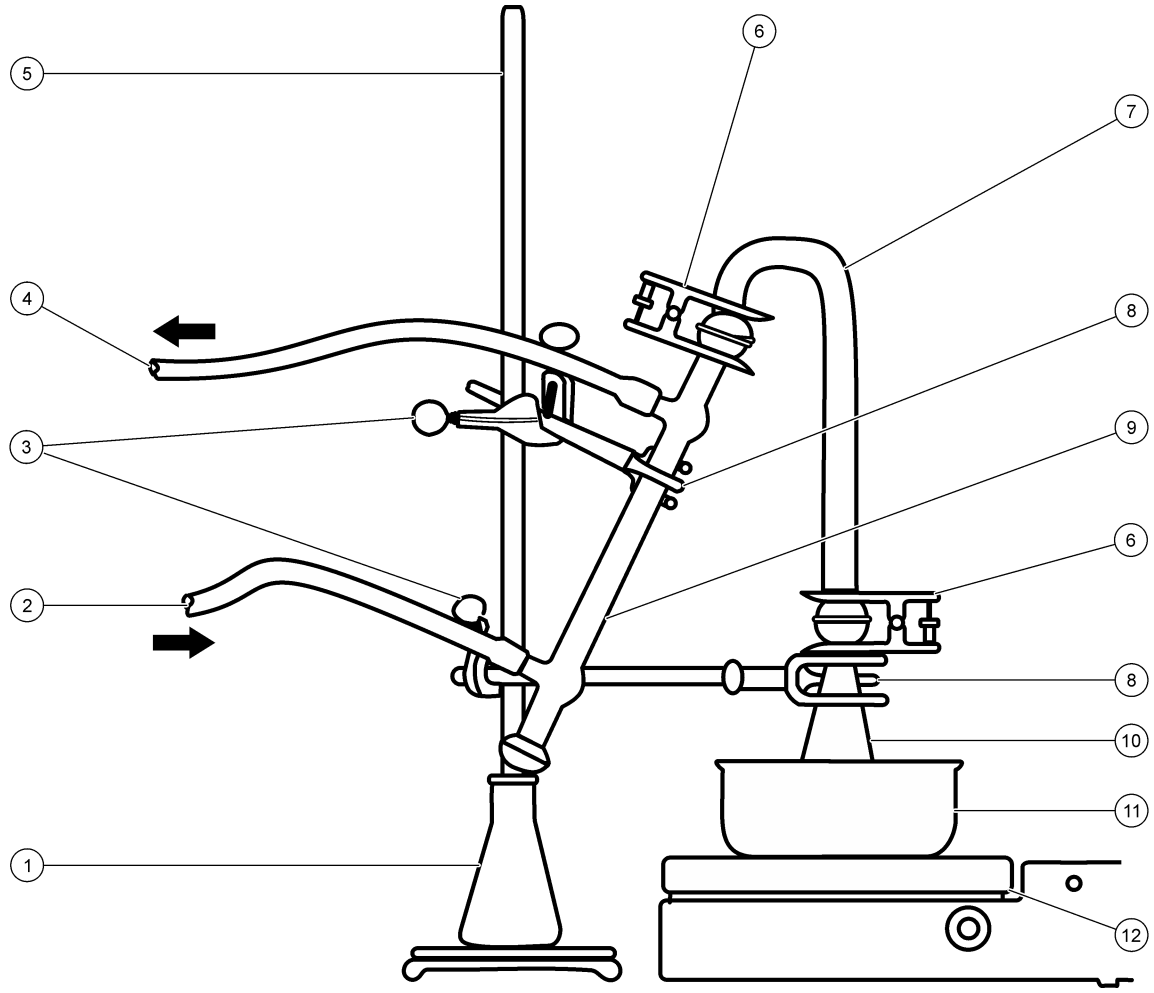
Refer to Consumables and replacement items on page 13 for order information.

Assemble the distillation apparatus

The distillation apparatus is necessary to determine HEM. Refer to Figure 1.

Note: *If only SGT-HEM is determined and the HEM is known, distillation is not necessary.*

Figure 1 Distillation apparatus assembly



1 Receiving flask	**5** Support stand and rod assembly	**9** Condenser
2 Water in	**6** Pinch clamp	**10** Distillation flask
3 Clamp holders	**7** J-Shaped connector	**11** Water bath
4 Water out	**8** Clamp, 3-Prong	**12** Hot plate

Sample collection and storage

- Do not rinse the bottle or the separatory funnel with sample.
- Collect samples in wide-mouth glass bottles or directly in the separatory funnel for immediate analysis.
- If samples are collected directly in the separatory funnel determine the sample volume as follows.

  1. Measure 350 mL of water with a graduated cylinder.
  2. Pour the water into the separatory funnel.
  3. Use a laboratory pen to put a mark on the 350-mL level.
  4. Discard the water. Fill with sample to this mark.
- To preserve samples for later analysis, add 6 mL of 1:1 Hydrochloric Acid Solution for each liter or quart of sample. Use a glass rod and a pH paper to measure the sample pH after the acid addition.

  1. Put the glass rod into the sample momentarily.
  2. Let some drops of sample touch the pH paper. Do not put the pH paper into the sample.
  3. Rinse the glass rod with a small quantity of n-hexane back into the sample container to remove all grease or oil bonded to the rod.
- If necessary add more acid to adjust pH below 2.
- Keep the preserved samples at or below 6 °C (43 °F) for a maximum of 28 days.
- If prompt analysis is not possible, keep the sample at or below 6 °C (43 °F) for a maximum of 28 days.
- Let the sample temperature increase to room temperature before analysis.

Prepare analysis glassware

Before analysis, it is necessary to carefully clean and dry all of the glassware and boiling chips. Always use tongs or an anti-lint wipe to prevent contamination.

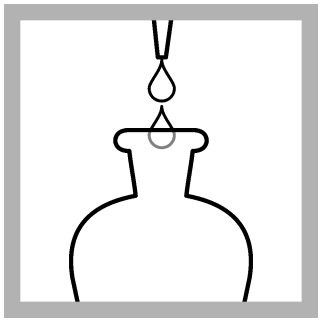
1. Clean the chips and distillation flask with hot water and detergent.
2. Rinse with distilled water. Then, rinse with acetone or n-hexane.
3. Put the cleaned flask and boiling chips in a drying oven at 105–115 °C (220–240 °F) for 2 hours.
4. Let the temperature of the flask and boiling chips decrease to room temperature in a desiccator for at least 30 minutes.
5. Keep the flask and boiling chips in the desiccator for the next use.

If the same flasks are used again and again, record the weight of the flasks (after each is dried in the oven with no boiling chips). Do not do the drying step, if the weight of a dried flask is the same as the weight of the flask after the acetone or n-hexane rinse. The weight of each boiling chip is not the same. Make sure to add the weight of the boiling chips to the flask weight.

Test procedure

1. Collect 350 mL of sample in a clean 500-mL separatory funnel.

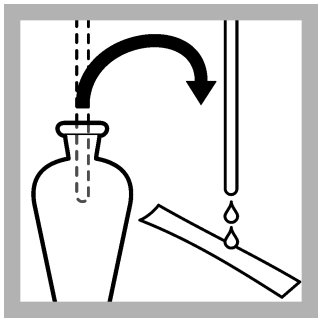
If the sample is not collected in the separatory funnel, set the empty container and lid aside for use in step 5.



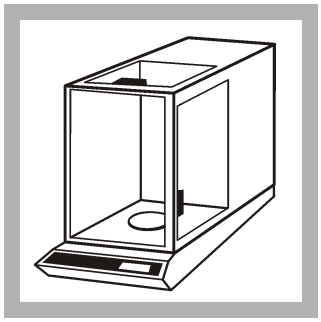
2. Use a pipet and a pipet filler to add 4 mL of 1:1 Hydrochloric Acid solution to the separatory funnel. Mix well.

The pH must be 2 or less to hydrolyze oils and grease and prevent a sodium sulfate interference.

Note: *Do not do the acid addition if the sample was preserved with 1:1 Hydrochloric Acid solution.*



3. Use a glass rod and a pH paper to measure the sample pH after the acid addition. Refer to Sample collection and storage on page 4.

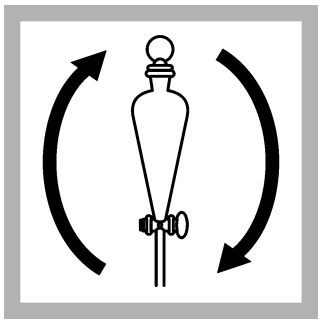


4. Clean and dry a 125-mL distillation flask that contains 3–5 boiling chips. Use an analytical balance to weigh the flask to the nearest 0.1 mg. Record the weight of the flask.

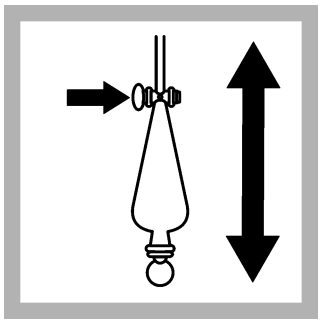
5. Add 20 mL of n-hexane to the separatory funnel.

If the sample was collected in a separate container, rinse the collecting vessel which contained the sample with 20 mL of n-hexane. If this step is for water layer extraction, rinse the volumetric flask that contained the water layer with 20 mL of n-hexane (refer to step 14).

Add the 20-mL n-hexane rinse to the separatory funnel.

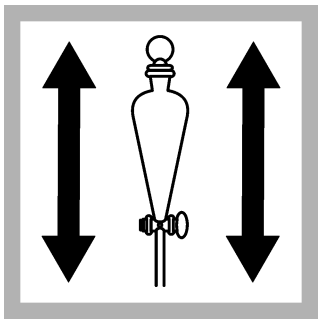


6. Put the stopper and invert the separatory funnel.

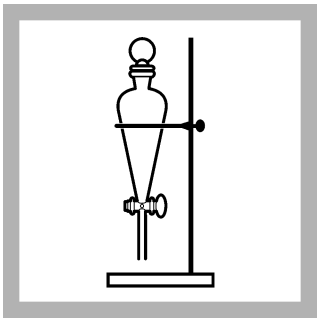


7. Release the gases through the stopcock.

To release gases from the separatory funnel, invert it and shake it once very hard. Make sure to hold the stopper. Under a hood, point the delivery tube in a safe direction. Slowly open the stopcock to release all of the gas. Close the stopcock. Do this procedure until the release of gas is not heard.



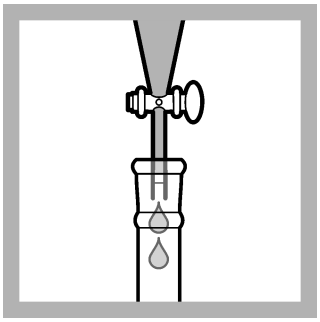
8. Vigorously shake the separatory funnel for 2 minutes.



9. Put the separatory funnel in the stand. Do not move the separatory funnel or the stand for a minimum of 10 minutes to let the separation of the lower water layer and the upper solvent layer.

If the solvent layer is brown, the sample can have oil with color on it.

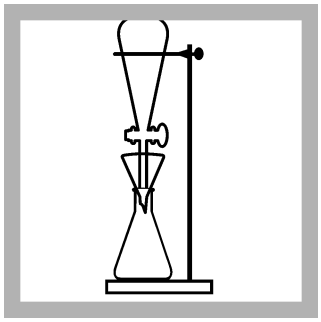
If this step is done again (for a third time), and the water layer is cloudy, do not move the separatory funnel for 20 minutes to make sure of the separation of the water and solvent layers.



10. Slowly drain the lower water layer from the separatory funnel into the initial sample container or a 500-mL volumetric flask. The drain must take approximately 3–4 minutes. Keep the water layer for use in step 13.

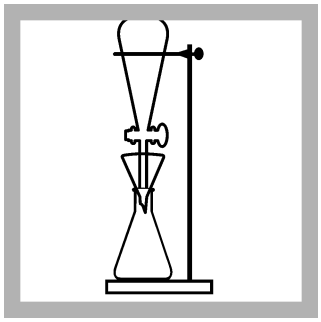
To make sure that water is not used in step 12, let some drops of solvent layer drain into the water layer until the solvent layer is visible on top of the water.

If the water layer drains too quickly, there will be too much water in the solvent layer. This causes sodium sulfate and water interference.



11. Set up the filtering funnel. Put the glass funnel in the neck of the distillation flask. Put a folded 12.5 cm filter paper in the funnel. Add 10 g of anhydrous sodium sulfate to the filter paper. Rinse the sodium sulfate with a small amount of n-hexane. Discard the n-hexane correctly.

For the second and third extractions, use the same filter, funnel and sodium sulfate. Between extractions, remove the large, hard sodium sulfate chunks to decrease sodium sulfate contamination.

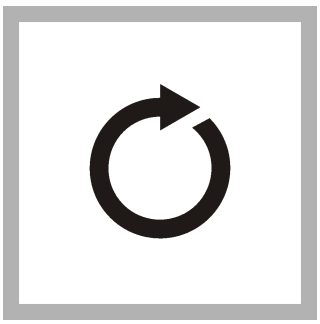


12. Drip-drain the solvent layer into the pre-weighed boiling flask through a funnel that contains filter paper and 10-g anhydrous sodium sulfate. Carefully stir the sodium sulfate with a glass rod while the solvent layer drains. Be careful and do not damage the filter paper.

Any spillage will cause inaccurate results. To reduce spillage, use the glass rod to route the sample solution into the filter.

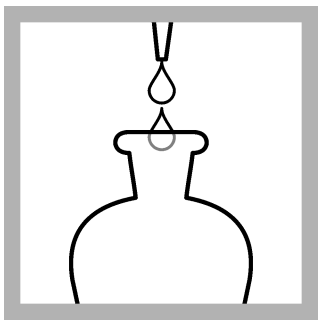
13. Return the water layer to the separatory funnel. Use the same glass funnel for the second and third extraction.

To reduce spillage, use a second funnel to pour the water layer into the separatory funnel.

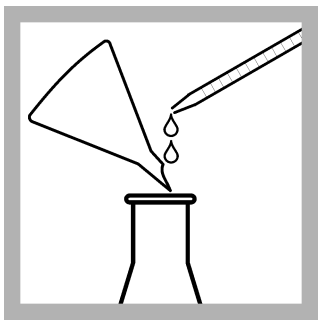


14. Do steps 5 through 13 again two more times. After the third extraction, discard the water layer.

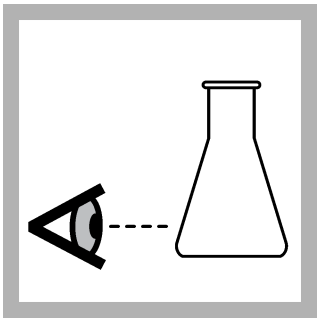
Make sure to correctly discard the water layer. The water layer can have small amounts of acetone and/or n-hexane on it.



15. Rinse the separatory funnel with three different 5-mL aliquots of fresh n-hexane to remove oil film that stayed on the funnel walls. Drain each aliquot through the funnel that contains the sodium sulfate into the distillation flask.

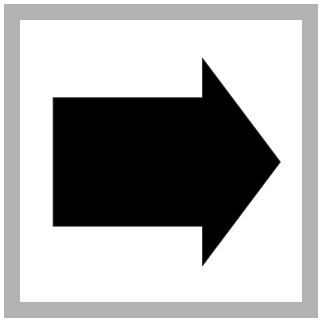


16. Rinse the tip of the glass funnel with 5 mL of n-hexane while removing it from the distillation flask.



17. Examine the distillation flask for sodium sulfate contamination.

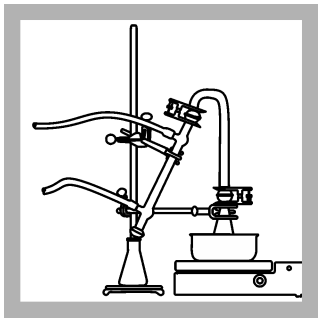
Sodium sulfate contamination will show as cubic crystals at the bottom of the distillation flask. If there is sodium sulfate contamination, filter the solvent layer again through filter paper without sodium sulfate. It is necessary to clean, dry and weigh the boiling flask and boiling chips again. Or make sure to have an additional boiling flask.



18. Continue with step 19 to determine HEM.

If the HEM is known and only the SGT-HEM is analyzed, go to step 26.

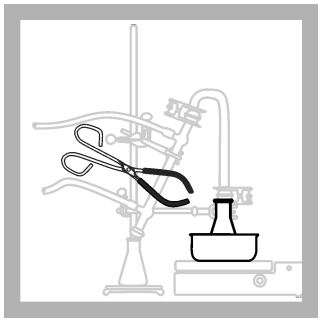
Note: *The HEM value is necessary to determine the quantity of silica gel necessary for the SGT-HEM. For each group of samples from a discharge, determine the HEM before the SGT-HEM.*



19. Use the distillation assembly shown in Figure 1 on page 3 to distill off the n-hexane. Distillation is complete when there are no boiling bubbles or the distillation flask is dry.

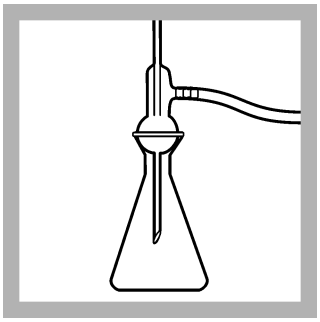
Use a steam bath or a hot plate to keep a water bath at the correct temperature for the distillation. Do not put the flask directly on a hot plate. This will cause low results and is dangerous because n-hexane is volatile.

Evaporation will be faster if the long vertical arm of the connector is wound with insulation (e.g., paper towel, cloth or asbestos insulating tape). The distillation is complete in 30 minutes or less.

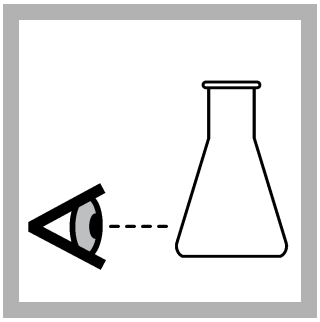


20. Disconnect the condenser/connector portion of the distillation assembly at the pinch clamp. Remove the distillation flask from the heat source with tongs or a lint-free cloth.

The distilled n-hexane is applicable for future HEM extractions, but is not recommended for SGT-HEM because of the possible increase of water content of the solvent.



21. Attach the vacuum connector/gas inlet adapter to remove the remaining solvent vapors from the distillation flask. Apply a vacuum for 1–2 minutes or until all n-hexane solvent vapors are removed.

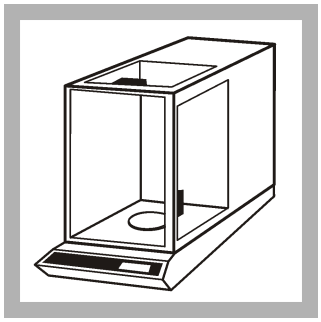


22. Examine the distillation flask for sodium sulfate contamination.

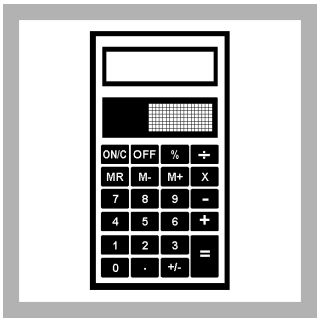
Sodium sulfate contamination will show as cubic crystals at the bottom of the distillation flask. If there is sodium sulfate contamination, dissolve the extract again in n-hexane, filter into another pre-weighed flask and do steps 18–20 again. This is not necessarily true for the “standard” extraction since stearic acid is crystalline below 69 °C (156 °F). If there is sodium sulfate in the standard, big cubical crystals (not the flattened stearic acid crystals) will show. Also, an unusually high yield compared to the expected value will result.

23. Put the flask in a desiccator for 30 minutes (or longer if necessary) until the flask temperature decreases to room temperature.

If the silica gel indicator changes to red, replace the silica gel.



24. Use an analytical balance to weigh the flask to the nearest 0.1 mg. Record this weight. Do not touch the flask it is weighted because fingerprints add weight. Always use a tong or a lint-free wipe to touch the flask. Precise weigh measurement is necessary for accurate results. Multiple weight measurements are recommended. Clean the flask again before each measurement to make sure that all contaminants are removed. Record each weight and use the lowest repeatable value for calculations.



25. Calculate the test results:

[(A – B) ÷ Sample volume] x 1000 = mg/L HEM

Where:

A = Weight (mg) of residue

B = Weight (mg) of flask with boiling chips (step 4)

Example:

A = 92.4659 g

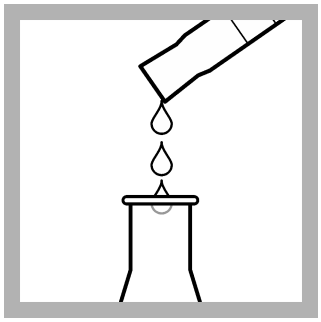
B = 92.4206 g

Sample volume = 0.350 L (350 mL)

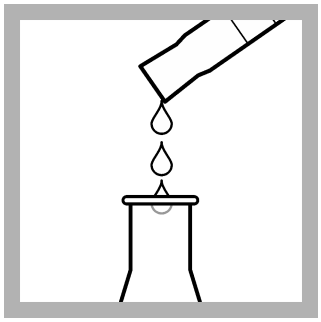
[(92.4659 – 92.4206) ÷ 0.350] × 1000 = 129.4 mg/L HEM

If yield is less than 15 mg/L and additional precision is needed, use a 1-liter sample.

For HEM determination stop here and do not continue the procedure. Continue with next step to determine SGT-HEM.



26. Dissolve the residue again with approximately 85 mL of fresh n-hexane. Heat slightly to make sure that all HEM materials are dissolved.



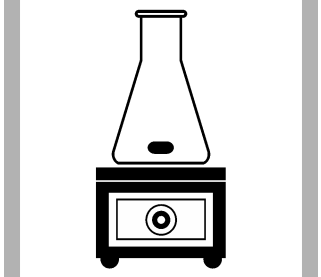
27. If necessary, dilute the dissolved HEM. For a 350-mL water sample, dilution is necessary if the HEM is more than 2850 mg/L (more than 1000 mg/L for a 1-L water sample).

To dilute to a 1000 mg/L sample, pour the dissolved HEM into a 100-mL volumetric flask. Rinse the distillation flask 3–4 times with 2–3 mL of n-hexane. Fill the volumetric flask to volume with n-hexane. Mix well. Use a volumetric pipet to add into a 100-mL beaker the quantity (Va) determined by this equation:
$V_a = 10{,}000 \div W_h$

Where:

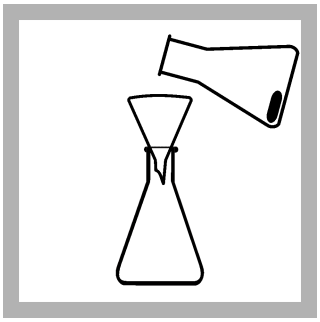
V_a = Volume of aliquot to be withdrawn (mL) to get 1000 mg of HEM

W_h = Weight of HEM (mg) (A – B) x 1000 in step 24 (mg). Dilute to about 100 mL with n-hexane.

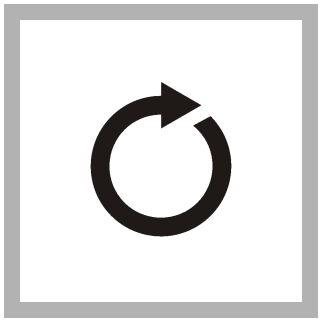


28. Put a magnetic stir bar and the correct amount of silica gel (based on the equation below) into the flask with the solvent/ product from step 27.
(3 × mg/L HEM) ÷ 100 = silica gel (g ± 0.3)

29. Stir the solution on a magnetic stirrer for a minimum of 5 minutes.



30. Put a funnel on a clean, dry distillation flask with 3–5 boiling chips in it. Put a 12.5-cm filter paper in the funnel. Pre-moisten the filter paper with fresh n-hexane. Filter the solution through filter paper. Rinse the beaker that contains the remaining silica gel three times with 5-mL aliquots of fresh n-hexane. Pour the aliquots into the distillation flask.



31. Do steps 19 through 25. Weigh the product that remains in the bottom of the flask. Calculate the results with this equation:

(A – B) ÷ Sample Volume = mg/L SGT-HEM

Where:

A = Weight (mg) of residue

B = Weight (mg) of flask with boiling chips.

Interferences

Substances extracted from samples will change from source to source. This change is dependent on the diversity of the site where the samples are collected. Some samples can contain high quantities of detergents or particulates that can interfere with the extraction procedure. For these samples, use a 350-mL sample as an alternative to the 1-liter sample (which is an option). In this condition, the 350-mL sample is EPA accepted for reporting. Wash all glassware in hot water with detergent, rinse with tap and distilled water and rinse with n-hexane or acetone.

If an emulsion forms between the two phases (at step 9) and is more than one-third of the volume of the solvent layer, filter the emulsion and solvent layer through a funnel with glass wool in it. Other possible solutions to remove the emulsion are: stir the solvent and emulsion layer with a stir bar, use the solvent phase separation paper, use centrifugation, use an ultrasonic bath with ice, add NaCl or apply other physical methods. Solid phase or other extraction techniques are performance-based modifications.

If there is water in the solvent layers, a milky solvent/product layer shows in the distillation flask. Do not move the flask for 1 hour to let the water collect at the bottom. Filter the solvent layer again through sodium sulfate to remove the remaining water.

Extremely low yields could indicate an unsatisfactory extraction (step 6 through step 11) and a high yield could indicate a problem in the drying process of the solvent (step 11). Follow these steps very carefully. Do a test in the blank before the test in the samples to identify possible interferences related to these steps. If the blank shows a yield above 1 mg for each test, do not continue until the source of contamination is identified. Usual contamination sources are sodium sulfate contamination and improperly rinsed glassware.

The method can measure HEM and SGT-HEM in the range of 15–3000 mg/L when a 350-mL sample is used. The lower limit can decrease to 5 mg/L if a 1-liter sample is used. If the 1-liter sample volume is used, refer to Accuracy check on page 11 for the amount of reagents to use.

Detection limit

This method is not applicable to measurements of materials that volatilize at temperatures below approximately 85 °C (185 °F). Petroleum fuels from gasoline through #2 fuel oil can be partially lost in the solvent removal operation. Some crude oils and

heavy fuel oils contain a important percentage of materials that are not soluble in n-hexane. Recoveries of these materials can be low.

Accuracy check

Standard preparation

Items to collect:

- Stearic acid, 98% minimum
- Hexadecane, 98% minimum
- Acetone for Organic Residue Analysis, residue less than 1 mg/L
- 100-mL Class A volumetric flask
- 10.0-mL Class A volumetric pipet

1. Put 400 (± 4) mg stearic acid and 400 (± 4) mg hexadecane into a 100-mL volumetric flask.
2. Add 75 mL of acetone to the flask. Cover with a small beaker. Stir the solution gently. Heat slightly until all material is dissolved. Over-heating with the lid on causes pressure build up.
3. Fill to volume with acetone. Cover with a small beaker. Let the solution temperature decrease to room temperature. Continue to fill to volume until solution is at stable volume.
4. Use a pipet to add 5 mL of the solution from step 3 into 350 mL of deionized reagent water. This standard solution must be 114.3-mg/L HEM or 57.1-mg/L SGT-HEM. If 1-liter reagent water is used, 5 mL gives concentrations of 40 mg/L HEM and 20 mg/L SGT-HEM.

   Note: *To verify the concentration, use a pipet to add 5 mL of the solution from step 3 in a pre-weighed flask. Put the flask in a hood to let the acetone dry. Weigh the flask. Verify that the weight difference before and after solution addition is 40 (± 1) mg.*

EPA monitoring

If the Oil and Grease tests are used for compliance reporting to the USEPA, make the changes that follow to the procedure:

1. Use a 1-liter sample in a 2000-mL separatory funnel rather than a 350-mL sample in a 500-mL separatory funnel (step 1).
2. Use 6 mL (instead of 4 mL) of 1:1 hydrochloric acid to adjust the pH below 2 (step 2) and 30 mL of n-hexane instead of 20 mL of n-hexane for the extraction (step 5).

MDL standard solution

The recommended standard concentration to determine the minimum detection limit (MDL) is approximately 5 mg/L.

1. To prepare the standard for HEM complete steps 1–3 in Standard preparation on page 11, but change step 1 to transfer 100 (± 4) mg stearic acid and 100 (± 4) mg hexadecane to a 250-mL volumetric flask.
2. To prepare the standard for SGT-HEM standard, put 200 (± 4) mg of decahexane only into a 250-mL volumetric flask. Transfer 5 mL of one ot the two standards into 1-liter of reagent water.

Analysis of the standard must give 5 mg/L for HEM or SGT-HEM.

IPR standard solution

Use deionozed water—void of any oil and grease—as the blank (standard solution) for the initial precision and recovery (IPR).

Complete the procedure four separate times with 5 mL of the standard (40 mg/L 1:1 stearic acid/hexadecane) diluted into 1 liter of demineralized water. Refer to EPA requirements for MDL and IPR on page 12.

EPA requirements for MDL and IPR

Before analysis on real samples for oil and grease, the user must get a MDL less than or equal to the EPA reported MDL and to report an IPR. It is highly recommended that the laboratory reagent water blanks are measured to remove all interferences before the MDL and IPR are measured.

MDL: Complete the procedure seven separate times with the standard solution. Find the standard deviation and multiply the standard deviation by 3.143 (Student's t test). The permitted limits are:

- HEM: ≤ 1.4 mg/L
- SGT-HEM: ≤ 1.6 mg/L

IPR: Complete the procedure for HEM and SGT-HEM (if necessary) four separate times with the standard solution. Report the average percent recovery (x) and the standard deviation for both HEM and SGT-HEM. The permitted limits are:

- HEM: Precision(s) ≤10 %; Recovery (x) 83–101 %
- SGT-HEM: Precision(s) ≤13 %; Recovery (x) 83–116 %

If not within these ranges, correct the problem and do IPR again.

After get satisfactory values for the MDL and IPR, keep records for USEPA verification.

Report the test results to the EPA

Include the data that follows with the HEM and/or SGT-HEM results for each set of 10 (maximum) samples for each discharge source.

1. **Blank value**: The value must be less than 5.0 mg/L for HEM and SGT-HEM.

   Note: *Use a standard that agrees with the regulatory concentration limit. This concentration is 1–5 times higher than the concentration of the sample (B) or is the same concentration as the OPR, the one that is highest. Divide the concentration of the spike (T) by 2 for SGT-HEM if the standard is used (40 mg/L 1:1 stearic acid/hexadecane).*

2. **OPR (Ongoing Precision and Recovery)**: Add 5 mL of the standard (40 mg/L 1:1 stearic acid/hexadecane) to a 1-liter sample and complete the test. The permitted limits for recovery are:

   - HEM: 70–114%
   - SGT-HEM: 66–114%

   If recovery is lower, there is a possible interference or the technique is not correct. Identify the cause and do OPR again until within the range.

3. **MS and MSD (matrix spike and matrix spike duplicate)**: Measure the HEM and SGT-HEM concentration of the sample (B). Spike two 1-L samples with 5 mL of the standard and measure the concentration after spiking (A).

   Calculate the Percent Recovery (P) as follows:

   $P_{HEM(40\ mg/L)} = [100 \times (A - B)] \div T$

   $P_{SGT-HEM} = [100 \times (A - B)] \div (T \div 2)$

   Where:

   A = concentration of the unspiked sample

   B = concentration of the spiked sample

   T = concentration of the spike solution

   If the recovery for HEM and SGT-HEM is within the permitted limits for OPR, then calculate the Relative Percent Difference (RPD).

   $RPD = [(Conc_{MS} - Conc_{MSD}) \div (Conc_{MS} + Conc_{MSD})] \times 200$

   If the RPD for HEM is ≤ 18 and for SGT-HEM ≤ 24, then continue to the next step. If the recovery is lower than the RPD, there is a possible interference. Identify and correct the interference, then do the MS and MSD measurement again.

   After every five MS/MSD tests, calculate the average percent recovery (Pa) and standard deviation of the percent recovery (sp). Record these numbers as Pa ± 2sp.

Update the accuracy assessment on a regular basis (e.g., after 5–10 new accuracy measurements).

4. **Balance calibration**: Measure a 2 mg and a 1000 mg class “S” weight on the analytical balance before and after each analytical batch. If the values are not within 10% of the actual weight, calibrate the balance.

Each laboratory must first verify the MDL and IPR and make sure that they are within correct parameters before oil and grease test results are reported to the EPA. Once this is established for a laboratory, it does not need to be done again.

For each 10 samples of each discharge source, calibrate the balance, report one blank, one OPR, one MS and one MSD. The user must keep logs on percent recovery and relative percent differences for MS/MSD tests. For each five MS/MSD test, calculate and record the average percent recovery and standard deviation.

Summary of method

Oil and Grease and Total Petroleum Hydrocarbons (TPH) include any material collected as a substance that is soluble in the n-hexane extractant. These include substances such as relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related materials. When measuring oil and grease (HEM) gravimetrically, the substances are removed from the sample with n-hexane, then the n-hexane is dried. The residue left is weighed to determine the concentration of oil and grease materials in mg/L.

When Total Petroleum Hydrocarbons (SGT-HEM) is gravimetrically measured, the substances are removed from the sample with n-hexane, then mixed with silica gel to absorb non-TPH components. Then, the n-hexane is dried. Like the HEM, the residue left is weighed to determine the concentration of total petroleum hydrocarbons.

Definition of HEM and SGT-HEM

The term oil and grease was used to define pollutants of this nature. The newer term n-Hexane Extractable Materials (HEM) shows that can apply this method to materials other than oils and greases.

Likewise, the term Total Petroleum Hydrocarbons (TPH) was used to classify aliphatic hydrocarbon materials. The newer term Silica Gel Treated n-Hexane Extractable Material (SGT-HEM) shows that can apply this method to materials other than aliphatic petroleum hydrocarbons that are not adsorbed by silica gel.

Note: *Careful technique is necessary for accurate results.*

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Hydrochloric Acid Solution, 6.0 N (1:1)	varies	500 mL	88449
Hexane, ACS grade	100–200 mL	500 mL	1447849
pH paper	varies	100/pkg	2601300
Silica gel with indicator (for desiccator)	varies	454 g	1426901
Silica gel, 100–200 mesh (for SGT-HEM)	1–30 g	500 g	2665034
Sodium sulfate, anhydrous	10 g	113 g	709914

Required apparatus

Description	Quantity/test	Unit	Item no.
Adapter, vacuum connector/gas inlet, 28/15	1	each	1433900
Aspirator, vacuum pump	1	each	213100
Balance, analytical, 115 VAC	1	each	2936801

Required apparatus (continued)

Description	Quantity/test	Unit	Item no.
Boiling chips, silicon carbide	2–3	500 g	2055734
Clamp, 3-prong	1	each	42200
Clamp holder	1	each	32600
Clamp, pinch type, No. 28, F/Glass Joints	2	each	1433800
Condenser, reflux, with ground glass joints, 28/15	1	each	1433700
Cylinder, graduated, 500 mL	1	each	50849
Cylinder, graduated, 50 mL	1	each	50841
Desiccator	1	each	2088800
Desiccator plate, ceramic	1	each	1428400
Filter funnel, 65-mm, short stem	1	each	2664700
Filter paper, 12.5-cm, folded, pore size 8 to 12 µm	1	100/pkg	69257
Flask, Erlenmeyer, 125 mL	2	each	50543
Flask, Erlenmeyer, 125-mL, with ground glass joint 28/15	2	each	1434000
Funnel, separatory, 500 mL	1	each	52049
Marker, laboratory	1	each	2092000
Oven, drying, 120 VAC	1	each	1428900
Pipet filler, safety bulb	1	each	1465100
Pipet, serological, 5 mL	1	each	53237
Ring support, 4-inch	1	each	580-01
Rod, glass	1	3/pkg	177001
Steam bath, 8-inch, 5-ring	1	each	2347900
Hot plate, 7 inch x 7 inch, digital, 120 VAC	1	each	2881500
Stir bar, 22.2 x 7.9 mm	1	each	2095350
Support, Ring Stand, 5-inch x 8-inch base	1	each	56300
Tongs, crucible, 9 inch	1	each	56900
Tube, connecting, J-shaped, with ground glass joint, 28/15	1	each	1814300
Tubing, rubber, 7.9 mm x 2.4 mm	varies	12 ft	56019

Recommended standards

Description	Unit	Item no.
Hexadecane, 99%, 400 mg	100 mL	2664842
Stearic Acid, 400 mg	500 g	2664934

Optional reagents and apparatus

Description	Unit	Item no.
Acetone, ACS	500 mL	1442949
Separatory funnel, 2-liters	each	52054
Beaker, 50 mL	each	50041H
Weight set	each	2617601

Optional reagents and apparatus (continued)

Description	Unit	Item no.
Hotplate/Stirrer 7.25 x 7.25 in., 220–240 VAC	each	2881602
Ring support, 4.5 in.	each	2656300
Furnace, Muffle, 120 VAC	each	1429600
Pipet, volumetric 5.0 mL	each	14515-37
Flask, volumetric	100 mL	14574-452
Cylinder, graduated, 100 mL	each	508-42

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02/2015, Edition 9

Oil and Grease

DOC316.53.01186

USEPA[1] Solid Phase Extraction Method — Method 10300

5 to 1000 mg/L HEM and SGT-HEM — Hexane Extractable Gravimetry

Scope and application: For water, wastewater, brine solutions, produced waters and hydraulic fracturing waters.

[1] This procedure is equivalent to USEPA Method 1664A, Solid Phase Extraction (SPE)

Test preparation

Before starting

Make sure to obey the instructions in Sample collection and storage on page 3 for sample collection and acidification.
Refer to Figure 1 on page 2 to assemble the Xenosep SPE apparatus. Make sure to put the waste collection tube in the large flask before the funnel assembly is installed. Refer to Figure 2 on page 3 to assemble the funnel. Make sure to put the pattern side of the SPE filter down in the SPE filter support.
Wash all glassware in hot water with detergent, rinse with tap and distilled water. Then, rinse with acetone or n-hexane.
Fully rinse all glassware with n-hexane to make sure that the analyte is removed from the apparatus. One incorrect rinse will cause low recovery.
Determine a blank value (1 liter of distilled or deionized water) with each new lot of reagents. If the blank result is greater than 5 mg, correct the source of error or remove interferences before analysis.
To analyze SGT-HEM rinse the inner cavity of the aluminum dish with a few milliliters of acetone. Then, use a few milliliters of n-hexane to remove all possible artifacts.
Put the dishes in a drying oven at 103–105 °C (217–221 °F) for 1 hour. Keep the dishes in the desiccator for the next use .
Make sure to remove the aluminum dish from the hot plate before the solution has fully evaporated. Do not apply too much heat to the solution because it will cause low recovery.
Use a vacuum pump that can generate a minimum of 1 CFM free air flow (3 CFM recommended). If the SPE dish is not sufficient dried, it will cause low recovery.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Description	Quantity
Hydrochloric Acid Solution, 6 N (1:1)	6 mL
Hexane (n-hexane) in Teflon-FEP wash bottle	1 wash bottle
Methanol in PE wash bottle	1 wash bottle
Deionized water in PE wash bottle	1 wash bottle
SPE Starter Kit, EPA Method 1664A	1 kit
SPE Consumables Kit	1 kit
SPE Solvent Recovery Kit	1 kit
Aluminum weighing dish	1
Hot plate (Thermolyne)	1
Pump, vacuum, 27 in. Hg, 1.3 CFM	1
pH paper, 0–14 pH units	1

Items to collect (continued)

Description	Quantity
Lab stand	1
Clamp, swivel	2
Desiccator	1
For SGT-HEM	
Silica gel	1 bottle
125-mL Erlenmeyer flask	1
100-mL volumetric flask (for HEM results over 1000 mg/L)	1
Magnetic stir plate	1
Aluminum weighing dish	1
Additional sodium sulfate column	1

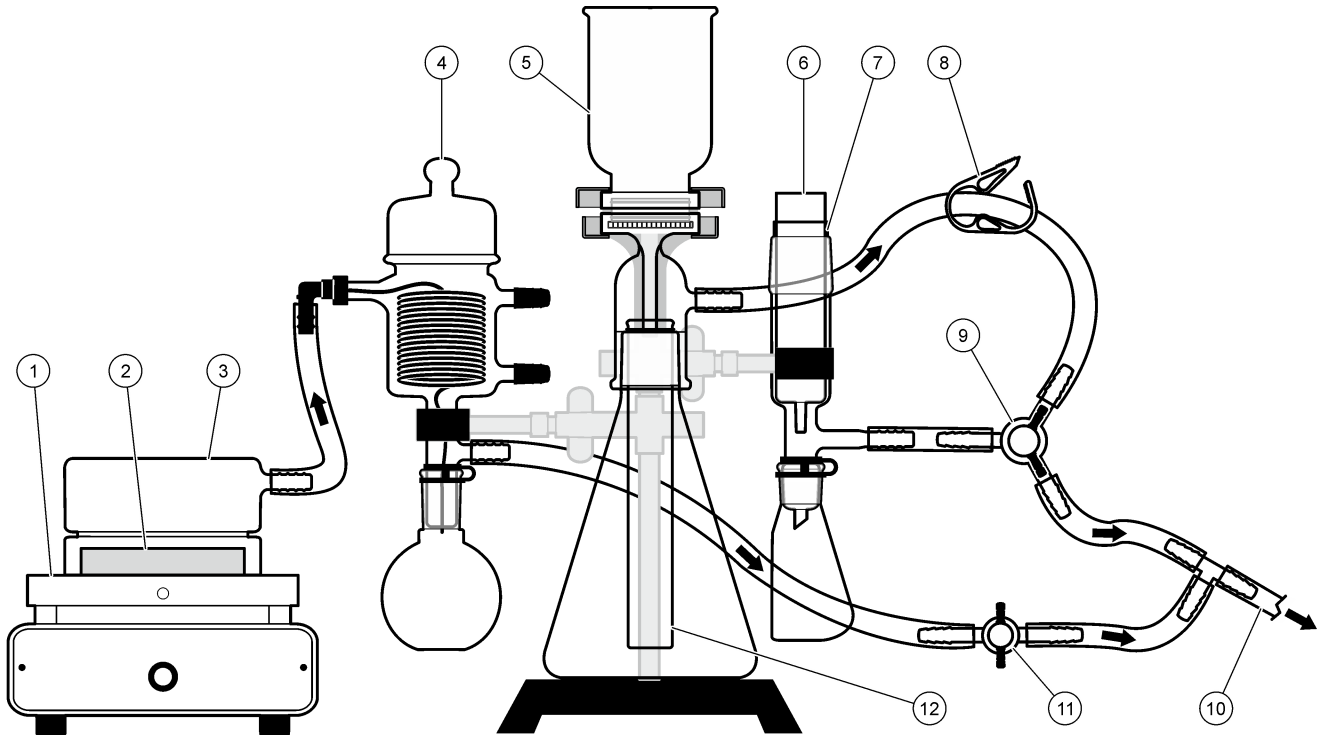
Refer to Consumables and replacement items on page 12 for order information.

Assemble the SPE apparatus

Refer to Figure 1 to assemble the Xenosep SPE apparatus. Make sure to put the waste collection tube in the large flask before the funnel assembly is installed.

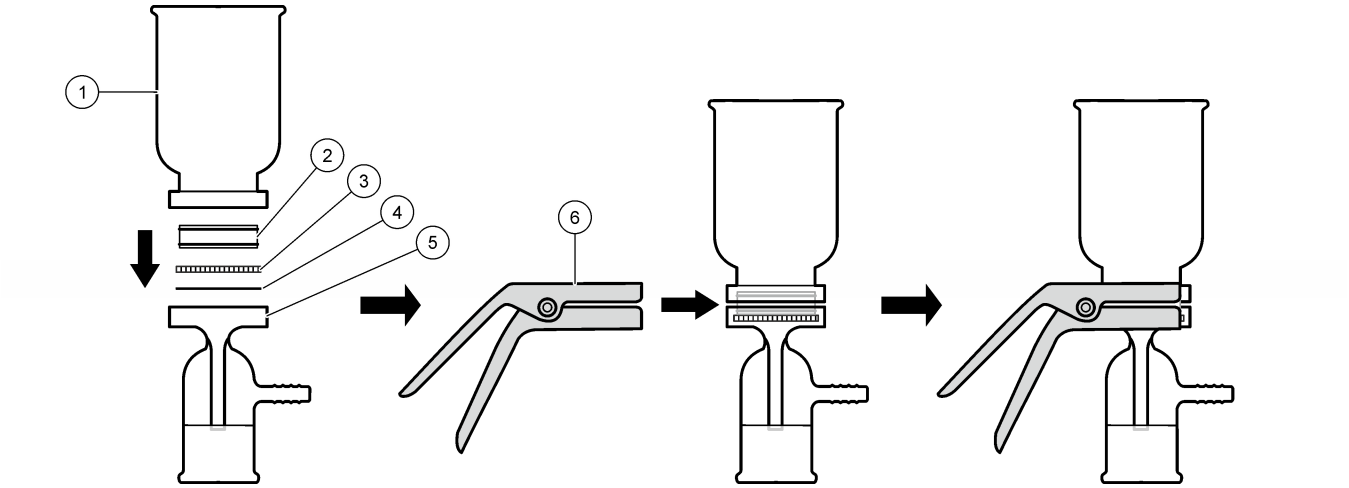
Refer to Figure 2 to assemble the funnel. Make sure to put the pattern side of the SPE filter down in the SPE filter support.

Figure 1 Apparatus assembly for solid phase extraction



1 Hot plate	**5** Funnel assembly (refer to Figure 2)	**9** 3-way valve
2 Aluminum dish	**6** Sodium sulfate column	**10** 2-way valve
3 Glass dome	**7** Eluter tube	**11** To vacuum
4 Solvent recovery assembly	**8** Tube clamp	**12** Waste collection tube with O-ring

Figure 2 Funnel assembly



1 Funnel	**4** Stainless steel support
2 Coupler with O-rings	**5** SPE starter holder
3 SPE filter with pattern side down	**6** Aluminum clamp

Sample collection and storage

- Do not rinse the bottle with sample before collection.
- Collect 1 L (950–1050 mL) of sample in a wide-mouth glass bottle.
- Let the sample temperature increase to room temperature before analysis.
- Adust the sample pH to less than 2 with 1:1 hydrochloric acid (HCl) solution before analysis.

Sample volume

Complete the steps that follow to measure the sample volume:

1. Use a laboratory pen to put a mark on the sample bottle at the liquid level of the sample.
2. When the test is complete, fill the bottle to this mark with tap water.
3. Pour the tap water into a 1-L graduated cylinder and record the volume.
4. Use this volume for the sample volume in the final step of the test procedure for HEM or SGT-HEM.

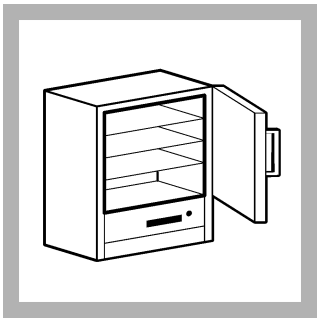
Sample acidification

Complete the steps that follow to find the volume of HCl to use:

1. Collect a separate aliquot of sample.
2. Add HCl until the pH is less than 2.
3. Add this volume of acid to each sample bottle before collection.

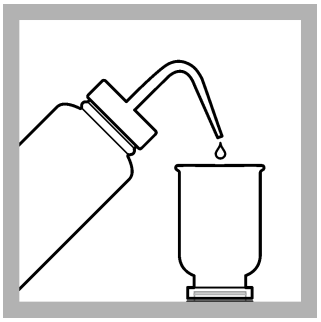
   Note: *Do not put pH paper, a pH electrode, a glass rod or other materials into the sample because oil and grease in the sample can bond to these items.*

Test procedure—HEM

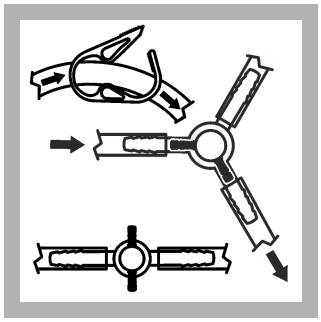


1. Put an aluminum dish in a drying oven at 103–105 °C (217–221 °C) for 1 hour.

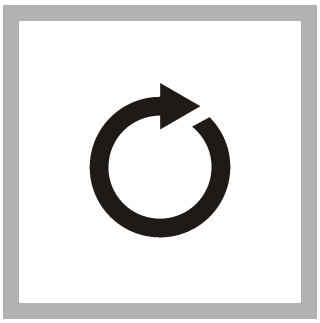
2. Remove the dish from the oven. Let the dish temperature decrease to room temperature in a desiccator.



3. Add approximately 10 mL of n-hexane to the funnel. Wait 5 seconds.

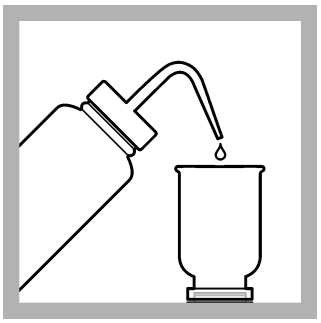


4. Set the vacuum to on and then to off to pull the solvent into the waste collection tube. Make sure that the valves are set to apply vacuum from the funnel holder and the tubing clamp is open.

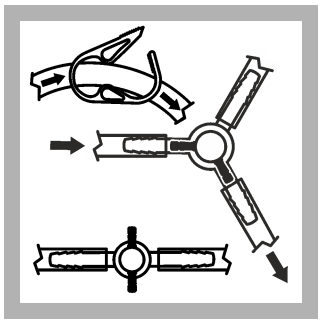


5. Do steps 3–4 again.

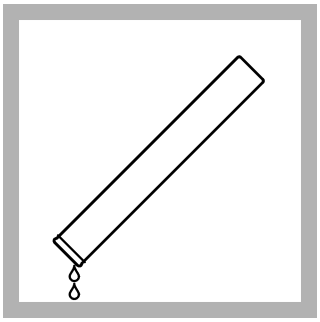
6. Set the vacuum to on for 1 minute to dry the filter. When the timer expires, set the vacuum to off.



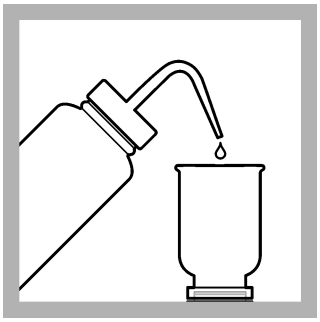
7. Add approximately 10 mL of methanol to the funnel. Wait 5 seconds.



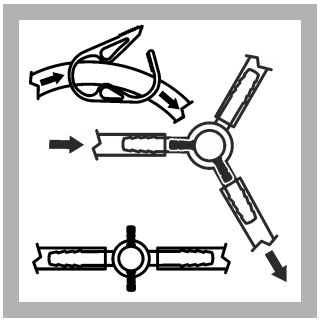
8. Set the vacuum to on and off to pull the solvent into the waste collection tube. Do not let the filter become dry.



9. Remove the waste collection tube. Discard the solvent waste.

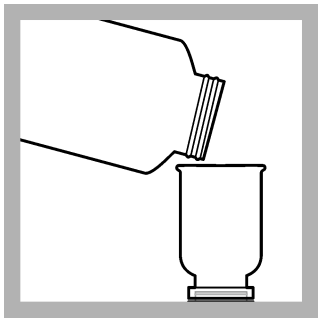


10. Add approximately 20 mL of deionized water to the funnel. Wait 5 seconds.



11. Set the vacuum to on and then to off to pull water into the flask. Do not let the filter become dry.

If the filter becomes dry, do steps 7–11 again.

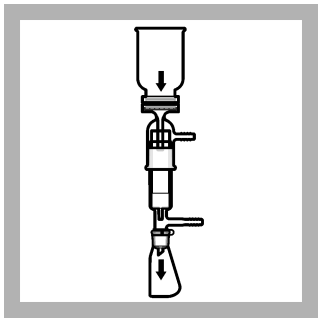


12. Slowly pour the acidified sample into the funnel and set the vacuum to on. Use deionized water to rinse all contamination from the walls of the funnel.

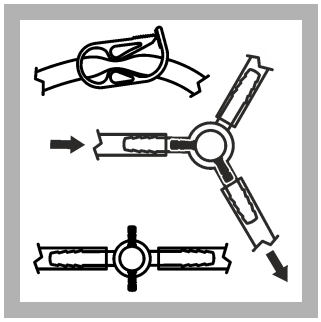
Refer to Sample acidification on page 3.

13. Keep the vacuum on for 4–8 minutes to air dry the filter. When the timer expires, set the vacuum to off.

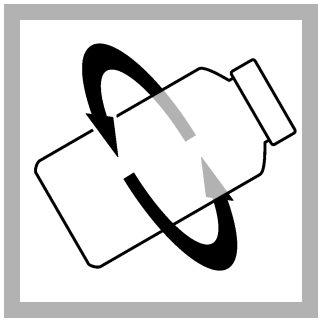
Do not leave the vacuum on for more than 8 minutes.



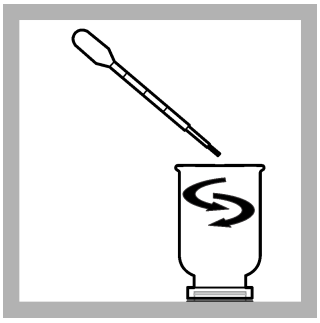
14. Put the funnel assembly on the eluter tube.



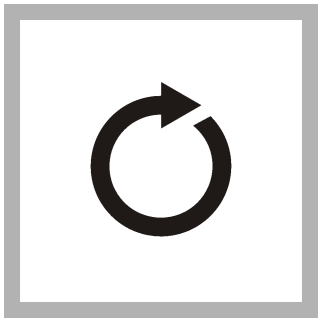
15. Turn the valve to apply vacuum to the eluter tube. Close the tubing clamp on the funnel holder tube.



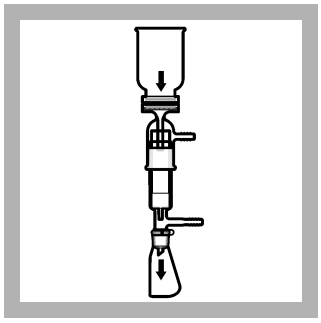
16. Add 10 mL of n-hexane to the empty sample bottle. Swirl the bottle in a horizontal, circular movement for 10 seconds to rinse the bottle.



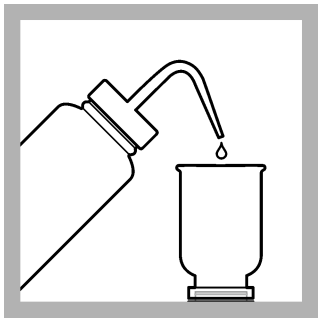
17. Use a transfer pipet to collect the n-hexane from the top of the sample bottle. Slowly rinse the walls of the funnel with the n-hexane. Go around the funnel at least three times.



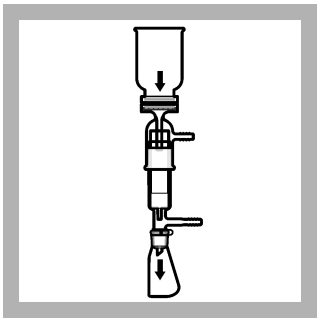
18. Do steps 16–17 again two more times.



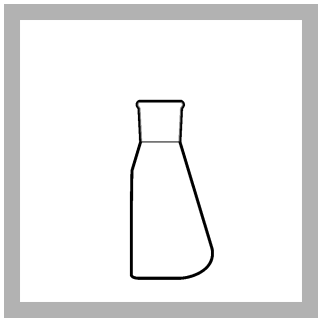
19. Set the vacuum to on and then to off to pull the solvent into the flat-sided flask.



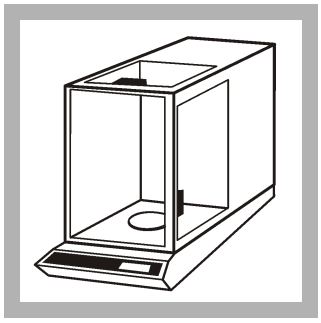
20. Rinse the walls of the funnel with approximately 10 mL of n-hexane. Wait 5 seconds.



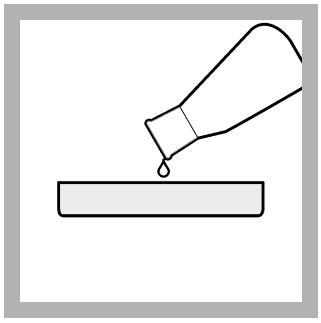
21. Set the vacuum power to on, then to off.



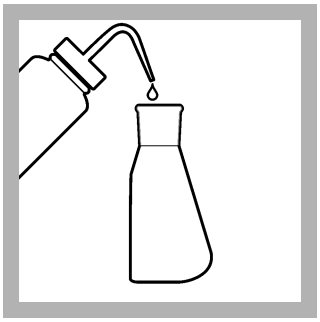
22. Remove the flat-sided flask from the eluter tube.



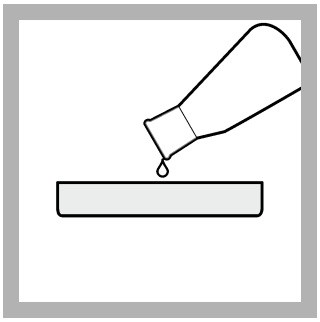
23. Use an analytical balance to weigh the dish to the nearest 0.1 mg (0.0001 g). Record this mg value as B.



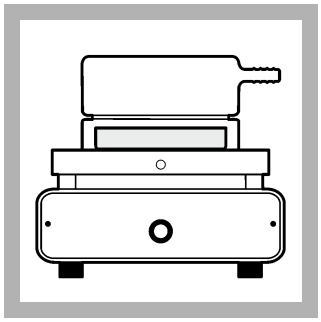
24. Add the n-hexane to the dish.



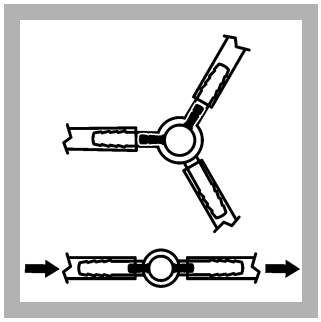
25. Rinse the flat-sided flask with approximately 5 mL of n-hexane.



26. Add the n-hexane to the dish.

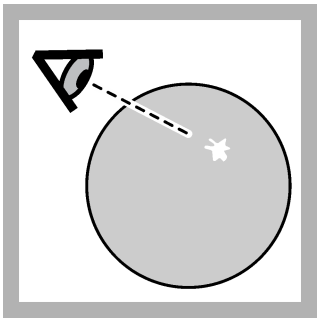


27. Put the dish on the hot plate. Put on the glass cover.



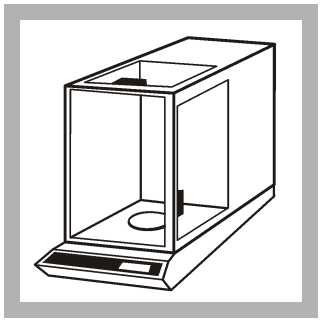
28. Close the 3-way valve and open the 2-way valve to apply vacuum from the solvent recovery apparatus.

29. Set the vacuum to on. Set the hot plate to on at low heat (35–85 ºC). Keep the vacuum and hot plate on for approximately 2 minutes.

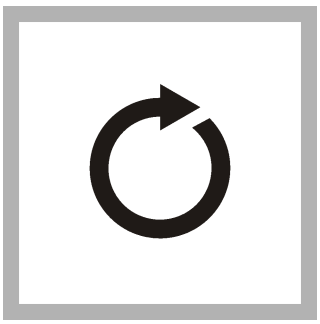


30. Examine the dish for dry spots. As soon as there is a dry spot remove the dish from the hot plate. Put the dish in a fume hood until the rest of the n-hexane has dried.

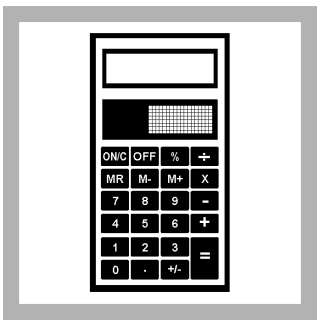
31. When the dish is dry, put the dish in a desiccator for 30 minutes.



32. Weigh the dish to the nearest 0.1 mg.



33. Do steps 31–33 again until the weight loss is less than 0.5 mg from the previous weight. Record this mg value as A.



34. Calculate the test results:

[(A – B) ÷ Sample volume] × 1000 = mg/L HEM

Where:
A = weight of dish with residue (g)

B = weight of dish (g)

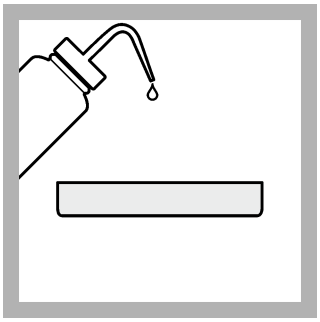
Example:
A = 6.2394 g

B = 6.2318 g

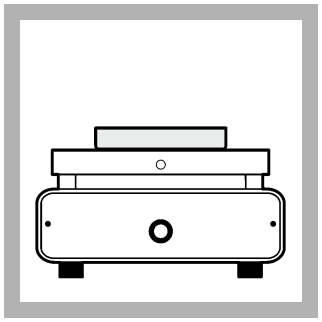
Sample volume = 0.950 L

[(6.2394–6.2318) ÷ 0.950] × 1000 = 8.0 mg/L HEM

Test procedure—SGT-HEM (< 1000 mg/L)



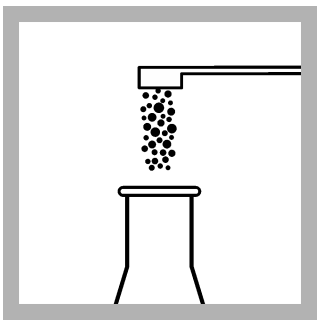
1. Add approximately 60 mL of n-hexane to the residue in the aluminum dish from the HEM test.



2. Use a hot plate to apply low heat to the dish and dissolve all of the residue.

3. Pour the mixture into a 125-mL Erlenmeyer flask. Rinse the pan and funnel several times with n-hexane. Add the mixture to the flask.

4. Add n-hexane to approximately the 100-mL mark.

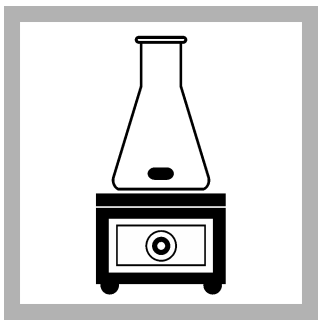


5. Add 3 (± 0.3) g of silica gel to each 100 mg of HEM:

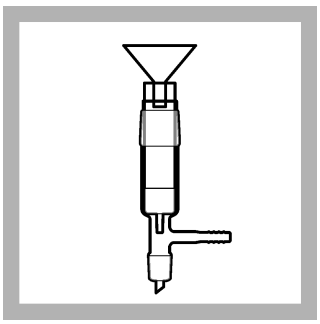
(3 × mg/L HEM) ÷ 100 = silica gel (g)

Example: If the HEM value is 735 mg, round 7.35 g up to the next whole gram increment (8 g or 800 mg) and add 3 × 800/100 = 24 g of silica gel.

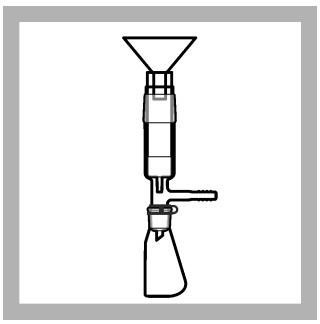
Do not add more than 30 g of silica gel.



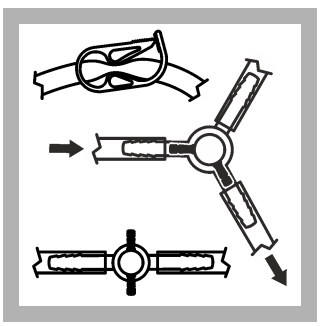
6. Add a stir bar to the flask. Stir for 5 minutes.



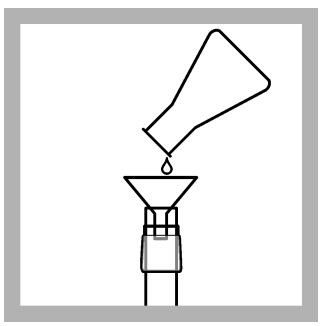
7. Put a new sodium sulfate column into the eluter tube. Put the funnel on the eluter tube.



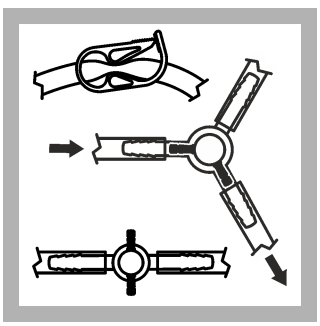
8. Install a clean flat-sided flask.



9. Adjust the valves to apply vacuum from the eluter tube.

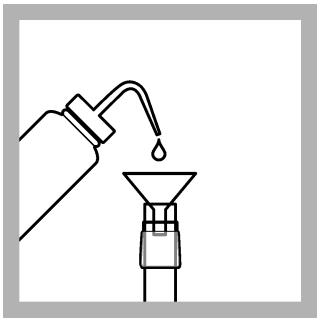


10. Pour the solution from the Erlenmeyer flask into the funnel.

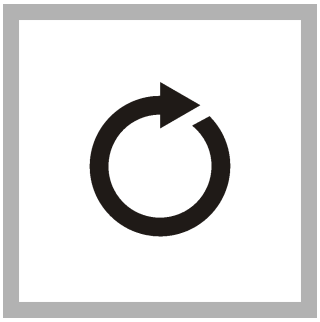


11. Set the vacuum to on and then to off to pull the solution into the flat-sided flask.

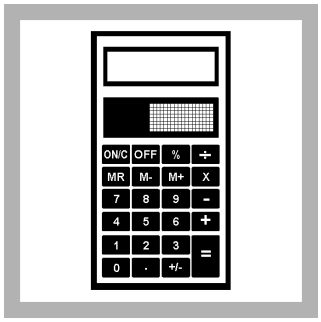
12. Rinse the Erlenmeyer flask with 5 mL of n-hexane. Add the n-hexane to the funnel. Set the vacuum to on and then to off.



13. Rinse the walls of the funnel with approximately 5 mL of n-hexane. Set the vacuum to on and then to off.



14. Complete steps 22–33 of the Test procedure—HEM on page 4 to evaporate the solvent.



15. Calculate the test results:

[(A – B) ÷ Sample volume] × 1000 = mg/L SGT-HEM

Where:
A = weight of dish with residue (g)

B = weight of dish (g)

Example:
A = 6.2360 g

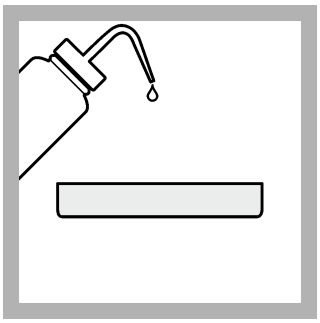
B = 6.2320 g

Sample volume = 0.950 L

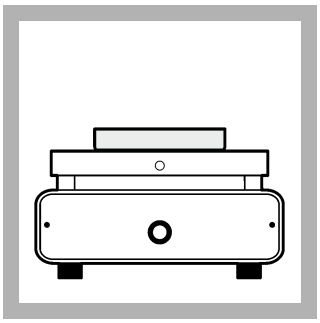
[(6.2360–6.2320) ÷ 0.950] × 1000 = 4.2 SGT-HEM

Report result as ≤ 5 mg/L SGT-HEM

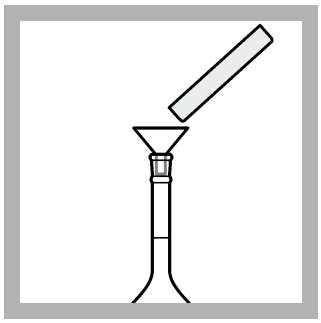
Test procedure—SGT-HEM (> 100 mg/L)



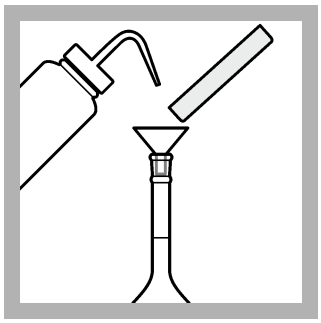
1. Add approximately 60 mL of n-hexane to the residue in the aluminum dish from the HEM test.



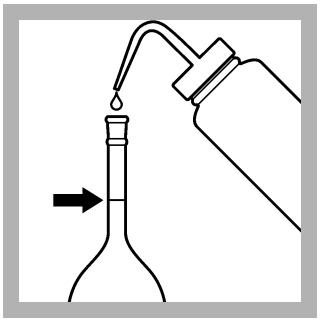
2. Use a hot plate to apply low heat to the dish and dissolve all of the residue.



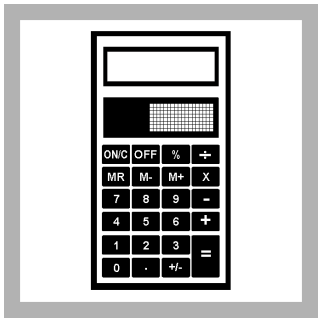
3. Pour the mixture into a 100-mL volumetric flask.



4. Rinse the pan and funnel several times with n-hexane. Add the rinse to the volumetric flask.



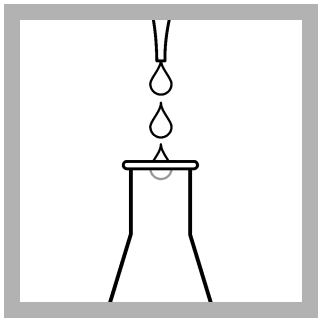
5. Dilute to the mark with n-hexane. Mix well.



6. Calculate the volume to remove for the silica gel treatment:

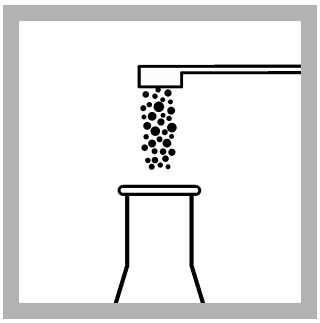
V_{1000} = 100,000 ÷ HEM value

V_{1000} = volume that contains 1000 mg HEM



7. Remove the amount calculated in step 6 from the volumetric flask and add it to a 125-mL Erlenmeyer flask.

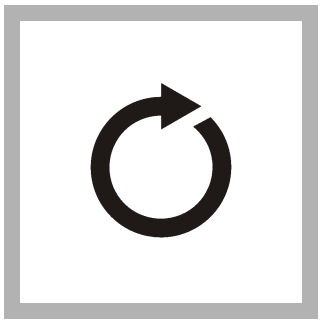
8. Add n-hexane to approximately the 100-mL mark.



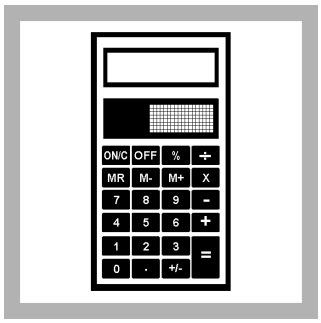
9. Add 30 g of silica gel to the flask. Mix well.

If the volume added in step 7 contained less than 1000 mg HEM, calculate the amount of silica gel to add based on the mg HEM that was added to the flask.

(3 × mg HEM in alliquot) ÷ 100 = silica gel (g)



10. Complete steps 6–15 in Test procedure—SGT-HEM (< 1000 mg/L) on page 7.



11. Correct the test result for the reduced volume that was treated with the silica gel:

$W_d \times (100 \div V_{1000}) = W_c$

Where:

W_d = result from step 15.

V_{1000} = volume removed for silica gel treatment

W_c = corrected SGT-HEM result

Interferences

For samples that are known to contain extremely high levels of oil and grease use a smaller sample volume. Correct the volume difference to give the result as a 1-L sample.

High concentrations of particulates in the water sample can clog the SPE filter or keep high levels of water, which can lower the extraction efficiency. Inorganic particulates are easier to filter than organic particulates. The techniques that follow can help to filter samples that contains high levels of particulates:

- Decanting—Let the sample to settle and pour the top portion into the funnel first. Just before dryness, add the rest of the sample. Remove all possible sediment from the bottle and add it to the SPE filter. Use deionized water to rinse any sediment that remains in the bottle.
- Prefilters or prefilter fibers—Put the prefilter or prefilter fibers into the coupler before the funnel is attached.
- Drying agents—Add magnesium sulfate to the SPE filter or to the prefilter to remove water from the particulates.

- Filtration aids—Add materials such as sodium chloride, sand, diatomaceous earth or glass beads to help speed the complete filtration of samples that contain organic particulates.

Detection limit

This method is not applicable to measurements of materials that volatilize at temperatures below approximately 85 °C (185 °F). Petroleum fuels from gasoline through #2 fuel oil can be partially lost in the solvent removal operation. Some crude oils and heavy fuel oils contain a important percentage of materials that are not soluble in n-hexane. Recoveries of these materials can be low.

Accuracy check

Standard preparation

Items to collect:

- Stearic acid, 98% minimum
- Hexadecane, 98% minimum
- Acetone for Organic Residue Analysis, residue less than 1 mg/L
- 100-mL Class A volumetric flask
- 10.0-mL Class A volumetric pipet
- 15.0-mL Class A volumetric pipet

1. Put 200 (± 2) mg stearic acid and 200 (± 2) mg hexadecane into a 100-mL volumetric flask.
2. Pour 75–85 mL of acetone and shake vigorously until all material has dissolved.
3. Let the solution temperature decrease to room temperature. Fill to volume with acetone. Mix well. The concentration of this stock solution is 4000 mg/L HEM (2000 mg/L SGT-HEM).
4. Use a volumetric pipet to dilute the stock solution for use in the minimum detection limit (MDL) and the initial precision and recovery (IPR) measurements. Refer to MDL standard solution on page 10 and IPR (OPR) standard solution on page 10.

MDL standard solution

1. Add 15 mL of the stock solution into a clean 100-mL volumetric flask. Dilute to the mark with acetone. Mix well.
2. Use a pipet to add 10 mL for HEM (or 20 mL for SGT-HEM) into a 1-L volumetric flask.
3. Dilute to the mark with deionized water at pH less than 2. Mix well.
   The concentration of this standard solution is 6 mg/L HEM (or 6 mg/L SGT-HEM)

Complete the procedure seven separate times with a 6 mg/L standard solution. Refer to EPA requirements for MDL and IPR on page 10.

IPR (OPR) standard solution

Add 10 mL of the stock solution into 1 liter of deionized water. Mix well.

The concentration of this solution is 40 mg/L HEM (20 mg/L SGT-HEM).

Note: *To verify the concentration, use a pipet to add 10 mL of the IPR standard solution in a pre-weighed flask. Put the flask in a hood to let the acetone dry. Weigh the flask. Verify that the weight difference before and after solution addition is 40 (± 1) mg.*

Complete the procedure for HEM and SGT-HEM (if necessary) four separate times with a 40 mg/L HEM (20 mg/L SGT-HEM) standard solution. Refer to EPA requirements for MDL and IPR on page 10.

EPA requirements for MDL and IPR

Before analysis on real samples for oil and grease, the user must get a MDL less than or equal to the EPA reported MDL and to report an IPR. It is highly recommended that the

laboratory reagent water blanks are measured to remove all interferences before the MDL and IPR are measured.

MDL: Complete the procedure seven separate times with the standard solution. Find the standard deviation and multiply the standard deviation by 3.143 (Student's t test). The permitted limits are:

- HEM: ≤ 1.4 mg/L
- SGT-HEM: ≤ 1.6 mg/L

IPR: Complete the procedure for HEM and SGT-HEM (if necessary) four separate times with the standard solution. Report the average percent recovery (x) and the standard deviation for both HEM and SGT-HEM. The permitted limits are:

- HEM: Precision(s) ≤10 %; Recovery (x) 83–101 %
- SGT-HEM: Precision(s) ≤13 %; Recovery (x) 83–116 %

If not within these ranges, correct the problem and do IPR again.

After get satisfactory values for the MDL and IPR, keep records for USEPA verification.

Report the test results to the EPA

Include the data that follows with the HEM and/or SGT-HEM results for each set of 20 (maximum) samples for each discharge source.

1. **Blank value**: The value must be less than 5.0 mg/L for HEM and SGT-HEM.

   Note: *Use a standard that agrees with the regulatory concentration limit. This concentration is 1–5 times higher than the concentration of the sample (B) or is the same concentration as the OPR, the one that is highest. Divide the concentration of the spike (T) by 2 for SGT-HEM if the standard is used (40 mg/L HEM (20 mg/L SGT-HEM)).*

2. **OPR (Ongoing Precision and Recovery)**: Add 5 mL of the standard (40 mg/L HEM (20 mg/L SGT-HEM)) to a 1-liter sample and complete the test. The permitted limits for recovery are:

   - HEM: 78–114%
   - SGT-HEM: 64–132%

   If recovery is lower, there is a possible interference or the technique is not correct. Identify the cause and do OPR again until within the range.

3. **MS and MSD (matrix spike and matrix spike duplicate)**: Measure the HEM and SGT-HEM concentration of the sample (B). Spike two 1-L samples with 10 mL of the standard and measure the concentration after spiking (A).

   Calculate the Percent Recovery (P) as follows:

   $P_{HEM(40\ mg/L)} = [100 \times (A - B)] \div T$

   $P_{SGT-HEM} = [100 \times (A - B)] \div (T \div 2)$

   Where:

   A = concentration of the unspiked sample

   B = concentration of the spiked sample

   T = concentration of the spike solution

   If the recovery for HEM and SGT-HEM is within the permitted limits for OPR, then calculate the Relative Percent Difference (RPD).

   $RPD = [(Conc_{MS} - Conc_{MSD}) \div (Conc_{MS} + Conc_{MSD})] \times 200$

   If the RPD for HEM is ≤ 18 and for SGT-HEM ≤34, then continue to the next step. If the recovery is lower than the RPD, there is a possible interference. Identify and correct the interference, then do the MS and MSD measurement again.

   After every five MS/MSD tests, calculate the average percent recovery (Pa) and standard deviation of the percent recovery (sp). Record these numbers as Pa ± 2sp.

Update the accuracy assessment on a regular basis (e.g., after 5–10 new accuracy measurements).

4. **Balance calibration**: Measure a 2 mg and a 1000 mg class “S” weight on the analytical balance before and after each analytical batch. If the values are not within 10% of the actual weight, calibrate the balance.

Each laboratory must first verify the MDL and IPR and make sure that they are within correct parameters before oil and grease test results are reported to the EPA. Once this is established for a laboratory, it does not need to be done again.

For each 20 samples of each discharge source, calibrate the balance, report one blank, one OPR, one MS and one MSD. The user must keep logs on percent recovery and relative percent differences for MS/MSD tests. For each five MS/MSD test, calculate and record the average percent recovery and standard deviation.

Summary of method

Oil and Grease and Total Petroleum Hydrocarbons (TPH) include any material collected as a substance that is soluble in the n-hexane extractant. These include substances such as relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related materials. When measuring oil and grease (HEM) gravimetrically, the substances are removed from the sample with n-hexane, then the n-hexane is dried. The residue left is weighed to determine the concentration of oil and grease materials in mg/L.

When Total Petroleum Hydrocarbons (SGT-HEM) is gravimetrically measured, the substances are removed from the sample with n-hexane, then mixed with silica gel to absorb non-TPH components. Then, the n-hexane is dried. Like the HEM, the residue left is weighed to determine the concentration of total petroleum hydrocarbons.

Definition of HEM and SGT-HEM

The term oil and grease was used to define pollutants of this nature. The newer term n-Hexane Extractable Materials (HEM) shows that can apply this method to materials other than oils and greases.

Likewise, the term Total Petroleum Hydrocarbons (TPH) was used to classify aliphatic hydrocarbon materials. The newer term Silica Gel Treated n-Hexane Extractable Material (SGT-HEM) shows that can apply this method to materials other than aliphatic petroleum hydrocarbons that are not adsorbed by silica gel.

Note: *Careful technique is necessary for accurate results.*

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Hydrochloric Acid Solution, 6.0 N (1:1)	varies	500 mL	88449
Hexane, for Organic Residue Analysis	100–200 mL	1 L	2510253
Methanol, ACS grade	10 mL	500 mL	1446449
Silica gel, 100–200 mesh (for SGT-HEM)	1–30 g	500 g	2665034

Required apparatus

Description	Quantity/test	Unit	Item no.
Balance, analytical, 115 VAC	1	each	2936801
Bottle, wash, 500-mL Teflon, FEP	1	each	2505100
Bottle, wash, 500-mL	1	3/pkg	2927204
Bottle, wide-mouth, 1-L	1	each	2951401
Clamp, swivel	2	each	2503400

Required apparatus (continued)

Description	Quantity/test	Unit	Item no.
Cylinder, graduated, 1-L	1	each	108153
Desiccator	1	each	2088800
Desiccator plate, ceramic	1	each	1428400
Flask, Erlenmeyer, 125 mL	2	each	50543
Hot plate (Thermolyne), 120 VAC, 50 Hz	1	each	2344100
Marker, laboratory	1	each	2092000
Oven, drying, 120 VAC	1	each	1428900
Pump, vacuum, 27 in. Hg, 1.3 CFM	1	each	2824800
SPE Consumables Kit	1	24/pkg	2943800
SPE Starter Kit, EPA Method 1664A	1	each	2943231
SPE Solvent Recovery Kit	1	each	2514300
Stirrer, magnetic, 120 VAC	1	each	2343600
Stir bar, 22.2 x 7.9 mm	1	each	2095350
Support stand	1	each	2504900
Tongs, crucible, 9 inch	1	each	56900

Recommended standards

Description	Unit	Item no.
Hexadecane, 99%, 400 mg	100 mL	2664842
Stearic Acid, 400 mg	500 g	2664934

Optional reagents and apparatus

Description	Unit	Item no.
Acetone, for Organic Residue Analysis	1 L	2510153
Flask, volumetric, Class A, 100-mL	each	1457442
Flask, volumetric, Class A, 1-L	each	1457453
pH paper, 0–14 pH units	100/pkg	2601300
Pipet filler, safety bulb	each	1465100
Pipet, serological, 10-mL	each	53238
Pipet, volumetric, Class A, 10 mL	each	1451538
Pipet, volumetric, Class A, 15 mL	each	1451539
Silica gel with indicator (for desiccator)	454 g	1426901

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02/2015, Edition 9

Organic Carbon, Total

DOC316.53.01334

USEPA[1] Direct Method — Method 10267

1.5 to 30.0 mg/L C (LR) — TNTplus 810

Scope and application: For wastewater, drinking water, surface water and process water analyses.

[1] Hach Method 10267 is USEPA approved for the determination of total organic carbon (TOC) in drinking water, Federal Register Volume 81, Number 138 (Tuesday, July 19, 2016).

Test preparation

Before starting

DR3900, DR3800, DR2800: Install the light shield in Cell Compartment #2 before this test is started.
Review the safety information and the expiration date on the package.
Use the DRB reactor with 13-mm wells for the digestion. If the reactor has 16-mm wells, put adapter sleeves into the wells.
Make sure to digest the samples at 100 °C. Higher temperatures may cause the vials to break apart.
Be careful with the vials after the digestion. Pressure increases in the vials during the digestion and can cause the vials to break apart.
Use only the TOC-X5 shaker to remove total inorganic carbon (TIC) from the sample.
Carbon dioxide from the air can contaminate the sample. Do not open the indicator vial before the shaker operation is complete. Immediately install the double cap on the indicator vial after the cap is removed, then immediately install the other side of the double cap on the sample vial.
The formation of crystals in the sample vial does not affect the result.
The recommended temperature for reagent storage is 2–8 °C (35–46 °F).
The recommended sample pH is 3–10.
If the sample contains particles, dilute the sample. Use the diluted sample in the test procedure. Multiply the test result by the dilution factor.
After both vials are attached to the double cap, keep the vial assembly together. Put the vial assembly in the plastic packaging after the analysis.
DR1900: Go to All Programs>LCK or TNTplus Methods>Options to select the TNTplus number for the test. Other instruments automatically select the method from the barcode on the vial.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

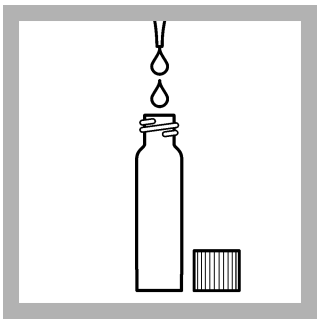
Description	Quantity
Total Organic Carbon, LR TNTplus 810 Reagent Set	1
DRB200 reactor with 13-mm wells	1
TOC-X5 shaker	1
Pipet, adjustable volume, 1.0–5.0 mL	1
Pipet tips, for 1.0–5.0 mL pipet	1
Test tube rack	1

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

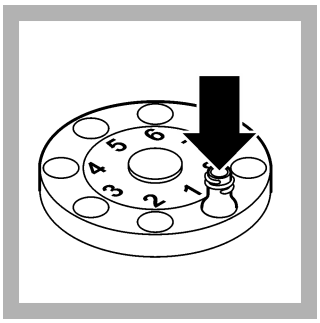
Sample collection

- Collect samples in clean glass bottles.
- Homogenize samples that contain solids to get a representative sample.
- Rinse the sample bottle several times with the sample to be collected.
- Fill the bottle completely full, then tighten the cap on the bottle.
- Analyze the samples as soon as possible for best results.
- Acid preservation is not recommended.

Test procedure

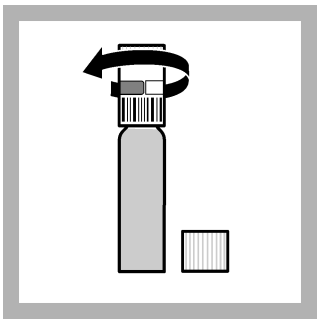


1. Remove the cap from a clear vial. Use a pipet to add 2 mL of sample to the vial.

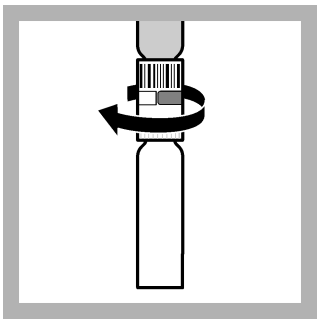


2. Insert the uncapped sample vial into the TOC-X5 shaker. Make sure that the vial is pushed all the way down into the shaker. Move the fan over the vial.

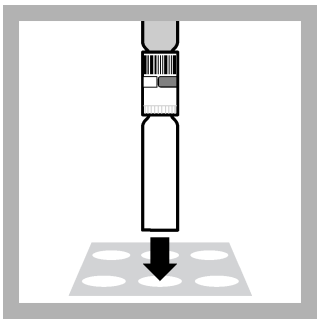
3. Push the on/off switch to start the shaker. Operate the shaker for 5 minutes.



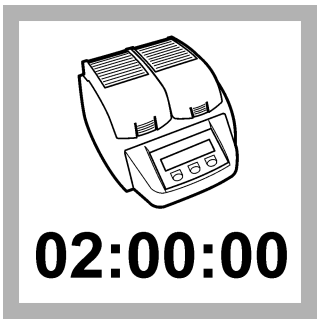
4. When the shake time is complete, remove the cap from a blue indicator vial. Immediately install and tighten a double cap on the indicator vial with the barcode label toward the vial.



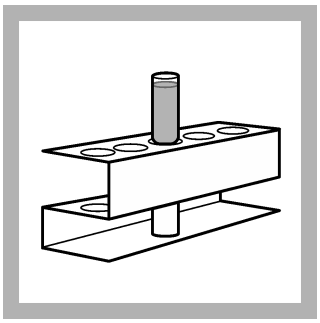
5. Immediately invert the indicator vial, then install and tighten the other side of the double cap on the sample vial. Hold the vial assembly vertically.



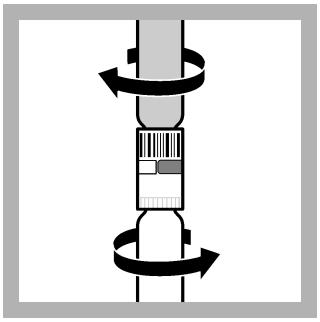
6. Insert the vial assembly into the DRB reactor (indicator vial on top).



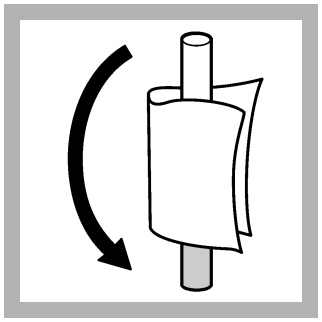
7. Increase the vial assembly temperature for 2 hours at 100 °C.



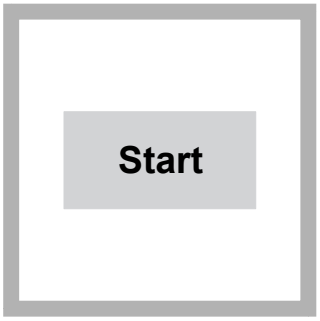
8. Let the vial assembly cool completely to room temperature. Make sure that the vials cool completely. Warm vials will give high results.



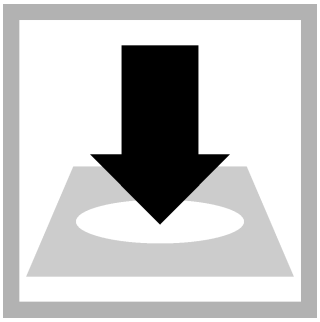
9. Tighten the double cap on both vials.



10. Invert the vial assembly so the indicator vial is on the bottom. Clean the indicator vial.



11. DR1900 only: Select program 810. Refer to Before starting on page 1.



12. Insert the vial into the cell holder. DR1900 only: Push **READ**.
Results show in mg/L C.

Interferences

The table that follows shows the substances that were tested for interference and did not interfere up to the levels shown.

Interfering substance	Interference level
Ammonium	200 mg/L
Calcium	2000 mg/L as $CaCO_3$
Chloride	1000 mg/L
Magnesium	2000 mg/L as $CaCO_3$
TIC	250 mg/L

Accuracy check

Standard solution method

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

Items to collect:

- 1000-mg/L C TOC Standard Solution
- 500-mL volumetric flask, Class A
- 200-mL volumetric flask, Class A
- 50-mL volumetric pipet, Class A and pipet filler safety bulb
- 20-mL volumetric pipet, Class A and pipet filler safety bulb
- Organic-free water

1. Prepare a 100-mg/L C stock solution as follows:
   a. Use a pipet to add 20 mL of a 1000-mg/L C standard solution into a 200-mL volumetric flask.
   b. Dilute to the mark with organic-free water. Mix well.
2. Prepare a 10-mg/L C standard solution as follows:
   a. Use a pipet to add 50 mL of a 100-mg/L C stock solution into a 500-mL volumetric flask.
   b. Dilute to the mark with organic-free water. Mix well. Prepare this solution daily.
3. Use the test procedure to measure the concentration of the prepared standard solution.
4. Compare the expected result to the actual result.

   Note: *The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then*

used for all test results. This adjustment can increase the test accuracy when there are small variations in the reagents or instruments.

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
TNTplus 810	10 mg/L C	9.72–10.28 mg/L C	0.4 mg/L C

Summary of method

The total inorganic carbon (TIC) in the sample is first removed during the shaker operation. The sample is then digested to oxidize the total organic carbon (TOC) in the sample to carbon dioxide (CO_2). The CO_2 from the digested sample goes through the membrane in the double cap to the indicator vial and causes the indicator solution to change color. The color of the indicator solution is measured by the spectrophotometer. The measurement wavelength is 435 nm.

Consumables and replacement items

Description	Quantity/test	Unit	Item no.
Total Organic Carbon Reagent Set, LR, TNTplus	1	25/pkg	TNT810

Required apparatus

Description	Quantity/test	Unit	Item no.
DRB200 Reactor, 115 VAC option, 9 x 13 mm + 2 x 20 mm, 1 block	1	each	DRB200-01
DRB200 Reactor, 230 VAC option, 9 x 13 mm + 2 x 20 mm, 1 block	1	each	DRB200-05
Pipet, adjustable volume, 1.0–5.0 mL	1	each	BBP065
Pipet tips, for 1.0–5.0 mL pipet	1	75/pkg	BBP068
Test tube rack	1	each	1864100
TOC-X5 shaker	1	each	LQV148.99.00002
Wipes, disposable	1	280/pkg	2097000

Recommended standards

Description	Unit	Item no.
TOC Standard Solution Ampule (KHP Standard, 1000-mg/L C)	5/pkg	2791505

Optional reagents and apparatus

Description	Unit	Item no.
Reactor adapter sleeves, 16 mm to 13 mm diameter, for TNTplus vials	5/pkg	2895805
Ampule Breaker, 2-mL PourRite Ampules	each	2484600
Flask, volumetric, Class A, 500 mL, glass	each	1457449
Flask, volumetric, Class A, 200 mL	each	1457445
Pipet, volumetric, Class A, 50 mL	each	1451541
Pipet, volumetric Class A, 20 mL	each	1451520
Pipet filler, safety bulb	each	1465100

Optional reagents and apparatus (continued)

Description	Unit	Item no.
Potassium Acid Phthalate (KHP), ACS	500 g	31534
Water, organic-free	500 mL	2641549

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04/2017, Edition 4

Organic Carbon, Total

DOC316.53.01335

USEPA[1] Direct Method — Method 10267

30 to 300 mg/L C (HR) — TNTplus 811

Scope and application: For wastewater, drinking water, surface water and process water analyses.

[1] Hach Method 10267 is USEPA approved for the determination of total organic carbon (TOC) in drinking water, Federal Register Volume 81, Number 138 (Tuesday, July 19, 2016).

Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows the adapter and light shield requirements for the applicable instruments that can use TNTplus vials.

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

Table 1 Instrument-specific information for TNTplus vials

Instrument	Adapters	Light shield
DR6000, DR5000	—	—
DR3900	—	LZV849
DR3800, DR2800	—	LZV646
DR1900	9609900 or 9609800 (A)	—

Before starting

DR3900, DR3800, DR2800: Install the light shield in Cell Compartment #2 before this test is started.
Review the safety information and the expiration date on the package.
Use the DRB reactor with 13-mm wells for the digestion. If the reactor has 16-mm wells, put adapter sleeves into the wells.
Make sure to digest the samples at 100 °C. Higher temperatures may cause the vials to break apart.
Be careful with the vials after the digestion. Pressure increases in the vials during the digestion and can cause the vials to break apart.
Use only the TOC-X5 shaker to remove total inorganic carbon (TIC) from the sample.
Carbon dioxide from the air can contaminate the sample. Do not open the indicator vial before the shaker operation is complete. Immediately install the double cap on the indicator vial after the cap is removed, then immediately install the other side of the double cap on the sample vial.
The formation of crystals in the sample vial does not affect the result.
The recommended temperature for reagent storage is 2–8 °C (35–46 °F).
The recommended sample pH is 3–10.
If the sample contains particles, dilute the sample. Use the diluted sample in the test procedure. Multiply the test result by the dilution factor.
After both vials are attached to the double cap, keep the vial assembly together. Put the vial assembly in the plastic packaging after the analysis.
DR1900: Go to All Programs>LCK or TNTplus Methods>Options to select the TNTplus number for the test. Other instruments automatically select the method from the barcode on the vial.

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

Items to collect

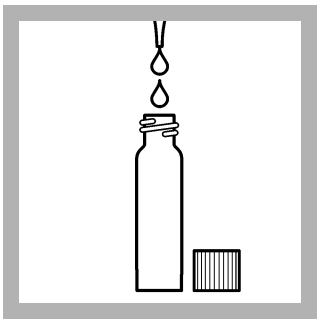
Description	Quantity
Total Organic Carbon, HR TNTplus 811 Reagent Set	1
DRB200 reactor with 13-mm wells	1
TOC-X5 shaker	1
Pipet, adjustable volume, 1.0–5.0 mL	1
Pipet tips, for 1.0–5.0 mL pipet	1
Test tube rack	1

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

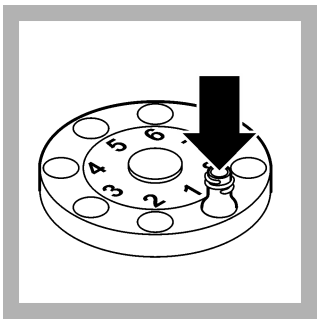
Sample collection

- Collect samples in clean glass bottles.
- Homogenize samples that contain solids to get a representative sample.
- Rinse the sample bottle several times with the sample to be collected.
- Fill the bottle completely full, then tighten the cap on the bottle.
- Analyze the samples as soon as possible for best results.
- Acid preservation is not recommended.

Test procedure

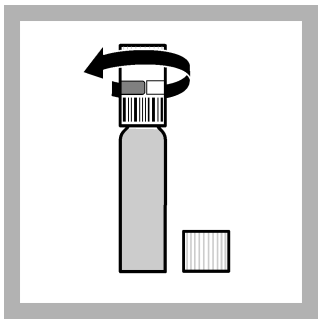


1. Remove the cap from a clear vial. Use a pipet to add 1 mL of sample to the vial.

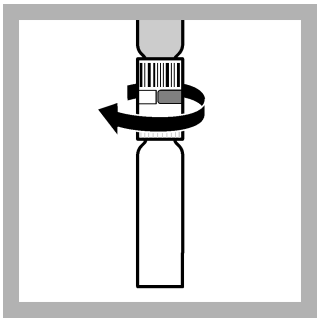


2. Insert the uncapped sample vial into the TOC-X5 shaker. Make sure that the vial is pushed all the way down into the shaker. Move the fan over the vial.

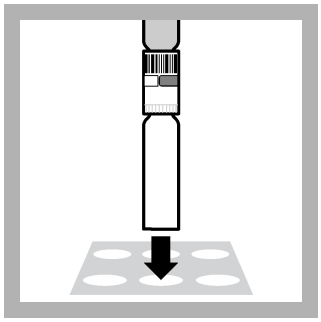
3. Push the on/off switch to start the shaker. Operate the shaker for 5 minutes.



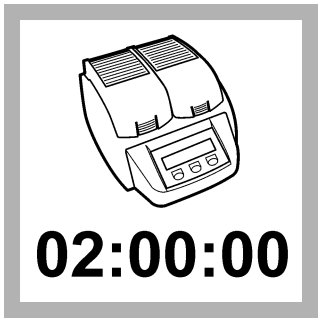
4. When the shake time is complete, remove the cap from a blue indicator vial. Immediately install and tighten a double cap on the indicator vial with the barcode label toward the vial.



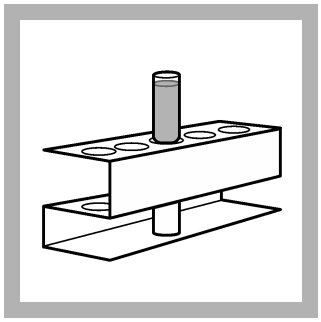
5. Immediately invert the indicator vial, then install and tighten the other side of the double cap on the sample vial. Hold the vial assembly vertically.



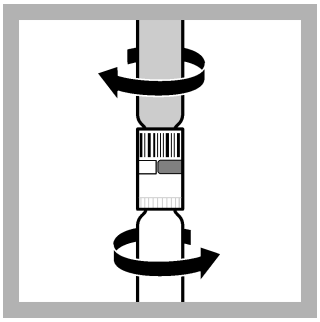
6. Insert the vial assembly into the DRB reactor (indicator vial on top).



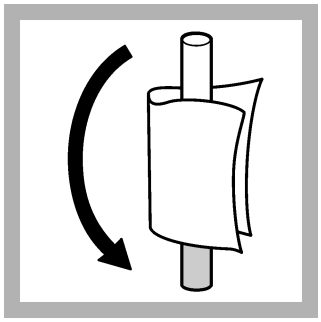
7. Increase the vial assembly temperature for 2 hours at 100 °C.



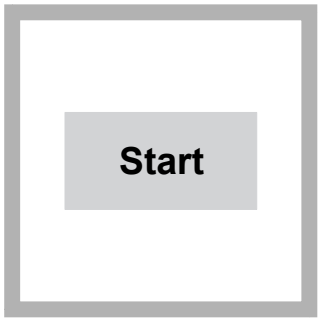
8. Let the vial assembly cool completely to room temperature. Make sure that the vials cool completely. Warm vials will give high results.



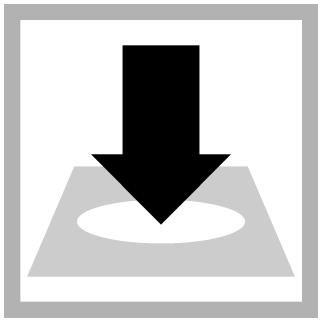
9. Tighten the double cap on both vials.



10. Invert the vial assembly so the indicator vial is on the bottom. Clean the indicator vial.



11. DR1900 only: Select program 811. Refer to Before starting on page 1.



12. Insert the vial into the cell holder. DR1900 only: Push **READ**.
Results show in mg/L C.

Interferences

The table that follows shows the substances that were tested for interference and did not interfere up to the levels shown.

Interfering substance	Interference level
Ammonium	2000 mg/L
Calcium	2000 mg/L as $CaCO_3$
Chloride	1400 mg/L
Magnesium	2000 mg/L as $CaCO_3$
TIC	250 mg/L

Accuracy check

Standard solution method

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

Items to collect:

- 1000-mg/L C, TOC Standard Solution
- 200-mL volumetric flask, Class A
- 20-mL volumetric pipet, Class A and pipet filler safety bulb
- Organic-free water

1. Prepare a 100-mg/L C standard solution as follows:
   a. Use a pipet to add 20 mL of a 1000-mg/L C standard solution into the volumetric flask.
   b. Dilute to the mark with organic-free water. Mix well. Prepare this solution daily.
2. Use the test procedure to measure the concentration of the prepared standard solution.
3. Compare the expected result to the actual result.

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

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
TNTplus 811	50 mg/L C	48.84–51.16 mg/L C	3.5 mg/L C

Summary of method

The total inorganic carbon (TIC) in the sample is first removed during the shaker operation. The sample is then digested to oxidize the total organic carbon (TOC) in the sample to carbon dioxide (CO_2). The CO_2 from the digested sample goes through the membrane in the double cap to the indicator vial and causes the indicator solution to change color. The color of the indicator solution is measured by the spectrophotometer. The measurement wavelength is 435 nm.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Total Organic Carbon Reagent Set, HR, TNTplus	1	25/pkg	TNT811

Required apparatus

Description	Quantity/test	Unit	Item no.
DRB200 Reactor, 115 VAC option, 9 x 13 mm + 2 x 20 mm, 1 block	1	each	DRB200-01
DRB200 Reactor, 230 VAC option, 9 x 13 mm + 2 x 20 mm, 1 block	1	each	DRB200-05
Pipet, adjustable volume, 1.0–5.0 mL	1	each	BBP065
Pipet tips, for 1.0–5.0 mL pipet	1	75/pkg	BBP068
Test tube rack	1	each	1864100
TOC-X5 shaker	1	each	LQV148.99.00002
Wipes, disposable	1	280/pkg	2097000

Recommended standards

Description	Unit	Item no.
TOC Standard Solution Ampule (KHP Standard, 1000-mg/L C)	5/pkg	2791505

Optional reagents and apparatus

Description	Unit	Item no.
Reactor adapter sleeves, 16 mm to 13 mm diameter, for TNTplus vials	5/pkg	2895805
Ampule Breaker, 2-mL PourRite Ampules	each	2484600
Flask, volumetric, Class A, 200 mL	each	1457445
Pipet, volumetric Class A, 20 mL	each	1451520
Pipet filler, safety bulb	each	1465100
Potassium Acid Phthalate (KHP), ACS	500 g	31534
Water, organic-free	500 mL	2641549

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04/2017, Edition 4

Oxygen, Dissolved

DOC316.53.01098

Indigo Carmine Method **Method 8316**

6 to 800 µg/L O_2 (spectrophotometers) **AccuVac® Ampuls**

10 to 1000 µg/L O_2 (colorimeters)

Scope and application: For boiler feedwater

Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows sample cell and adapter requirements for AccuVac Ampul tests.

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

Table 1 Instrument-specific information for AccuVac Ampuls

Instrument	Adapter	Sample cell
DR 6000 DR 5000 DR 900	—	2427606 
DR 3900	LZV846 (A)	
DR 1900	9609900 or 9609800 (C)	
DR 3800 DR 2800 DR 2700	LZV584 (C)	2122800 

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
The dissolved oxygen reading is only stable for 30 seconds. After 30 seconds, the Ampul solution will absorb oxygen from the air.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Description	Quantity
Low Range Dissolved Oxygen AccuVac® Ampuls	1
Polypropylene beaker, 50-mL	1
Stoppers, for 18-mm tubes and AccuVac Ampuls	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	1

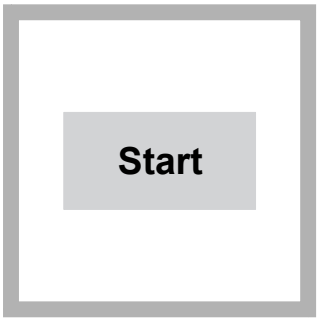
Refer to Consumables and replacement items on page 3 for order information.

Sample collection

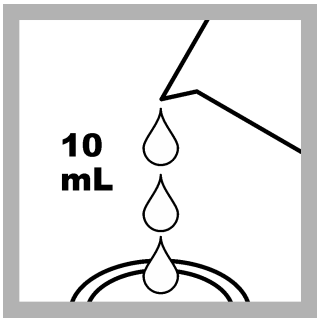
The main consideration with sample collection is to prevent contamination of the sample with atmospheric oxygen.

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- For best results, collect the sample from a stream of water that is hard-plumbed to the sample source.
- Use a funnel to maintain a continuous flow of sample and also to collect a sufficient volume to fill the Ampul.
- Do not introduce air into the sample.
- Rubber tubing, if used, will introduce unacceptable amounts of oxygen into the sample unless the length of tubing is minimized and the flow rate is maximized.
- Flush the sampling system with sample for at least 5 minutes.

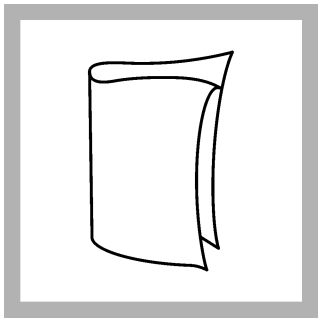
AccuVac® Ampul procedure



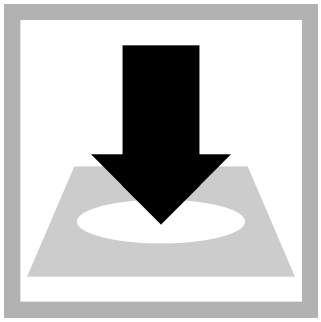
1. Start program **446 Oxygen, Dis LR AV**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



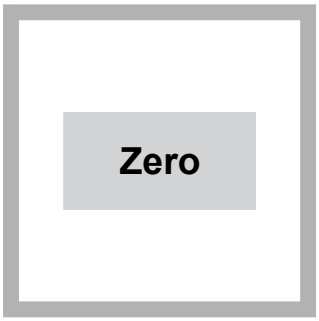
2. Prepare the blank: Fill the sample cell with 10 mL of sample.



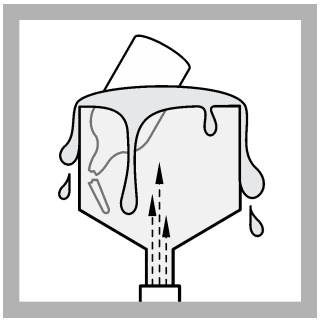
3. Clean the blank sample cell.



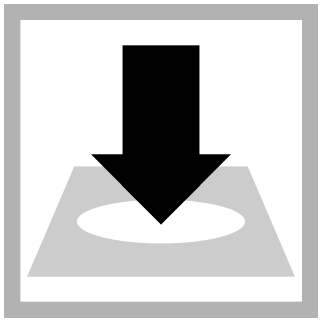
4. Insert the blank into the cell holder.



5. Push **ZERO**. The display shows 0 µg/L O_2.



6. Prepare the sample: Immerse the AccuVac Ampul in the sample and fill the Ampul with sample. For best results, collect the sample from a stream of water that is hard-plumbed to the sample source. Refer to Sample collection on page 2.



7. Immediately clean and then insert the Ampul into the cell holder.

8. Push **READ**. Results show in µg/L O_2.

Interferences

Excess amounts of thioglycolate, ascorbate, ascorbate + sulfite, ascorbate + cupric sulfate, nitrite, sulfite, thiosulfate and hydroquinone will not reduce the oxidized form of the indicator and do not cause significant interference.

Interfering substance	Interference level
Hydrazine	A 100,000-fold excess will start to reduce the oxidized form of the indicator solution.
Sodium hydrosulfite	Reduces the oxidized form of the indicator solution and will cause a significant interference.

Accuracy check

Reagent blank measurement

A reagent blank for this test can be measured as follows:

1. Fill a 50-mL beaker with sample.
2. Add one sodium hydrosulfite powder pillow and mix.
3. Fill a Low Range Dissolved Oxygen AccuVac Ampul with this sample.
4. Measure the dissolved oxygen concentration as shown in the test procedure. The result should be 0 ± 6 µg/L O_2.

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
446	N/A	not determined	6 µg/L O_2

Summary of method

The Low Range Dissolved Oxygen AccuVac Ampul contains reagent vacuum-sealed in an Ampul. When the AccuVac Ampul is broken open in a sample containing dissolved oxygen, the yellow solution will turn blue. The blue color development is proportional to the concentration of dissolved oxygen. Test results are measured at 610 nm.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Low Range Dissolved Oxygen AccuVac Ampul	1	25/pkg	2501025

Required apparatus

Description	Quantity/test	Unit	Item no.
Beaker, polypropylene, 50 mL, low form	1	each	108041

Recommended standards

Description	Unit	Item no.
Hydrosulfite Reagent Powder Pillows	100/pkg	2118869

Optional reagents and apparatus

Description	Unit	Item no.
AccuVac Ampul Snapper	each	2405200
AccuVac Sampler	each	2405100
AccuVac Ampul vials for sample blanks	25/pkg	2677925
Stoppers for 18-mm tubes and AccuVac Ampuls	6/pkg	173106

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01/2014, Edition 9

pH

DOC316.53.01323

USEPA electrode method

Method 10257

pH meter

Scope and application: For water, wastewater, brine solutions, produced waters and hydraulic fracturing waters[1].

[1] Adapted from Standard Method 4500-H+B, ASTM Method D1293-84(90)/(A or B) and USEPA Method 150.

Test preparation

Instrument-specific information

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

Table 1 Instrument-specific information

Meter	Standard probe	Rugged probe
HQ1110, HQ2100, HQ2200, HQ4100, HQ4200, HQ4300 HQ40d, HQ30d or HQ11d	Gel: PHC101 Liquid: PHC301	PHC10105, PHC10110, PHC10115, PHC10130

Before starting

Refer to the meter documentation for meter settings and operation. Refer to probe documentation for probe preparation, maintenance and storage information.
Prepare the probe before initial use. Refer to probe documentation.
When an Intellical probe is connected to an HQ meter or an HQd meter, the meter automatically identifies the measurement parameter and is prepared for use.
Condition the electrode for the best response time. To condition the electrode, soak the electrode for several minutes in a solution that has almost the same pH and ionic strength as the sample.
Calibrate the probe before initial use. Refer to Calibration procedure on page 3.
For rugged electrodes, it may be necessary to remove the shroud before measurement and calibration.
Air bubbles under the sensor tip can cause slow response or measurement errors. To remove the bubbles, carefully shake the probe.
To save data automatically, set the measurement mode to Press to Read or Interval. When the measurement mode is Continuous, select Store to save data manually.
Rinse the electrode between measurements to prevent contamination.
Keep the electrode in a pH storage solution when not in use. Refer to the probe documentation.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.
This procedure is specified for the HQ meters and HQd meters. The Sension+ meters can be used, but the menus and navigation will be different.

Items to collect

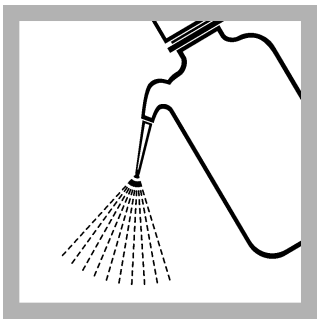
Description	Quantity
Beaker or sample containers	3
Wash bottle with deionized water	1
pH buffers (4.0, 7.0, 10.0)	3

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

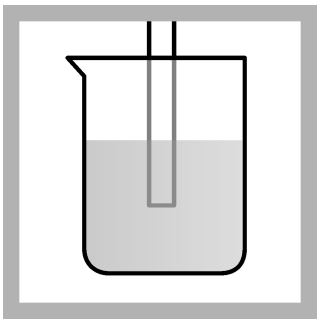
Sample collection

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Collect samples in clean glass or plastic bottles.

Test procedure

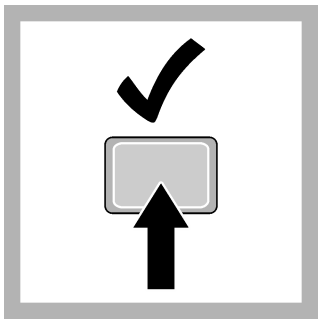


1. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

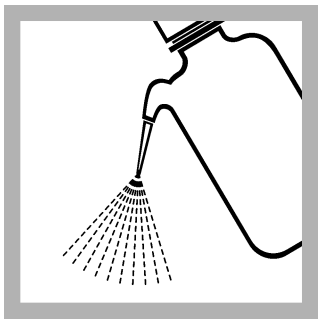


2. Laboratory test: Put the probe in a beaker that contains the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip. Stir the sample at a slow to moderate rate.
Field test: Put the probe in the sample. Move the probe up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

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

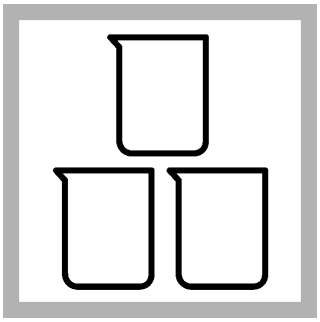


3. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.



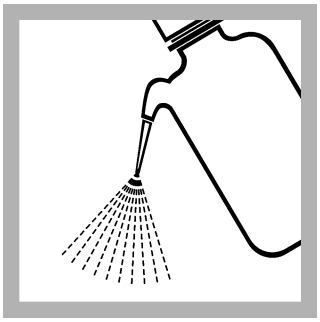
4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

Calibration procedure

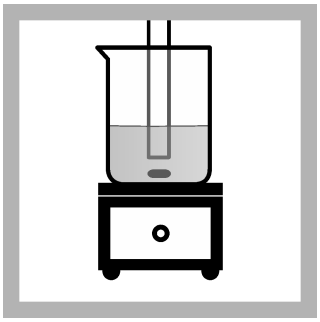


1. Prepare two or three fresh buffer solutions in separate beakers. If two buffers are used, use a 7.0 and a 4.0 or a 7.0 and a 10.0 pH buffer solution.

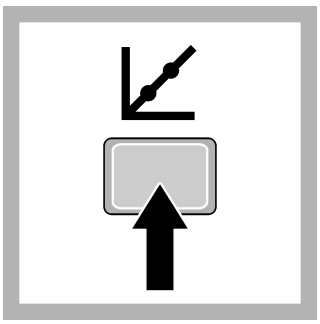
2. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



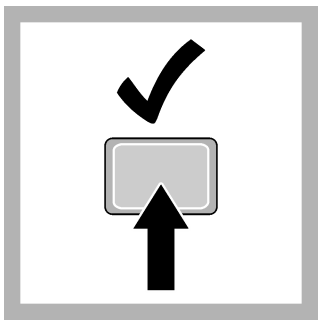
3. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



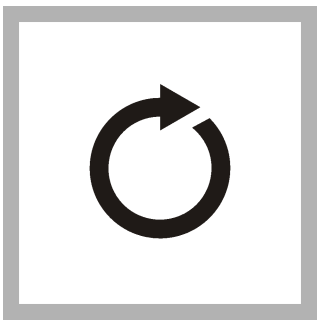
4. Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.



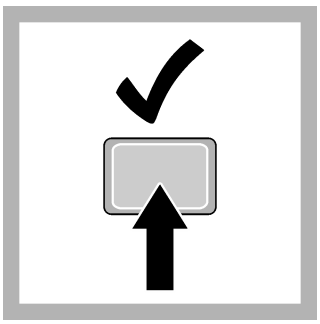
5. Push **Calibrate**. The standard solution value is shown.



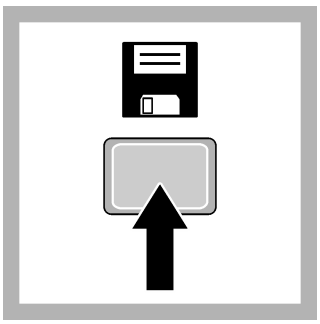
6. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.



7. Measure the remaining buffer solutions.



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



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

Interferences

The sodium error is low but increases at pH values that are higher than pH 11. The acid error is negligible. Refer to the electrode or the meter documentation.

Accuracy check

Slope test

The electrode operation is satisfactory when the calibration slope is within the specified range (typically –58 mV (±3) at 25 °C).

Calibration accuracy

Measure the pH of a fresh buffer solution. A calibration is satisfactory when the measured pH value agrees with the known pH value of the buffer solution.

Clean the probe

Clean the probe regularly to remove contamination and to keep the reference junction open. Symptoms of contamination:

- Incorrect or irregular readings
- Slow stabilization times
- Calibration errors
- Sample material stays on the probe

1. Rinse the probe with deionized water. Use warm (35–45 °C (95–113 °F)) deionized water to remove storage solution that dries on the probe. Dry the probe body with a lint-free cloth.
2. Rinse or soak the probe for 1 minute in deionized water. Dry the probe body with a lint-free cloth.
3. Soak the probe in pH 4 buffer for 20 minutes.
4. Rinse the probe with deionized water. Dry the probe body with a lint-free cloth.

Table 2 Cleaning solution

Contamination	Cleaning solution	Active component	Soak time
General contamination	Electrode cleaning solution for regular maintenance	KATHON™ CG, DECONEX®11	12–16 hours
Minerals	Electrode cleaning solution for minerals/inorganic contamination	Phosphoric acid (~10%)	10–15 minutes
Fats, grease and oils	Electrode cleaning solution for fats, oils and grease contamination	KATHON™ CG, TRITON® X	2 hours maximum
Proteins	Electrode cleaning solution for proteins/organic contamination	Pepsin in HCl	3 hours maximum
Wastewater and organic compounds	Electrode cleaning solution, extra strong	Sodium hypochlorite	5–10 minutes

Method performance

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

Summary of method

A combination pH electrode develops an electrical potential at the glass/liquid interface. At a constant temperature, this potential varies linearly with the pH of the solution.

The pH is a measure of the hydrogen ion activity in a solution and is defined as $-\log_{10}aH+$, where aH+ is the activity of the hydrogen ion. The sample pH can change when carbon dioxide is absorbed from the atmosphere. In water that has a high conductivity, the buffer capacity is typically high and the pH does not change significantly.

Consumables and replacement items

HQ meters and probes

Description	Unit	Item no.
HQ1110 portable one input, pH/ORP meter	each	LEV015.53.1110A
HQ2100 portable one input, multi-parameter meter	each	LEV015.53.2100A
HQ2200 portable two input, multi-parameter meter	each	LEV015.53.2200A

HQ meters and probes (continued)

Description	Unit	Item no.
HQ4100 portable one input, multi-parameter meter	each	LEV015.53.4100A
HQ4200 portable two input, multi-parameter meter	each	LEV015.53.4200A
HQ4300 portable three input, multi-parameter meter	each	LEV015.53.4300A
Intellical pH gel probe, standard with 1 m cable	each	PHC10101
Intellical pH gel probe, standard with 3 m cable	each	PHC10103
Intellical pH liquid probe, standard with 1 m cable	each	PHC30101
Intellical pH liquid probe, standard with 3 m cable	each	PHC30103
Intellical pH gel probe, rugged with 5 m cable	each	PHC10105
Intellical pH gel probe, rugged with 10 m cable	each	PHC10110
Intellical pH gel probe, rugged with 15 m cable	each	PHC10115
Intellical pH gel probe, rugged with 30 m cable	each	PHC10130

Refill solution and storage

Description	Unit	Item no.
pH filling solution[1], 3 M KCl, saturated with AgCl	28 mL	2841700
pH electrode storage solution	500 mL	2756549

Recommended standards

Description	Unit	Item no.
pH 4.01 buffer solution, Singlet one-use packets, 20 mL each	20/pkg	2770020
pH 7.00 buffer solution, Singlet one-use packets, 20 mL each	20/pkg	2770120
pH 10.01 buffer solution, Singlet one-use packets, 20 mL each	20/pkg	2770220
pH 4.01 and pH 7.00 buffer solution kit, Singlet one-use packets, 20 mL each	2 x 10/pkg	2769920
pH 7.00 and 10.01 buffer solution kit, Singlet one-use packets, 20 mL each	2 x 10/pkg	2769820
pH color-coded buffer solution kit (NIST), 500 mL, includes:	1	2947600
pH 4.01 ± 0.02 pH buffer (NIST)	500 mL	2283449
pH 7.00 ± 0.02 pH buffer (NIST)	500 mL	2283549
pH 10.01 ± 0.02 pH buffer (NIST)	500 mL	2283649
Powder pillows:		
pH 4.01 ± 0.02 pH buffer powder pillow (NIST)	50/pkg	2226966
pH 7.00 ± 0.02 pH buffer powder pillow (NIST)	50/pkg	2227066
pH 10.01 ± 0.02 pH buffer powder pillow (NIST)	50/pkg	2227166
Radiometer Analytical (IUPAC Series certified pH standards):		
pH 1.679 ± 0.010 at 25 °C (77 °F)	500 mL	S11M001
pH 4.005 ± 0.010 at 25 °C (77 °F)	500 mL	S11M002
pH 6.865 ± 0.010 at 25 °C (77 °F)	500 mL	S11M003
pH 7.000 ± 0.010 at 25 °C (77 °F)	500 mL	S11M004

[1] Use with the pH liquid probes.

Recommended standards (continued)

Description	Unit	Item no.
pH 9.180 ± 0.010 at 25 °C (77 °F)	500 mL	S11M006
pH 10.012 ± 0.010 at 25 °C (77 °F)	500 mL	S11M007
pH 12.45 ± 0.05 at 25 °C (77 °F)	500 mL	S11M008
pH buffer 1.09, technical	500 mL	S11M009
pH buffer 4.65, technical	500 mL	S11M010
pH buffer 9.23, technical	500 mL	S11M011

Accessories

Description	Unit	Item no.
Beaker, polypropylene, 50 mL, low form	each	108041
Beaker, polypropylene, 100-mL	each	108042
Bottle, wash, 500 mL	each	62011
Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.)	each	4531500
Stirrer, electromagnetic, 120 VAC, with electrode stand	each	4530001
Stirrer, electromagnetic, 230 VAC, with electrode stand	each	4530002
Sample bottle with screw-top cap, polypropylene, 500-mL	each	2758101
Water, deionized	4 L	27256

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02/2021, Edition 3

Salinity

DOC316.53.01180

Mercuric Nitrate Method **Method 10073**

0 to 100 ppt **Digital Titrator**

Scope and application: For seawater and brackish water.

Test preparation

Before starting

The reagents that are used in this test contain mercury. Collect the reacted samples for safe disposal.
The optional TitraStir Titration Stand can hold the Digital Titrator and stir the sample.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

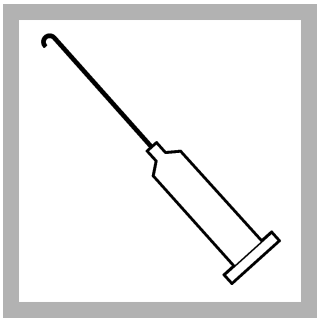
Description	Quantity
Diphenylcarbazone Reagent Powder Pillow	1
Mercuric Nitrate Titration Cartridge, 2.570 N	1
Syringe, 3-cc, Luer lock tip	1
Vial with 2-, 5-, 10-, 15-, 20- and 25-mL marks	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Water, deionized	varies

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

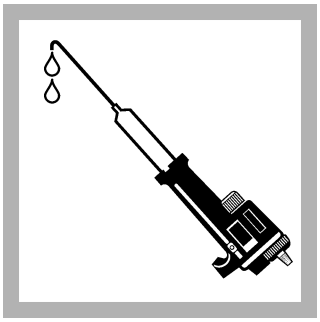
Sample collection

- Collect samples in clean glass or plastic bottles.
- If prompt analysis is not possible, keep the sample for a maximum of 7 days before analysis.

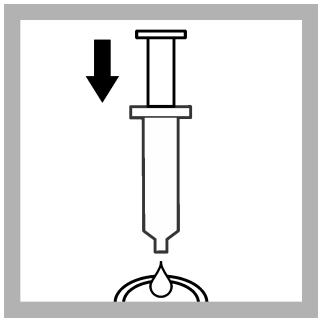
Test procedure



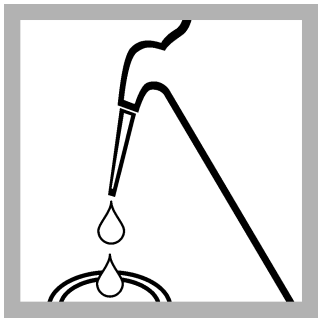
1. Insert a clean delivery tube into the Mercuric Nitrate Titration Cartridge. Attach the cartridge to the Digital Titrator.



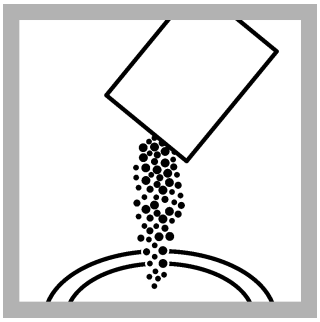
2. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



3. Use the 3-mL (3-cc) syringe to collect a 2.0-mL (2-cc) water sample. Add the sample to the plastic vial.

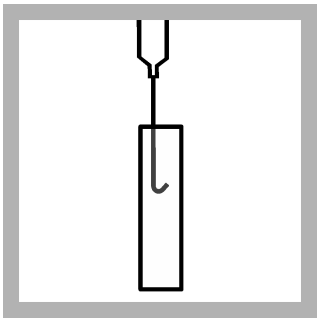


4. Fill the vial to the 10-mL mark with deionized water.

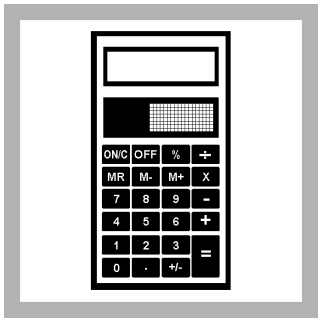


5. Add the contents of one Diphenylcarbazone Reagent Powder Pillow to the vial and mix.

A small amount of undissolved powder will not have an effect on the results.



6. Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes from yellow to light pink. Record the number of digits on the counter.



7. Calculate the salinity:

Digits x 0.1 = ppt salinity

Example: The counter showed 250 digits at the endpoint. The concentration is: 250 digits x 0.1 = 25 ppt salinity.

(ppt = parts per thousand)

Conversions

To change the units or chemical form of the test result, multiply the test result by the factor in Table 1.

Table 1 Conversions

ppt salinity to...	multiply by...	Example
mg/L chloride (Cl^-)	569	50 ppt salinity x 569 = 28,450 mg/L Cl^-
mg/L sodium chloride (NaCl)	940	50 ppt salinity x 940 = 47,000 mg/L NaCl

Pollution prevention and waste management

Reacted samples contain mercury and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations.

Summary of method

Mercuric ions in the titrant react with chloride in the sample to form mercuric chloride. After all of the chloride is in the form of mercuric chloride, the mercuric ions react with

diphenylcarbazone indicator to form a pink-purple complex, which shows the endpoint of the titration. The reagent powder contains the indicator and a buffer.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Diphenylcarbazone Reagent Powder Pillows	1	100/pkg	96799
Mercuric Nitrate Titration Cartridge, 2.570 N	1	each	2393701
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity/test	Unit	Item no.
Digital Titrator	1	each	1690001
Delivery tube for Digital Titrator, J-hook tip	1	5/pkg	1720500
Syringe, 3-cc, Luer lock tip	1	each	4321300
Vial with 2-, 5-, 10-, 15-, 20- and 25-mL marks	1	each	219300

Recommended standards and apparatus

Description	Unit	Item no.
Chloride Standard Solution, 12,500 mg/L as Cl^- (22 ppt salinity), 10-mL Voluette ampules	16/pkg	1425010
Chloride Standard Solution, 10,246 mg/L as NaCl (10.9 ppt salinity)	100 mL	2307442
Ampule Breaker, 10-mL Voluette Ampules	each	2196800

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12/2014, Edition 8

Silica

DOC316.53.01133

Silicomolybdate Method

Method 8185

1 to 100 mg/L SiO_2 (HR, spectrophotometers)

Powder Pillows

1 to 75 mg/L SiO_2 (HR, colorimeters)

Scope and application: For water and seawater.

Test preparation

Instrument-specific information

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

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

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR6000 DR3800 DR2800 DR2700 DR1900	The fill line is to the right.	2495402 
DR5000 DR3900	The fill line is toward the user.	
DR900	The orientation mark is toward the user.	2401906 

Before starting

Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
The sample temperature must be between 15–25 °C (59–77 °F) for accurate results.
Use the Standard Adjust option with each new lot of reagent for the best results. Refer to the Standard solution method in Accuracy check on page 3.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

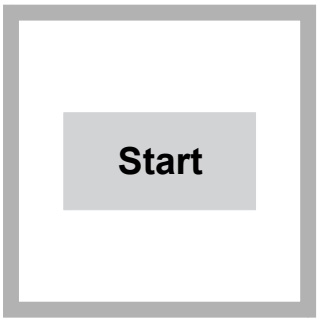
Description	Quantity
High Range SIlica Reagent Set	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

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

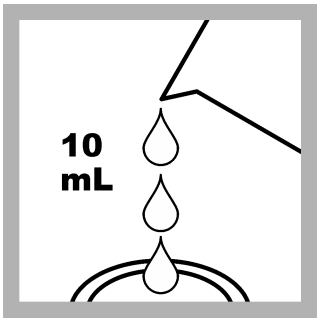
Sample collection

- Collect samples in clean plastic bottles with tight-fitting caps. Do not use glass bottles, which will contaminate the sample.
- Analyze the samples as soon as possible for best results.
- If prompt analysis is not possible, keep the samples at or below 6 °C (43 °F) for up to 28 days.
- Let the sample temperature increase to room temperature before analysis.

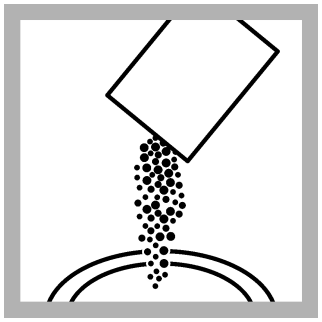
Powder pillow procedure



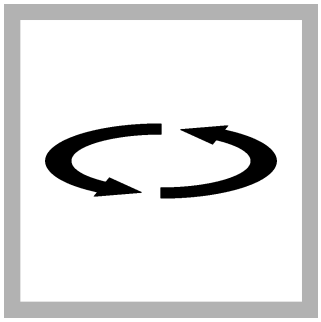
1. Start program **656 Silica HR**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



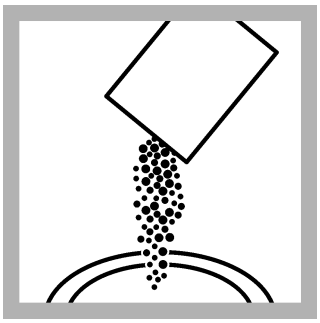
2. Prepare the sample: Fill a sample cell with 10 mL of sample.



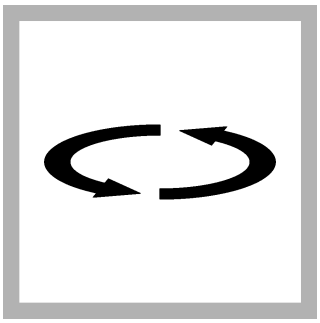
3. Add the contents of one Molybdate Reagent Powder Pillow for High Range Silica to the sample cell.



4. Swirl until the reagent is completely dissolved.

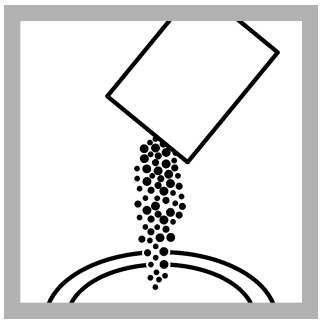


5. Add the contents of one Acid Reagent Powder Pillow for High Range Silica.
A yellow color shows if silica or phosphorus is present in the sample.



6. Swirl to mix.

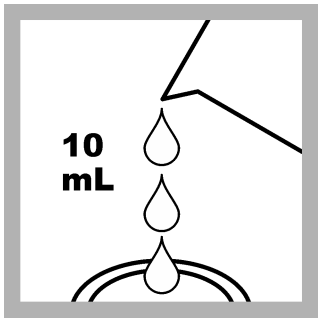
7. Start the instrument timer. A 10-minute reaction time starts.



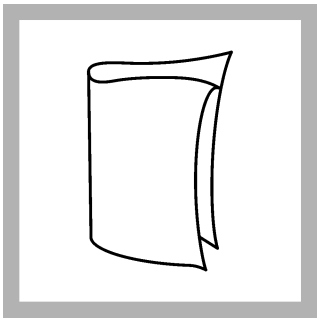
8. When the timer expires, add the contents of one Citric Acid Powder Pillow to the sample cell and swirl to mix.
Any yellow color caused by phosphorous is removed during this step.

9. Start the instrument timer. A 2-minute reaction time starts.

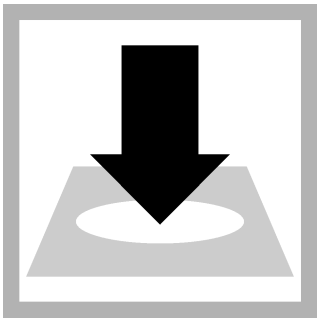
Complete the rest of the procedure within 3 minutes after the timer expires.



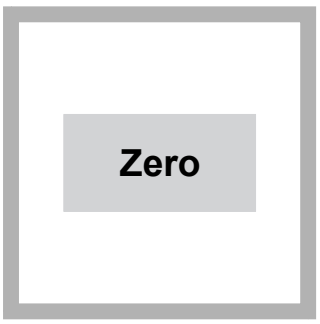
10. Prepare the blank: Fill a second sample cell with 10 mL of the original sample.



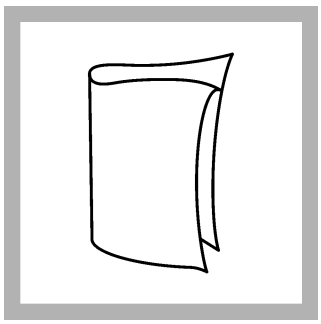
11. When the timer expires, clean the blank sample cell.



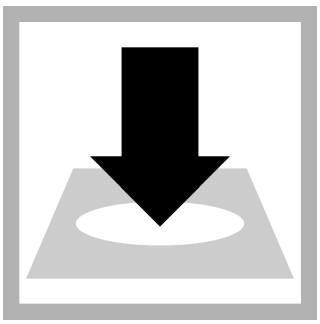
12. Insert the blank into the cell holder.



13. Push **ZERO**. The display shows 0 mg/L SiO_2.



14. Clean the prepared sample cell.



15. Insert the prepared sample into the cell holder.

16. Push **READ**. Results show in mg/L SiO_2.

Interferences

Interfering substance	Interference level
Color	Does not interfere when the original sample is used to zero the instrument.
Iron	Large amounts of both ferrous and ferric iron interfere.
Phosphate	Does not interfere at levels less than 50 mg/L PO_4^{3-}. At 60 mg/L PO_4^{3-}, an interference of –2% occurs. At 75 mg/L PO_4^{3-}, the interference is –11%.
Slow reacting forms of silica	Occasionally a sample contains silica which reacts very slowly with molybdate. The nature of these "molybdate-unreactive" forms is not known. A pretreatment with sodium bicarbonate, then sulfuric acid will make these forms reactive to molybdate. The pretreatment is given in *Standard Methods for the Examination of Water and Wastewater* under Silica-Digestion with Sodium Bicarbonate. A longer reaction time with the sample and the molybdate and acid reagents (before the citric acid is added) can help as an alternative to the bicarbonate pretreatment.
Sulfides	Interfere at all levels.
Turbidity	Small amounts of turbidity do not interfere when the original sample is used to zero the instrument.

Accuracy check

Standard additions method (sample spike)

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

Items to collect:

- Silica Standard Solution, 1000-mg/L
- Pipet, TenSette®, 0.1–1.0 mL

- Pipet tips

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 10-mL portions of fresh sample. Mix well.
6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Standard solution method

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

Items to collect:

- Silica Standard Solution, 50-mg/L

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

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

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
656	50 mg/L SiO_2	48–52 mg/L SiO_2	1.0 mg/L SiO_2

Summary of method

Silica and phosphate in the sample react with molybdate ion under acidic conditions to form yellow silicomolybdic acid complexes and phosphomolybdic acid complexes. Addition of citric acid destroys the phosphate complexes. Silica is then determined by measuring the remaining yellow color. The measurement wavelength is 452 nm for spectrophotometers or 420 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Water, deionized	varies	4 L	27256
High Range Silica Reagent Set, 10 mL	—	100 tests	2429600

Consumables and replacement items (continued)

Description	Quantity/test	Unit	Item no.
Includes:			
Acid Reagent Powder Pillow for High Range Silica, 10 mL	1	100/pkg	2107469
Citric Acid Powder Pillow, 10 mL	2	100/pkg	2106269
Molybdate Reagent Powder Pillow for High Range Silica, 10 mL	1	100/pkg	2107369

Recommended standards

Description	Unit	Item no.
Silica Standard Solution, 50-mg/L as SiO_2	200 mL	111729
Silica Standard Solution, 1000-mg/L as SiO_2	500 mL	19449

Optional reagents and apparatus

Description	Unit	Item no.
Sodium Bicarbonate	454 g	77601
Sulfuric Acid Standard Solution, 1 N	100 mL MDB	127032
Sampling bottle, with cap, low density polyethylene, 250 mL	12/pkg	2087076
Thermometer, non-mercury, –10 to +225 °C	each	2635700

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01/2014, Edition 9

Silica

DOC316.53.01132

Heteropoly Blue Method[1] — Method 8186

0.010 to 1.600 mg/L SiO_2 (spectrophotometers) — Powder Pillows

0.01 to 1.60 mg/L SiO_2 (colorimeters)

Scope and application: For boiler and ultrapure water.

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

Test preparation

Instrument-specific information

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

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

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR6000 DR3800 DR2800 DR2700 DR1900	The fill line is to the right.	2495402 
DR5000 DR3900	The fill line is toward the user.	
DR900	The orientation mark is toward the user.	2401906 

Before starting

Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
The reaction times in the test procedure are for samples that are at 20 °C (68 °F). If the sample temperature is 10 °C (50 °F), wait 8 minutes for the first (4-minute) reaction time and 2 minutes for the second (1-minute) reaction time. If the sample temperature is 30 °C (86 °F), wait 2 minutes for the first (4-minute) reaction time and 30 seconds for the second (1-minute) reaction time.
To test for very low concentrations, use the ULR rapid liquid method for the best results.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

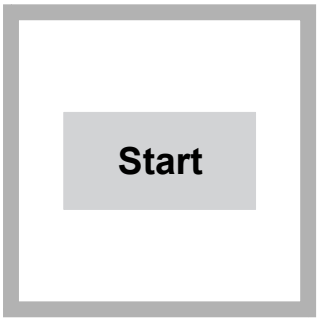
Description	Quantity
Amino Acid F Reagent powder pillows, 10-mL	1
Citric acid powder pillows, 10-mL	2
Molybdate 3 Reagent solution	1 mL
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

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

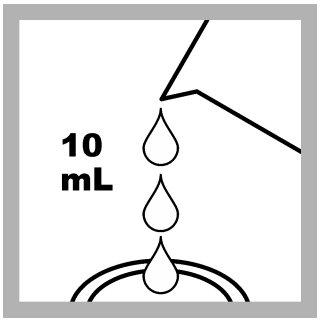
Sample collection

- Collect samples in clean plastic bottles with tight-fitting caps. Do not use glass bottles, which will contaminate the sample.
- Analyze the samples as soon as possible for best results.
- If prompt analysis is not possible, keep the samples at or below 6 °C (43 °F) for up to 28 days.
- Let the sample temperature increase to room temperature before analysis.

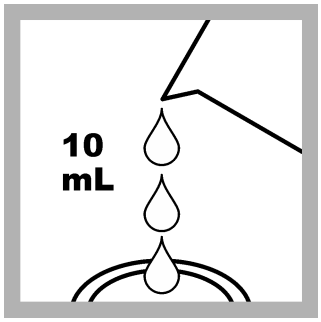
Powder pillow procedure



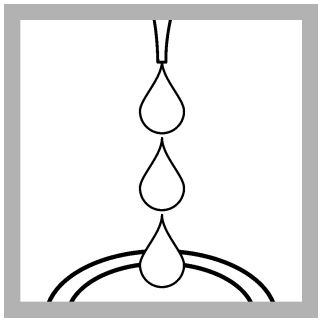
1. Start program **651 Silica LR**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



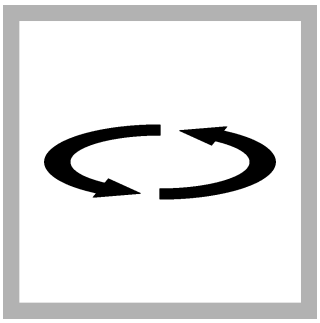
2. Prepare the blank: Fill a sample cell with 10 mL of sample.



3. Prepare the sample: Fill a second sample cell with 10 mL of sample.

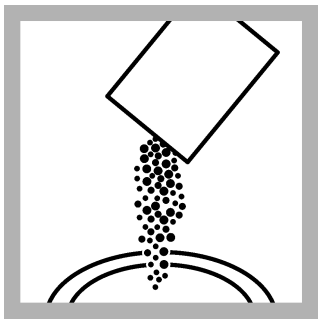


4. Add 14 drops of Molybdate 3 reagent solution to each cell.

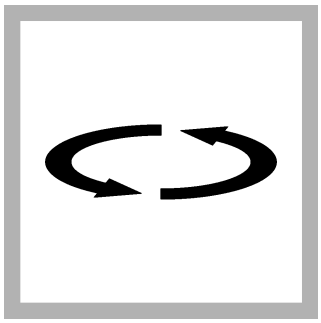


5. Swirl to mix.

6. Start the instrument timer. A 4-minute reaction time starts.



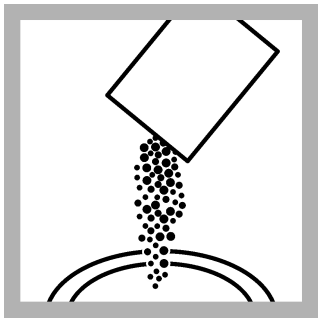
7. After the timer expires, add the contents of one Citric Acid Reagent powder pillow to each sample cell.



8. Swirl to mix.

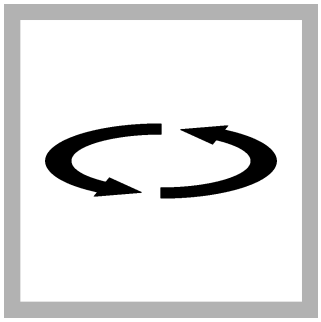
9. Start the instrument timer. A 1-minute reaction time starts.

The destruction of possible phosphate interference occurs during this period.



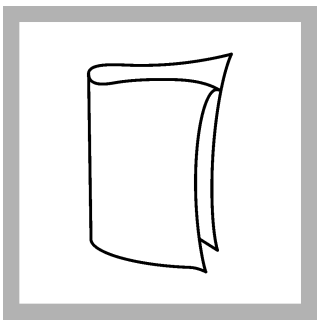
10. After the timer expires, add the contents of one Amino Acid F Reagent powder pillow to the prepared sample cell.

Blank: The sample without the Amino Acid F Reagent is the blank.

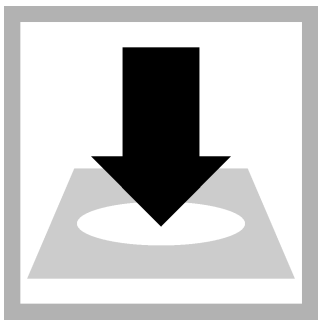


11. Swirl to mix.

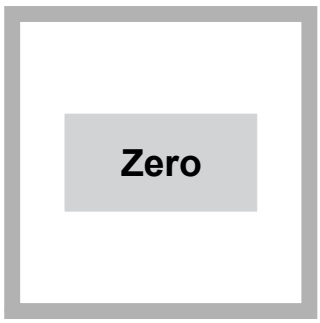
12. Start the instrument timer. A 2-minute reaction time starts.
A blue color shows if silica is present.



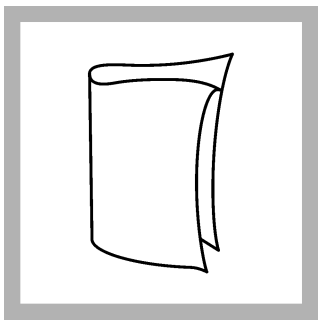
13. When the timer expires, clean the blank sample cell.



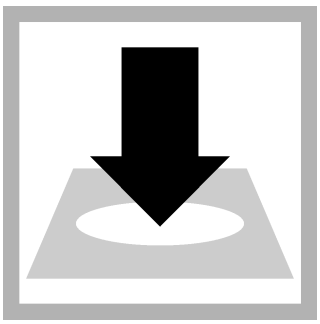
14. Insert the blank into the cell holder.



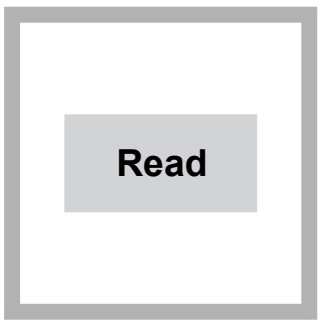
15. Push **ZERO**. The display shows 0.000 mg/L SiO_2. .



16. Clean the prepared sample cell.



17. Insert the prepared sample into the cell holder.



18. Push **READ**. Results show in mg/L SiO_2.

Interferences

Interfering substance	Interference level
Color	Does not interfere when the original sample is used to zero the instrument.
Iron	Large amounts of both ferrous and ferric iron interfere.
Phosphate	Does not interfere at levels less than 50 mg/L PO_4^{3-}. At 60 mg/L PO_4^{3-}, an interference of –2% occurs. At 75 mg/L PO_4^{3-}, the interference is –11%.

Interfering substance	Interference level
Slow reacting forms of silica	Occasionally a sample contains silica which reacts very slowly with molybdate. The nature of these "molybdate-unreactive" forms is not known. A pretreatment with sodium bicarbonate, then sulfuric acid will make these forms reactive to molybdate. The pretreatment is given in *Standard Methods for the Examination of Water and Wastewater* under Silica-Digestion with Sodium Bicarbonate. A longer reaction time with the sample and the molybdate and acid reagents (before the citric acid is added) can help as an alternative to the bicarbonate pretreatment.
Sulfides	Interfere at all levels.
Turbidity	Small amounts of turbidity do not interfere when the original sample is used to zero the instrument.

Accuracy check

Standard additions method (sample spike)

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

Items to collect:

- Silica Standard Solution, 25 mg/L SiO_2
- Pipet, TenSette®, 0.1–1.0 mL
- Pipet tips

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 10-mL portions of fresh sample. Mix well.
6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Standard solution method

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

Items to collect:

- Silica Standard Solution, 1.00-mg/L SiO_2

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

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

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
651	1.000 mg/L SiO_2	0.990–1.010 mg/L SiO_2	0.012 mg/L SiO_2

Summary of method

Silica and phosphate in the sample react with molybdate ion under acidic conditions to form yellow silicomolybdic acid complexes and phosphomolybdic acid complexes. Addition of citric acid destroys the phosphate complexes. An amino acid is then added to reduce the yellow silicomolybdic acid to an intense blue color, which is proportional to the silica concentration. The measurement wavelength is 815 nm for spectrophotometers (DR 1900: 800 nm) or 610 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Silica Reagent Set, low range, includes:	—	100 tests	2459300
Amino Acid F Reagent Powder Pillow, 10 mL	1	100/pkg	2254069
Citric Acid Powder Pillow, 10 mL	2	100/pkg	2106269
Molybdate 3 Reagent Solution	1 mL	50 mL	199526

Recommended standards and apparatus

Description	Unit	Item no.
Silica Standard Solution, 1-mg/L SiO_2	500 mL	110649
Silica Standard Solution, 25-mg/L as SiO_2	236 mL	2122531
Water, deionized	4 L	27256

Optional reagents and apparatus

Description	Unit	Item no.
Sodium Bicarbonate	454 g	77601
Sulfuric Acid Solution, 1.00 N	1000 mL	127053
Pipet, TenSette, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette Pipet, 0.1–1.0 mL	1000/pkg	2185628

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08/2019, Edition 10

Silica

DOC316.53.01130

Heteropoly Blue Method[1]

Method 8282

ULR 3 to 1000 µg/L SiO_2

Pour-Thru Cell

Scope and application: For testing trace levels of soluble silica in pure and ultrapure water.

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

Test preparation

Instrument specific table

Table 1 shows all of the instruments that have the program for this test. The table also shows sample cell and orientation requirements.

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

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Pour-Thru Kit	Adapter	Sipper Cell Kit
DR6000	The flow path is to the right.	LZV899, LZQ105 and LZQ102	—	LQV157.99.20002
DR3800		5940400	LZV585 (B)	—
DR2800		5940400	LZV585 (B)	—
DR2700		5940400	LZV585 (B)	—
DR1900		LZV899	—	—
DR5000	The flow path is toward the user.	LZV479	—	—
DR3900		LZV899	—	LQV157.99.10002

Before starting

Refer to the instrument documentation for Pour-Thru cell and module assembly and installation. Make sure to install the Pour-Thru cell correctly.
To protect the Pour-Thru Cell from contamination when not in use, invert a small beaker over the top of the glass funnel.
Refer to Clean the labware on page 5 and to Clean the Pour-Thru Cell on page 5 to clean the Pour-Thru Cell and all labware.
Refer to Prepare the reagents on page 4 to prepare the Amino Acid F Reagent.
The reaction times in the test procedure are for samples that are at 20 °C (68 °F). If the sample temperature is 10 °C (50 °F), wait 8 minutes for the first (4-minute) reaction time and 2 minutes for the second (1-minute) reaction time. If the sample temperature is 30 °C (86 °F), wait 2 minutes for the first (4-minute) reaction time and 30 seconds for the second (1-minute) reaction time.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Description	Quantity
Amino Acid F Reagent Solution	1
Citric Acid F Reagent	1
Molybdate 3 Reagent	1

Items to collect (continued)

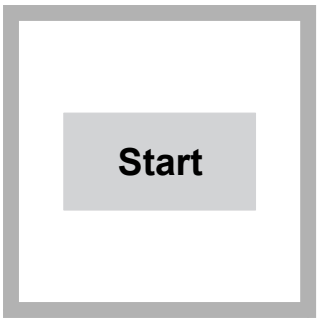
Description	Quantity
Cylinder, graduated, 50 mL, polypropylene	1
Flask, Polymethylpentene, screw cap, 250-mL	2
Pipet, TenSette, 0.1–1.0 mL	1
Pipet tips, for TenSette Pipet, 0.1–1.0 mL	2
Pour-Thru cell kit (refer to Table 1 on page 1)	1

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

Sample collection

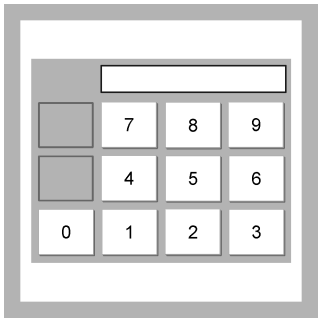
- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Collect samples in clean plastic bottles with tight-fitting caps. Do not use glass bottles, which will contaminate the sample.
- Soak the sample containers for several hours in a solution of one part Molybdate 3 Reagent to 50 parts of high quality deionized water of low silica concentration. Fully rinse with low-level silica water, drain and close. Repeat this cleaning periodically.
- Make sure to get a representative sample. It the sample is taken from a spigot or faucet, let the water flow for at least 1 or 2 minutes. Do not adjust the flow because this can add particulates.

Test procedure



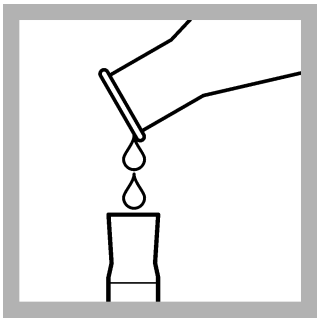
1. Start program **645 Silica ULR**. For information about sample cells, adapters or light shields, refer to Table 1 on page 1.

2. Set the reagent blank option to on to automatically subtract the reagent blank value from the sample results.

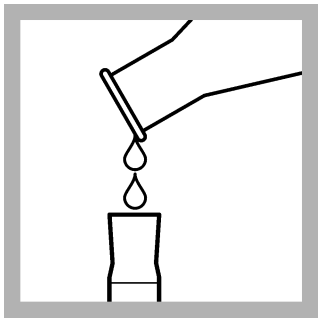


3. Enter the reagent blank value. The value is printed on the Molybdate 3 reagent label.

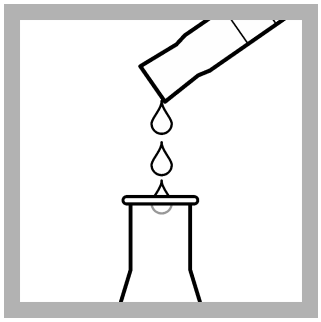
4. Fill two clean 250-mL Erlenmeyer flasks to overflowing with sample.



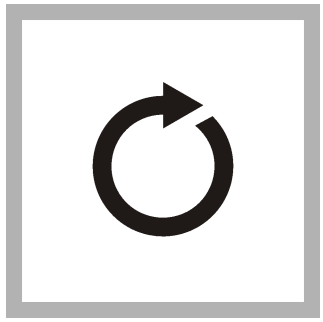
5. Fill a clean 50-mL plastic graduated cylinder with sample from one of the flasks. Then discard the contents of the cylinder. Do this procedure three times.



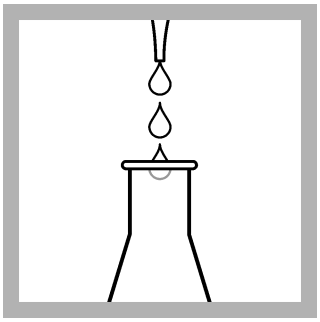
6. Fill the rinsed cylinder to the 50-mL mark with sample from the same flask. Discard any remaining sample in the flask.



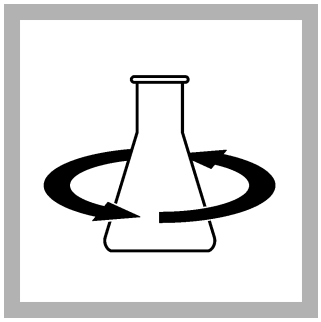
7. Pour the contents of the 50-mL cylinder back into the original flask.



8. Do steps 5 to 7 again for the second sample flask.

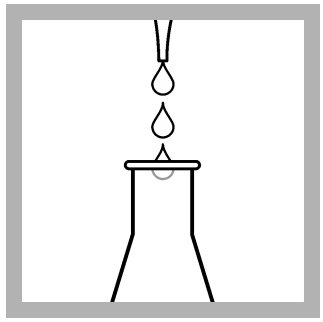


9. Use a TenSette Pipet to add 1.0 mL of Molybdate 3 Reagent to each flask.

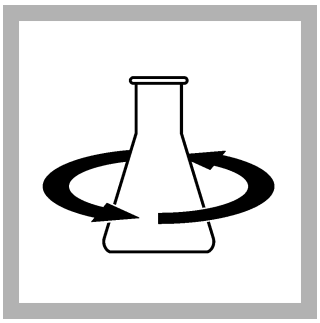


10. Swirl to mix.

11. Start the instrument timer. A 4-minute reaction time starts.

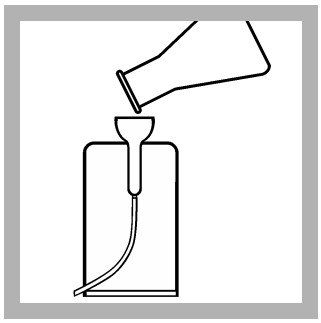


12. When the timer expires, add 1.0 mL of Citric Acid F Reagent to each flask.

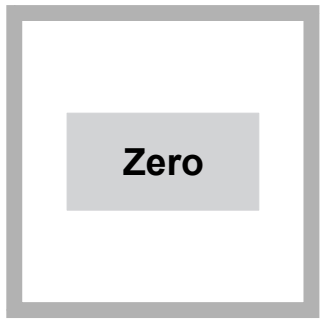


13. Swirl to mix.

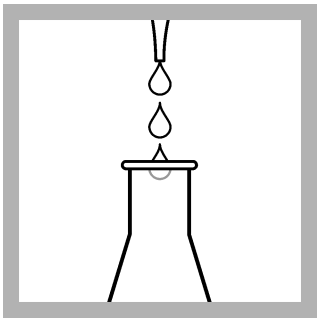
14. Start the instrument timer. A 1-minute reaction time starts.
The destruction of possible phosphate interference occurs during this period.



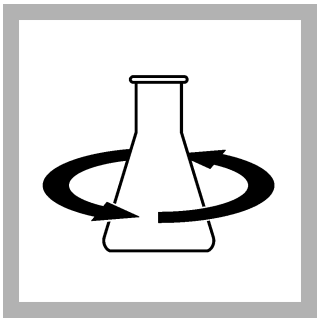
15. When the timer expires, pour the contents of one flask into the Pour-Thru Cell.



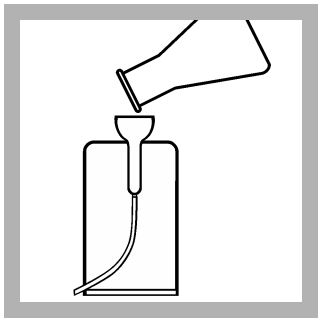
16. When the flow stops, push **ZERO**. The display shows 0 µg/L SiO_2.



17. Add 1.0 mL of Amino Acid F Reagent to the remaining flask.

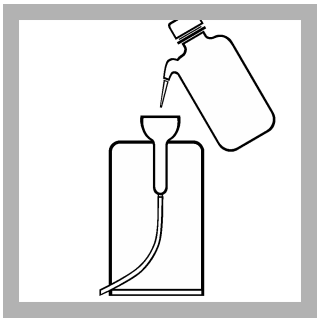


18. Swirl to mix.
A faint blue color forms if silica is in the sample.



19. Wait at least 15 seconds, then pour the contents of the second flask into the Pour-Thru Cell.

20. Push **READ**. Results show in µg/L SiO_2.



21. Flush the Pour-Thru Cell with at least 50-mL of deionized water immediately after use.

Interferences

Interfering substance	Interference level
Color	Eliminated by zeroing the instrument with the blank (follow procedure).
Iron	Interferes at high levels.
pH (extreme)	Adjust pH to less than 7.
Phosphate (PO_4^{3-})	Interferes at levels greater than 50 mg/L PO_4^{3-}.
Sulfides	Interfere at all levels.
Turbidity	Eliminated by zeroing the instrument with the blank (follow procedure).

Prepare the reagents

Amino Acid F Reagent Solution is available in 100-mL bottles or a package of 20 unit-dose ampules. The bottled reagent is stable for maximum of 1 year if the bottle is kept closed when not in use. The reagent ampule is sealed under argon and is more stable with a shelf life of more than 1 year.

Prepare other volumes of Amino Acid F Reagent as follows:

1. Dissolve the contents of one bottle of Amino Acid F Reagent Powder in one bottle of Amino Acid Reagent Dilution Solvent. These reagents are available as the Amino Acid F Reagent Package.
2. Install a bottle-top dispenser on the Amino Acid F, Molybdate 3 and Citric Acid Reagent bottles for fast reagent addition.
3. As an alternative, larger or smaller volumes can be prepared. Dissolve Amino Acid F Reagent Powder in Amino Acid F Reagent Solvent at a ratio of 11 grams per 100 mL of reagent solvent.

This reagent has a limited stability. Verify the test performance routinely with the 1-mg/L (1000 µg/L) Silica Standard Solution. Reduced sensitivity at high concentrations (1000 µg/L) indicates reagent instability. If the measured concentration is less than 950 µg/L, prepare fresh Amino Acid F Reagent Solution.

Clean the labware

Fully clean all containers that are used in this test to remove any traces of silica. Use plastic containers for all analysis and storage because glass can contaminate the sample with silica. Small bottles or flasks with screw-type closures work well.

1. Clean containers (do not use phosphate detergents), then rinse with high quality deionized water of low-level silica concentration.
2. Soak for 10 minutes with a 1:50 dilution of Molybdate 3 Reagent in low-level silica water.
3. Rinse repeatedly with either low-level silica water or the sample before use. Keep containers tightly closed when not in use.
4. Fill the Pour-Thru Cell with this same mixture of Molybdate 3 and water. Soak for 10 minutes.
5. Rinse with low-level silica water.

Clean the Pour-Thru Cell

The Pour-Thru Cell can collect a buildup of products with color, especially if the reacted solutions stay in the cell for long periods of time after measurement.

1. Rinse the Pour-Thru Cell with a 1:5 dilution of ammonium hydroxide solution to remove the color.
2. Fully rinse with deionized water.
3. Put a cover on the Pour-Thru Cell funnel when it is not in use.

Accuracy check

Standard additions method (sample spike)

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

Items to collect:

- 1-mg/L (1000-µg/L) Silica standard
- TenSette Pipet and Pipet tips
- 250-mL plastic Erlenmeyer flasks (3x)

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.2 mL, 0.4 mL and 0.6 mL of the standard solution, respectively, to three 50 mL portions of fresh sample. Mix well.
6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Standard solution method

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

Items to collect:

- 500-µg/L SiO_2 standard solution

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

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

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
645	500 µg/L silica	496–504 µg/L silica	13 µg/L silica

Summary of method

A number of modifications are necessary to adapt the Low Range Silica method for analyzing trace levels in the Ultra Low Range method. It is absolutely necessary to use the 1-inch Pour-Thru Cell and liquid reagents. The Pour-Thru Cell increases the reproducibility of the optics and reduces the instability of the readings that result from moveable sample cells. Liquid reagents produce more reproducible readings and lower blank values by eliminating slight turbidity that can remain with powdered reagents.

Silica and phosphate in the sample react with molybdate ions under acidic conditions to form yellow silicomolybdic acid complexes and phosphomolybdic acid complexes. Addition of citric acid destroys the phosphate complexes. Amino Acid F Reagent is then added to reduce the yellow silicomolybdic acid to an intense blue color, which is proportional to the silica concentration. The measurement wavelength is 815 nm for spectrophotometers (DR 1900: 800 nm).

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
ULR Silica Reagent Set (using Amino Acid F solution, 100 tests) includes:			2553500
Molybdate 3 Reagent Solution	2 mL	100 mL	199532
Citric Acid Reagent Solution	2 mL	100 mL	2254232
Amino Acid F Reagent	1 mL	100 mL	2386442
ULR Silica Reagent Set (using Amino Acid F ampules, 40 tests) includes:			2581400
Molybdate 3 Reagent Solution	2 mL	100 mL	199532
Citric Acid Reagent Solution	2 mL	100 mL	2254232
Amino Acid F Reagent, 1.2-mL ampule	1	20/pkg	2386420

Required apparatus

Description	Quantity/test	Unit	Item no.
Cylinder, graduated, 50 mL, polypropylene	1	each	108141
Flask, Polymethylpentene, screw cap, 250 mL	1	each	2089846
Pipet, TenSette, 0.1–1.0 mL	1	each	1970001
Pipet tips, for TenSette Pipet, 0.1–1.0 mL	2	50/pkg	2185696

Recommended standards

Description	Unit	Item no.
Silica Standard Solution, 1-mg/L SiO_2	500 mL	110649
Silica Standard Solution, 500-µg/L as SiO_2	3.78 L	2100817

Optional reagents and apparatus

Description	Unit	Item no.
Water, deionized	4 L	27256
Ammonium Hydroxide, 58%	500 mL	10649
Citric Acid Reagent Solution	500 mL	2254249
Molybdate 3 Reagent Solution	500 mL	199549
Molybdate 3 Reagent Solution	1 L	199553
PourRite Ampule Breaker, 2 mL	each	2484600
Sampling bottle with cap, low density polyethylene, 500 mL	12/pkg	2087079
Thermometer, non-mercury, –10 to +225 °C	each	2635700

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 10/2018, Edition 9

Sulfate

DOC316.53.01316

SulfaVer 4 Method[1]

Method 10248

2 to 70, 20 to 700, 200 to 7000 mg/L SO_4^{2-}

Powder Pillows

Scope and application: For brine solutions, produced waters and hydraulic fracturing waters.

[1] Adapted from *Standard Methods for the Examination of Water and Wastewater*, SM4500-SO_4^{2-}E.

Test preparation

Instrument-specific information

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

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

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR6000 DR3800 DR2800 DR2700 DR1900	The fill line is to the right.	2495402 
DR5000 DR3900	The fill line is toward the user.	
DR900	The orientation mark is toward the user.	2401906 

Before starting

For turbidimetric methods, install the instrument cap or cover on all instruments before ZERO or READ is pushed.
Use the Standard Adjust option with each new lot of reagent for the best results. Refer to the Standard solution method in Accuracy check on page 4.
For the best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to determine the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option.
Filter samples that are turbid with filter paper and a funnel.
Do not use the Pour-Thru Cell or sipper module (for applicable instruments) with this test.
The reagents that are used in this test contain barium chloride. Collect the reacted samples for safe disposal.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

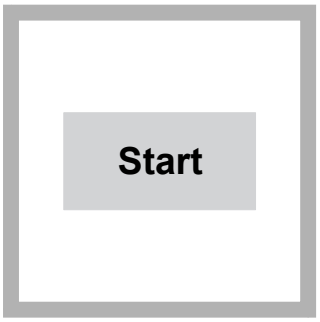
Description	Quantity
SulfaVer® 4 Reagent Powder Pillows, 10-mL	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	1

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

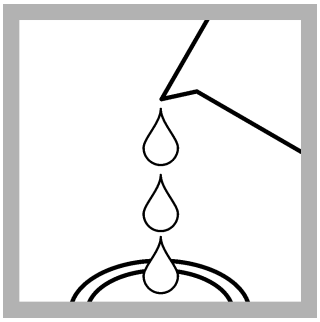
Sample collection and storage

- Collect samples in clean glass or plastic bottles.
- To preserve samples for later analysis, keep the samples at or below 6 °C (43 °F) for up to 28 days.
- Let the sample temperature increase to room temperature before analysis.

Powder pillow procedure



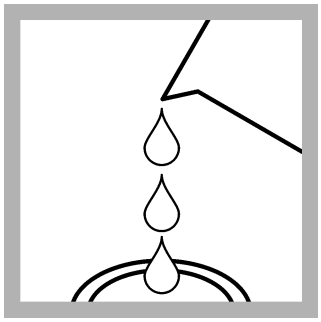
1. Start program **680 Sulfate**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



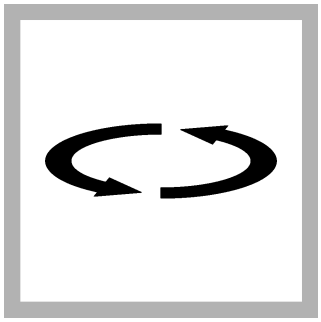
2. Add the sample volume that is specified for the test range to a sample cell:

- 2–70 mg/L: 10 mL
- 20–700 mg/L: 1.0 mL
- 200–7,000 mg/L: 0.1 mL

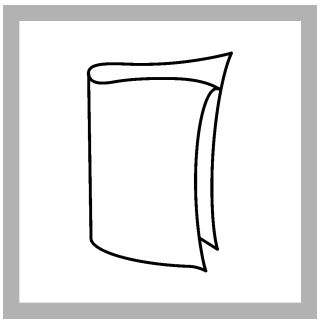
Use a TenSette Pipet or glass pipet to measure 0.1 mL or 1.0 mL.



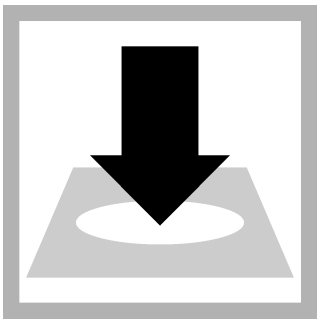
3. If the sample volume is less than 10-mL add deionized water to the 10-mL line.
For the dilution factor, refer to Set the dilution factor on page 3.



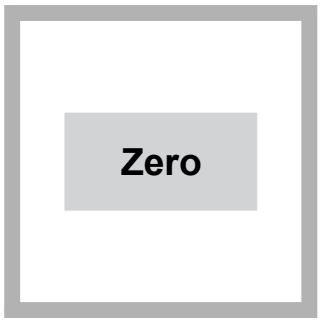
4. Swirl to mix.



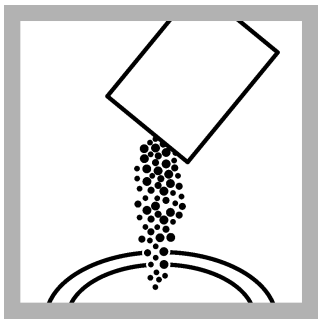
5. Clean the blank sample cell.



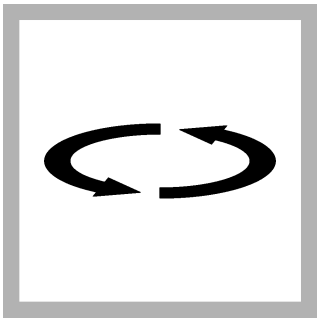
6. Insert the blank into the cell holder.



7. Push **ZERO**. The display shows 0 mg/L SO_4^{2-}.



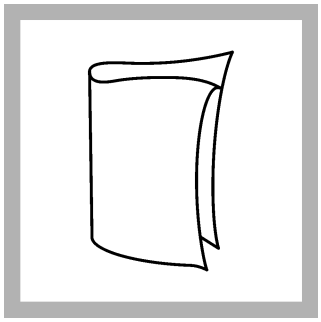
8. Add the contents of one SulfaVer 4 Reagent Powder Pillow to the sample cell. The sample will get cloudy if sulfate is present in the sample.



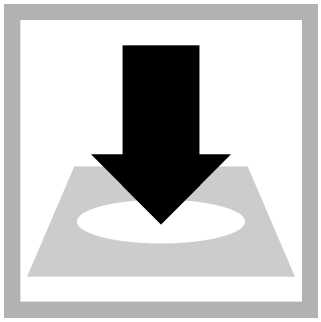
9. Swirl the sample cell to mix. Undissolved powder will not affect accuracy.

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

Do not move the sample cell during the reaction period.

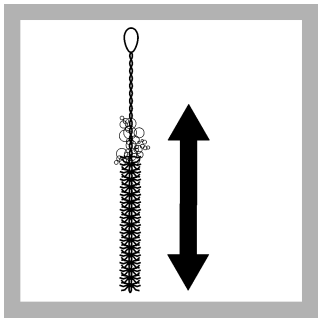


11. Clean the prepared sample cell.



12. Within 5 minutes after the timer expires, insert the prepared sample into the cell holder.

13. Push **READ**. Results show in mg/L SO_4^{2-}.



14. Clean the sample cell immediately after each test with soap, water and a brush.

Interferences

Interfering substance	Interference level
Barium	Interferes at all levels. The higher the relative barium concentration when compared to the sulfate concentration, the higher the error. Samples with high barium concentrations will generally give a result that is 20% lower than the actual sulfate concentration.
Calcium	More than 20,000 mg/L as $CaCO_3$
Chloride	More than 40,000 mg/L as Cl^-
Magnesium	More than 10,000 mg/L as $CaCO_3$
Silica	More than 500 mg/L SiO_2

Set the dilution factor

Instruments that have a dilution factor option can include the dilution factor in the result and show the concentration of the original, undiluted sample. For example, if the sample is diluted by a factor of 10, the instrument multiplies the result by 10 and shows the calculated result in the instrument display.

1. Select **Options>More>Dilution** factor from the instrument menu.

   Note: *DR1900: Select* ***Options>Advanced Options>Dilution Factors>On****.*

   Note: *Colorimeters include a dilution factor when the chemical form is set. Go to* ***Options>Advanced Options>Chemical Form*** *and select LR, MR or HR.*

2. Enter the dilution factor:

   - 1 mL sample diluted to 10 mL: dilution factor is 10.
   - 0.1 mL sample diluted to 10 mL: dilution factor is 100.

3. Push **OK** to confirm. Push **OK** again.
4. Push **RETURN** to go back to the measurement screen.

Accuracy check

Standard additions method (sample spike)

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

Items to collect:

- Sulfate Ampule Standard Solution, 2500 mg/L sulfate
- Ampule breaker
- Pipet, TenSette®, 0.1–1.0 mL and tips
- Mixing cylinders (3x), 25 mL

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 25-mL portions of fresh sample. Mix well.
6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Standard solution method

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

Items to collect:

- Sulfate standard solution, 1000 mg/L
- 100-mL volumetric flask, Class A
- 5-mL volumetric pipet, Class A and pipet filler safety bulb
- Deionized water

1. Prepare a 50 mg/L sulfate standard solution as follows:
   a. Use a pipet to add 5.0 mL of 1000 mg/L sulfate standard solution into the volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
2. Use the test procedure to measure the concentration of the prepared standard solution.
3. Compare the expected result to the actual result.

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

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
680	40 mg/L SO_4^{2-}	30–50 mg/L SO_4^{2-}	0.4 mg/L SO_4^{2-}

Summary of method

Sulfate ions in the sample react with barium in the SulfaVer 4 and form a precipitate of barium sulfate. The amount of turbidity formed is proportional to the sulfate concentration. The measurement wavelength is 450 nm for spectrophotometers or 520 nm for colorimeters.

Pollution prevention and waste management

Reacted samples contain barium and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
SulfaVer 4 Reagent Powder Pillow[1], 10-mL	1	100/pkg	2106769

Recommended standards

Description	Unit	Item no.
Sulfate Standard Solution, 1000-mg/L as SO_4^{2-}	500 mL	2175749
Sulfate Standard Solution, 2500-mg/L, 10-mL ampules as SO_4^{2-}	16/pkg	1425210

Optional reagents and apparatus

Description	Unit	Item no.
Mixing cylinder, graduated, 25 mL	each	189640
Mixing cylinder, graduated, 50 mL	each	189641
Ampule Breaker, 10-mL Voluette Ampules	each	2196800
Pipet, volumetric 5.00 mL	each	1451537
Pipet filler	1	1465000
Pipet, TenSette, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet, TenSette, 1.0–10.0 mL	each	1970010
Pipet tips for TenSette Pipet, 1.0–10.0 mL	50/pkg	2199796
Flask, volumetric, Class A, 100 mL, glass	each	1457442

[1] SulfaVer is a registered trademark of Hach Company.

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FAX: (970) 669-2932

10/2019, Edition 11

Sulfide, HR

DOC316.53.01319

Methylene Blue Method[1]

Method 10254

0.01 to 0.70, 0.1 to 7.0, 1 to 70 mg/L S^{2-}

Reagent Solution

Scope and application: For brine solutions, produced waters and hydraulic fracturing waters.

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

Test preparation

Instrument-specific information

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

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

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR6000 DR3800 DR2800 DR2700 DR1900	The fill line is to the right.	2495402 
DR5000 DR3900	The fill line is toward the user.	
DR900	The orientation mark is toward the user.	2401906 

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
Some sulfide loss can occur if dilution is necessary.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Description	Quantity
Sulfide 1 Reagent	1–2 mL
Sulfide 2 Reagent	1–2 mL
Pipet or mechanical pipettor (appropriate sample and reagent size)	1

Items to collect (continued)

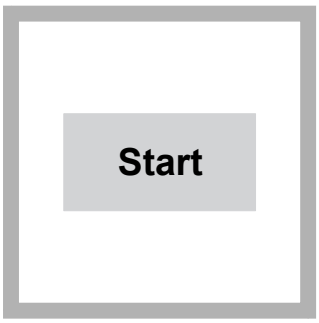
Description	Quantity
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2
Stoppers	2
Water, deionized	10 mL

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

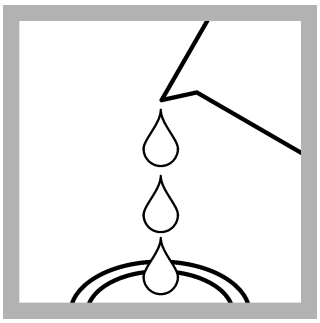
Sample collection

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Collect samples in clean glass or plastic bottles with tight-fitting caps. Completely fill the bottle and immediately tighten the cap.
- Prevent agitation of the sample and exposure to air.

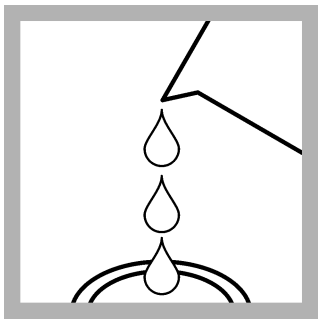
Methylene Blue method



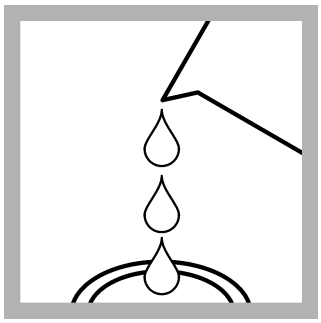
1. Start program **691 Sulfide HR**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



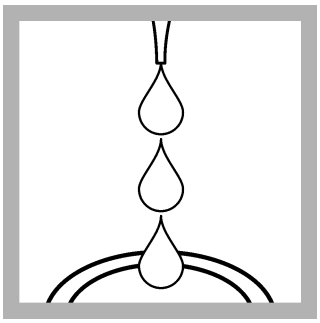
2. Prepare the blank: Fill a sample cell with deionized water. Use 10 mL for spectrophotometers and 25 mL for colorimeters.



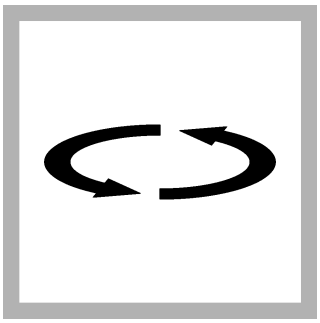
3. Prepare the sample: Add the sample volume that is specified for the test range to a clean sample cell. Refer to Table 2 on page 3.
Use a pipet to measure small volumes.



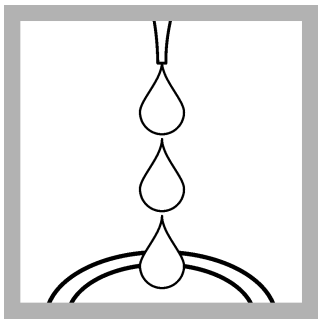
4. Spectrophotometers: Add deionized water to the 10-mL line. **Colorimeters:** Add deionized water to the 25-mL line.
To prevent sulfide loss, do not mix the sample more than necessary.



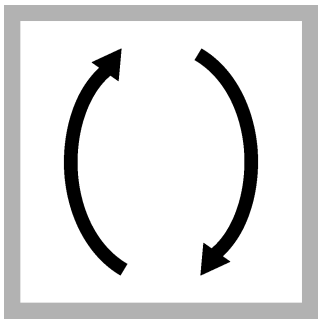
5. Add Sulfide 1 Reagent to each sample cell. Use 0.5 mL of reagent for spectrophotometers. Use 1.0 mL of reagent for colorimeters.



6. Swirl to mix.

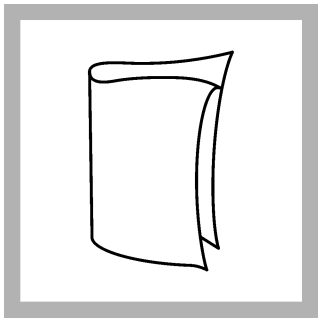


7. Add Sulfide 2 Reagent to each sample cell. Use 0.5 mL of reagent for spectrophotometers. Use 1.0 mL of reagent for colorimeters.

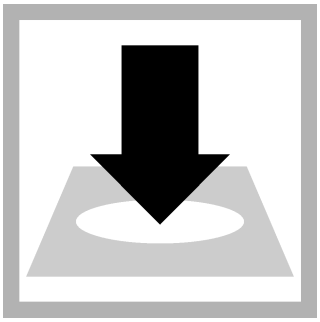


8. Put the stopper on both sample cells with a stopper. Invert to mix. The solution shows pink and then blue if sulfide is in the sample.

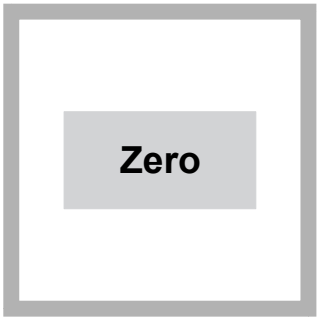
9. Start the instrument timer. A 5-minute reaction time starts.



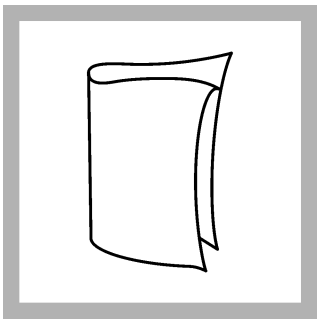
10. When the timer expires, clean the blank sample cell.



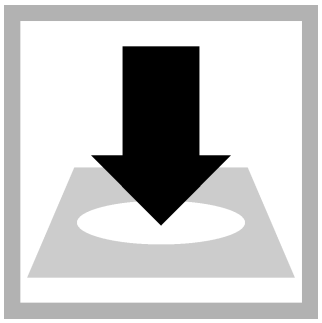
11. Insert the blank into the cell holder.



12. Push **ZERO**. The display shows 0 mg/L S^{2-}.



13. Clean the prepared sample cell.



14. Insert the prepared sample into the cell holder.

15. Push **READ**. Results show in mg/L S^{2-}.

Select a sample volume

Table 2 Sample volumes and ranges

Range	Spectrophotometer volume	Colorimeter volume
0.01–0.70 mg/L (LR)	10 mL	25 mL
0.1–7.0 mg/L (MR)	1.0 mL	2.5 mL
1–70 mg/L (HR)	0.1 mL	0.25 mL

Set the dilution factor

Instruments that have a dilution factor option can include the dilution factor in the result and show the concentration of the original, undiluted sample. For example, if the sample is diluted by a factor of 10, the instrument multiplies the result by 10 and shows the calculated result in the instrument display.

1. Select **Options>More>Dilution** factor from the instrument menu.

   Note: *DR1900: Select* ***Options>Advanced Options>Dilution Factors>On****.*

   Note: *Colorimeters include a dilution factor when the chemical form is set. Go to* ***Options>Advanced Options>Chemical Form*** *and select LR, MR or HR.*
2. Enter the dilution factor:
   - 1 mL sample diluted to 10 mL: dilution factor is 10.
   - 0.1 mL sample diluted to 10 mL: dilution factor is 100.
3. Push **OK** to confirm. Push **OK** again.
4. Push **RETURN** to go back to the measurement screen.

Soluble sulfides

To measure soluble sulfides, use a centrifuge to separate the solids. To make an estimate of the amount of insoluble sulfides in the sample, subtract the soluble sulfide concentration from the total (with solids) sulfide concentration.

1. Fill a centrifuge tube completely with sample and immediately cap the tube.
2. Put the tube in a centrifuge and run the centrifuge to separate the solids.
3. Use the supernatant as the sample in the test procedure.

Interferences

Interfering substance	Interference level
Barium	Concentrations more than 20 mg/L barium react with the sulfuric acid in Sulfide 1 Reagent and form a $BaSO_4$ (barite) precipitate. To correct for this interference: 1. Dilute the sample in the test procedure as follows: • Spectrophotometers: use a 0.1-mL or 1.0-mL sample volume and add deionized water to the 10-mL mark. • Colorimeters: use a 0.25-mL or 2.5-mL sample volume and add deionized water to the 25-mL mark. 2. Add both Sulfide 1 and Sulfide 2 reagents per the procedure steps. 3. After the 5-minute reaction period, pour the sample into a 50-mL beaker. 4. Pull the sample into a Luer-Lock syringe (10 cc for spectrophotometers or 60 cc for colorimeters). 5. Put a 0.45-µm filter disc on the Luer-Lock tip and filter the sample into a clean sample cell for measurement. Use deionized water to prepare the blank. 6. Set the instrument zero and read the result, per the procedure steps. 7. Multiply by the appropriate dilution factor for the dilution used (10 or 100).
Strong reducing substances such as sulfite, thiosulfate and hydrosulfite	Prevent the full color development or reduce the blue color
Sulfide, high levels	High concentrations of sulfide can inhibit the full color development. Use a diluted sample in the test procedure. Some sulfide loss can occur when the sample is diluted.
Turbidity	Pre-treat the sample to remove sulfide, then use the pre-treated sample as the blank in the test procedure. Prepare a sulfide-free blank as follows: 1. Measure 25 mL of sample into a 50-mL Erlenmeyer flask. 2. Add 30-g/L Bromine Water by drops with constant swirling until a yellow color remains. 3. Add 30-g/L Phenol Solution by drops with constant swirling until the yellow color is removed. 4. Use this solution to replace the deionized water blank in the test procedure.

Accuracy check

Standard solution method

Sulfide standard solutions are not stable and must be prepared by the user. Refer to Standard Methods, 4500S^{2-} for preparation and standardization instructions.

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
691	0.52 mg/L S^{2-}	0.50–0.54 µg/L S^{2-}	0.005 mg/L S^{2-}

Summary of method

Hydrogen sulfide and acid-soluble metal sulfides react with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration. High sulfide levels in oil field waters may be

determined after proper dilution. The measurement wavelength is 665 nm for spectrophotometers or 610 nm for colorimeters.

Pollution prevention and waste management

Reacted samples contain hexavalent chromium and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Water, deionized	varies	4 L	27256
Sulfide Reagent Set	—	—	2244500
Includes:			
Sulfide 1 Reagent	1–2 mL	100 mL MDB	181632
Sulfide 2 Reagent	1–2 mL	100 mL MDB	181732

Required apparatus

Description	Quantity/test	Unit	Item no.
Pipet, TenSette, 0.1–1.0 mL	1	each	1970001
Pipet tips, for TenSette Pipet, 0.1–1.0 mL	2	50/pkg	2185696
Pipet, TenSette 1.0–10.0 mL	1	each	1970010
Pipet tips, for TenSette Pipet, 1.0–10.0 mL	varies	50/pkg	2199796
Pipet, adjustable volume, 0.2–1.0 mL	1	each	BBP078
Pipet tips, for 0.2–1.0 mL pipet	2	100/pkg	BBP079
Pipet, adjustable volume, 1.0–5.0 mL	1	each	BBP065
Pipet tips, for 1.0–5.0 mL pipet	1	75/pkg	BBP068

Optional reagents and apparatus

Description	Unit	Item no.
Beaker, 50 mL	each	50041H
Bromine Water, 30 g/L	29 mL	221120
Mixing cylinder, graduated, 10 mL	each	2088638
Flask, Erlenmeyer, 50 mL	each	50541
Phenol Solution, 30-g/L	29 mL	211220
Pipet, serological, 10 mL	each	53238
Pipet filler, safety bulb	each	1465100
Syringe, 10 cc, Luer-Lock tip	each	2202400
Syringe, 60 cc, Luer-Lock tip	1	2258700
Syringe filter, 0.45 µm, 33 mm PVDF	50/pkg	2513603

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07/2014, Edition 11

Sulfite

DOC316.53.01181

Iodate-Iodide Method

Method 8216

4 to more than 400 mg/L as SO_3^{2-}

Digital Titrator

Scope and application: For boiler water.

Test preparation

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Let the sample temperature decrease to 50 °C (122 °F) or less before analysis.
Sulfite reacts quickly with oxygen in the air. Shaking or swirling the sample causes low results. Prevent agitation of the sample during the procedure.
As an alternative to the Dissolved Oxygen 3 Reagent Powder Pillow, use 0.5 mL of 19.2 N Sulfuric Acid Standard Solution.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

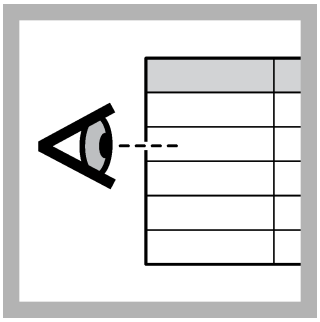
Description	Quantity
Dissolved Oxygen 3 Reagent Powder Pillows	1
Iodate-Iodide Titration Cartridge, 0.3998 N	1
Starch Indicator Solution	1 full dropper
Clippers	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (use a size that is applicable to the selected sample volume)	1
Erlenmeyer flask, 125 mL	1
Water, deionized	varies

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

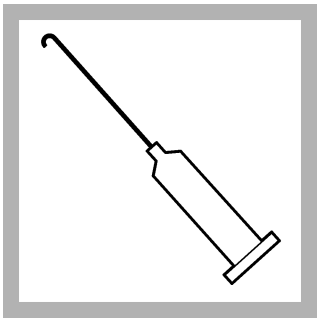
Sample collection

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Collect samples in clean glass or plastic bottles with tight-fitting caps. Completely fill the bottle and immediately tighten the cap.
- If the sample temperature is more than 50 °C (122 °F), decrease the sample temperature to 50 °C (122 °F) or lower before analysis.
- Prevent agitation of the sample and exposure to air.

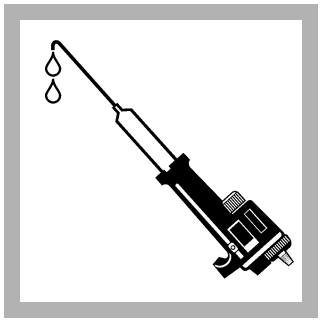
Test procedure



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

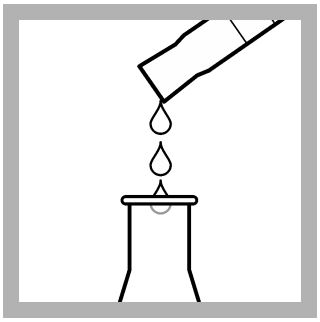


2. Insert a clean delivery tube into the Iodate-Iodide Titration Cartridge. Attach the cartridge to the Digital Titrator.

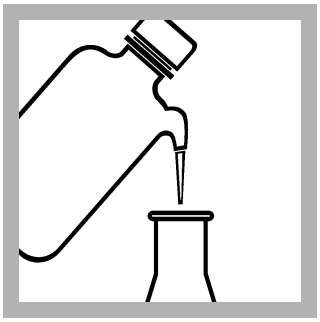


3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.

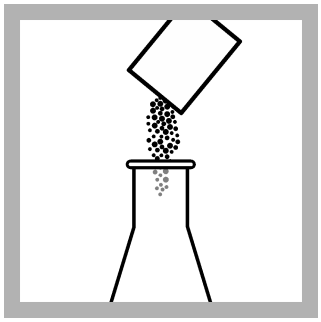
4. Use a graduated cylinder to measure the sample volume from Table 1 on page 3.



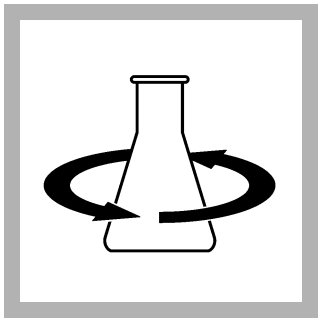
5. Pour the sample into a clean, 125-mL Erlenmeyer flask.



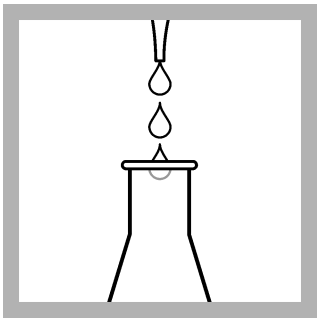
6. If the sample volume is less than 50 mL, dilute to approximately 50 mL with deionized water.



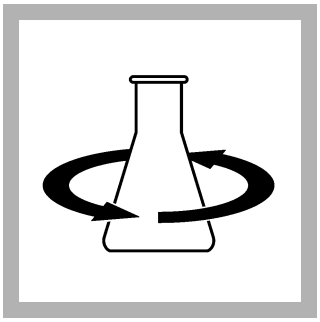
7. Add the contents of one Dissolved Oxygen 3 Reagent Powder Pillow.



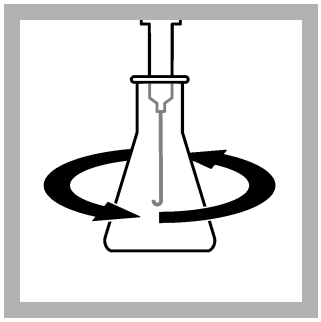
8. Swirl to mix.



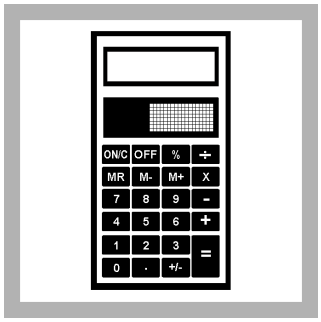
9. Add 1 mL of Starch Indicator Solution.



10. Swirl to mix.



11. Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes to a permanent blue color. Record the number of digits on the counter.



12. Use the multiplier in Table 1 on page 3 to calculate the concentration. Digits used × digit multiplier = mg/L sulfite SO_3^{2-}.

Sample volumes and digit multipliers

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

Example: A 50-mL sample was titrated with the 0.3998 N Iodate-Iodide Titration Cartridge and the counter showed 250 digits at the endpoint. The concentration is 250 digits x 0.4 = 100 mg/L sulfite SO_3^{2-}.

Table 1 Sample volumes and digit multipliers

Range (mg/L as SO_3^{2-})	Sample volume (mL)	Titration cartridge	Digit multiplier
a maximum of 160	50	0.3998 N KIO_3–KI	0.4
100–400	20	0.3998 N KIO_3–KI	1
200–800	10	0.3998 N KIO_3–KI	2
more than 400	5	0.3998 N KIO_3–KI	4

Conversions

To change the units or chemical form of the test result, multiply the test result by the factor in Table 2.

Table 2 Conversions

mg/L sulfite (SO_3^{2-}) to...	multiply by:	Example
mg/L bisulfite, hydrogen sulfite (HSO_3^-)	1.01	200 mg/L SO_3^{2-} x 1.01 = 202 mg/L HSO_3^-
mg/L sodium bisulfite, sodium hydrogen sulfite ($NaHSO_3$)	1.30	200 mg/L SO_3^{2-} x 1.30 = 260 mg/L $NaHSO_3$
mg/L sodium metabisulfite, sodium pyrosulfite ($Na_2S_2O_5$)	2.37	200 mg/L SO_3^{2-} x 2.37 = 474 mg/L $Na_2S_2O_5$
mg/L sodium sulfite (Na_2SO_3)	1.58	200 mg/L SO_3^{2-} x 1.58 = 316 mg/L Na_2SO_3

Interferences

Table 3 shows the substances that can interfere with this test.

Table 3 Interferences

Interfering substance	Interference level
Metals	Some metals, especially copper, catalyze the oxidation of sulfite to sulfate. Immediately add one Sulfamic Acid Powder Pillow or one Dissolved Oxygen 3 Powder Pillow for each liter of sample during sample collection to prevent the interference.
Nitrite	Reacts with sulfite and causes low results.
Organic compounds	Oxidizable organic compounds can cause high results.
Oxidizable compounds	Cause high results.
Sulfide	Causes high results.

Accuracy check

Standard additions method (sample spike)

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

Items to collect:

- Sulfite Voluette Ampule Standard, 5,000-mg/L SO_3^{2-}
- Ampule Breaker
- Pipet, TenSette, 0.1–1.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the sample.
2. Use a TenSette pipet to add 0.1 mL of the standard solution to the titrated sample.
3. Titrate the spiked sample to the endpoint. Record the number of digits on the counter.
4. Add one more 0.1-mL addition of the standard solution to the titrated sample.
5. Titrate the spiked sample to the endpoint. Record the number of digits on the counter.
6. Add one more 0.1-mL addition of the standard solution to the titrated sample.
7. Titrate the spiked sample to the endpoint. Record the number of digits on the counter.
8. Compare the actual result to the correct result. The correct result for this titration is 25 digits of the 0.3998 N Iodate-Iodide Titration Cartridge for each 0.1-mL addition of the standard solution. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

Standard solution method

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

Items to collect:

- Sodium Thiosulfate Standard Solution, 0.025 N
- 250-mL volumetric flask, Class A
- 10.0-mL volumetric pipet, Class A and pipet filler safety bulb
- Deionized water

1. Prepare a 40-mg/L sulfite-equivalent standard solution as follows:
   a. Use a pipet to add 10.0 mL of a 0.025 N sodium thiosulfate standard solution to the volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
2. Use the test procedure to measure the concentration of the prepared standard solution. Use 50 mL of the prepared standard solution.
3. Compare the actual result to the correct result. If much more or less titrant was used, there can be a problem with user technique, reagents or apparatus.

Summary of Method

The water sample is acidified and titrated with a potassium iodide-iodate standard solution. The acid releases free iodine, which is reduced to colorless iodide by the sulfite in the sample. When all of the sulfite is gone, the iodine reacts with the starch indicator to form a blue color.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Sulfite Reagent Set (approximately 100 tests):	—	each	2272300
Dissolved Oxygen 3 Reagent Powder Pillows	1	100/pkg	98799
Iodate-Iodide Titration Cartridge, 0.3998 N	varies	each	1496101
Starch Indicator Solution	1 dropperful	100 mL MDB	34932
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity/test	Unit	Item no.
Clippers for plastic pillows	1	each	96800
Cylinder, graduated, 5 mL	1	each	50837

Required apparatus (continued)

Description	Quantity/test	Unit	Item no.
Cylinder, graduated, 10 mL	1	each	50838
Cylinder, graduated, 25 mL	1	each	50840
Cylinder, graduated, 50 mL	1	each	50841
Digital Titrator	1	each	1690001
Delivery tube for Digital Titrator, J-hook tip	1	5/pkg	1720500
Flask, Erlenmeyer, 125 mL	2	each	50543

Recommended standards

Description	Unit	Item no.
Sulfite Equivalent Standard Solution, 10-mL Voluette® Ampule, 5,000-mg/L as SO_3^{2-}	16/pkg	2267410
Sulfite Equivalent Standard Solution, 15 mg/L as SO_3^{2-}	500 mL	2408449
Sodium Thiosulfate Standard Solution, 0.025 N	1 L	2409353

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette Ampules	each	2196800
Flask, volumetric, Class A, 250 mL	each	1457446
Pipet, volumetric, Class A, 10 mL	each	1451538
Pipet filler, safety bulb	each	1465100
Pipet, TenSette, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette Pipet, 0.1–1.0 mL	50/pkg	2185696
Sulfuric Acid Standard Solution, 19.2 N	100 mL	203832
TitraStir Titration Stand, 115 VAC	each	1940000
TitraStir Titration Stand, 230 VAC	each	1940010
Delivery tube for Digital Titrator, 90-degree bend for use with TitraStir Titration Stand	5/pkg	4157800

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12/2014, Edition 9

Solids, Total

DOC316.53.01203

USEPA Gravimetric Method[1, 2] Method 8271

Scope and application: For potable, surface and saline water and for domestic and industrial wastewater, brine solutions, produced waters and hydraulic fracturing waters.

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

Test preparation

Before starting

If applicable, use the test result in Method 8276—Solids, Total Volatile and Fixed
Dry the aluminum dishes at 103–105 °C for 1 hour. Keep dried dishes in a desiccator.
For larger samples, use a steam bath and evaporating dishes as an alternative to the aluminum dishes.

Items to collect

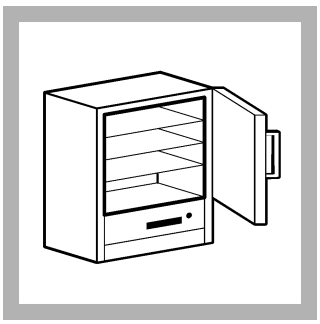
Description	Quantity
Weighing dish, aluminum	1
Drying oven	1
Cylinder, graduated, 50 mL	1
Desiccator with desiccant	1
Analytical balance	1
Tongs	1

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

Sample collection and storage

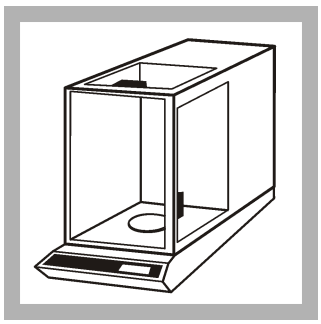
- Collect samples in clean glass or plastic bottles.
- To preserve samples for later analysis, keep the samples at or below 6 °C (43 °F) for up to 7 days.
- Let the sample temperature increase to room temperature before analysis.

Test procedure

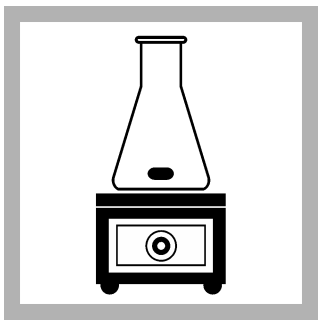


1. Put an aluminum dish in a drying oven at 103–105 °C (217–221 °C) for 1 hour.

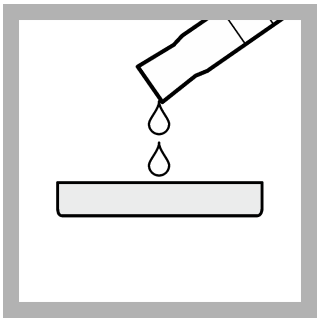
2. Remove the dish from the oven. Let the dish temperature decrease to room temperature in a desiccator.



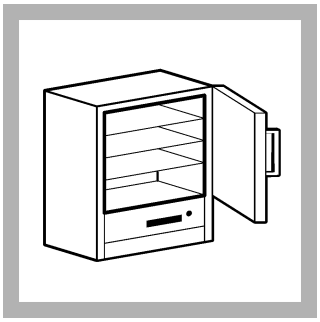
3. Use an analytical balance to weigh the dish to the nearest 0.1 mg (0.0001 g). Record this mg value as B.



4. Mix the sample. Use a blender or a beaker with stir bar and stir plate to mix the sample.



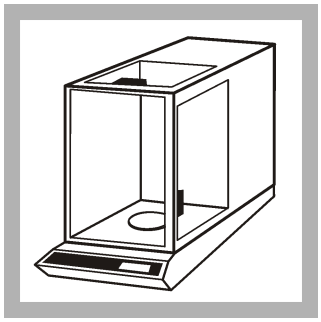
5. Use a graduated cylinder to add 50 mL of sample to the aluminum dish.



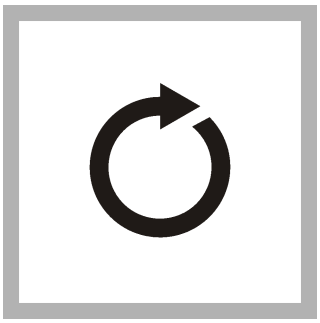
6. Put the sample in a preheated oven. Dry at 103–105 °C for approximately 6 hours. More time can be necessary for high mineralized water.

Note: *For larger samples, use a steam bath and an evaporating dish as an alternative to the drying oven. After the sample is dried on the steam bath, dry the dish to constant weight in a 103–105 °C drying oven.*

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

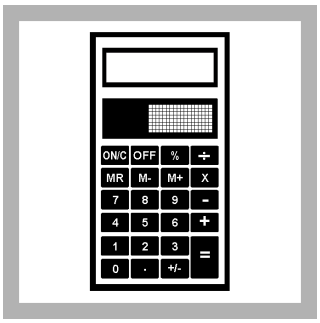


8. Use an analytical balance to weigh the dish to the nearest 0.1 mg (0.0001 g). Record this mg value as A.



9. Do steps 6–8 again until results do not change more than 0.4 mg.

Successive weight results that are identical for some wastewater samples are unlikely because of slow organic volatilization.



10. Calculate the test results:

[(A – B) × 1000] ÷ mL sample = mg/L Total Solids

Where:

A = Weight (mg)[1] of sample + dish

B = Weight (mg) of dish

Note: *If applicable, continue with Method 8276 for Volatile and Fixed Solids results.*

Summary of method

A well-mixed sample is dried in a pre-weighed dish to a constant weight in an oven at 102–105 °C. The difference of weight between the empty dish and the dried dish shows the total solids of the sample.

[1] Weight in mg = grams × 1000

Consumables and replacement items

Required reagents and apparatus

Description	Quantity/test	Unit	Item no.
Balance, analytical, 115 VAC	1	each	2936801
Cylinder, graduated, 50 mL	1	each	50841
Desiccant, indicating Drierite	1	each	2088701
Desiccator, without stopcock	1	each	1428500
Desiccator plate, ceramic	1	each	1428400
Water, deionized	varies	4 L	27256
Dish, aluminum (63 x 17.5 mm)	1	100/pkg	2164000
Oven, drying, 120 VAC	1	each	1428900
Oven, drying, 240 VAC	1	each	1428902
Tongs, crucible, 9 inch	1	each	56900

Optional reagents and apparatus

Description	Unit	Item No.
Blender, 1.2 liter, 120 VAC	each	2616100
Blender, 1.2 liter, 240 VAC	each	2616102
Stirrer, magnetic	each	2881200
Digital stirring/hot plate 7 x 7 in., 230 VAC	each	2881602
Beaker, 250 mL	each	50046H
Stir bar, 22 x 8 mm	each	2095350
Steam bath, 8 inch diameter	each	2347900
Evaporating dish, porcelain, 120 mL	each	52561
Sampling bottle with cap, low density polyethylene, 500 mL	12/pkg	2087079

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02/2015, Edition 9

Suspended Solids

DOC316.53.01139

Photometric Method[1]

Method 8006

5 to 750 mg/L TSS

Scope and application: For water and wastewater.

[1] Adapted from Sewage and Industrial Wastes, 31, 1159 (1959).

Test preparation

Instrument-specific information

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

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

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR6000 DR3800 DR2800 DR2700 DR1900	The fill line is to the right.	2495402 
DR5000 DR3900	The fill line is toward the user.	
DR900	The orientation mark is toward the user.	2401906 

Before starting

For turbidimetric methods, install the instrument cap or cover on all instruments before ZERO or READ is pushed.
Do not use the Pour-Thru Cell or sipper module (for applicable instruments) with this test.

Items to collect

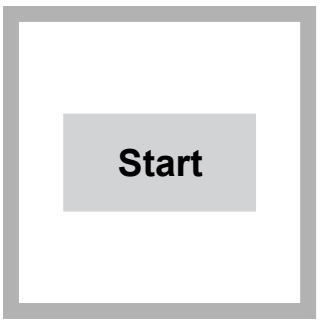
Description	Quantity
Beaker, 600-mL, polypropylene	1
Blender	1
Cylinder, 500-mL polypropylene, graduated	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

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

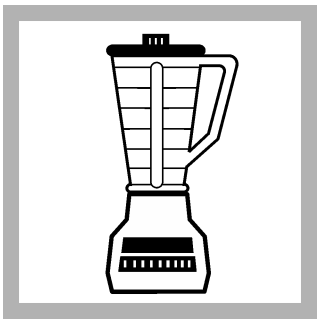
Sample collection and storage

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

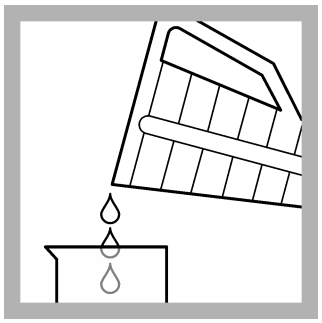
Photometric procedure



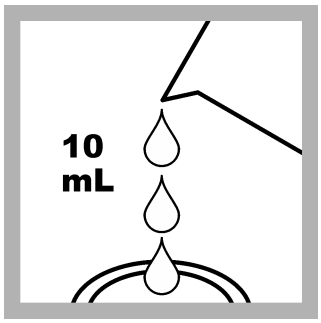
1. Start program **630 Suspended Solids**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



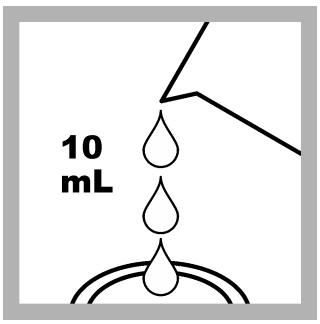
2. Blend 500 mL of sample in a blender at high speed for exactly two minutes.



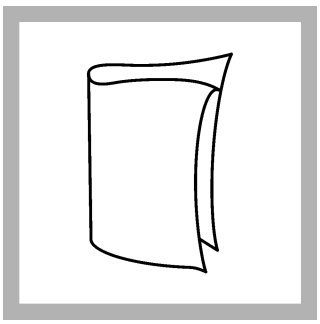
3. Pour the blended sample into a 600-ml beaker.



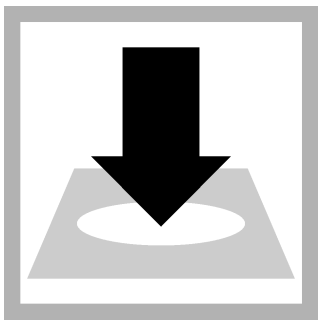
4. Prepare the sample: Stir the sample and immediately pour 10 mL of the blended sample into a sample cell.



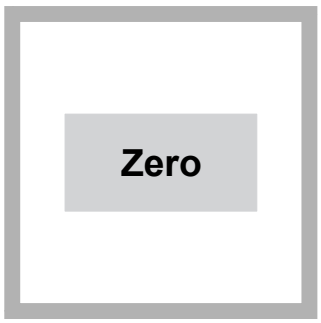
5. Prepare the blank: Fill a second sample cell with 10 mL of tap water or deionized water.



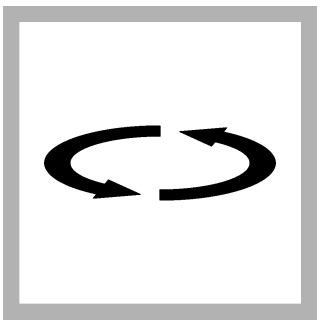
6. Clean the blank sample cell.



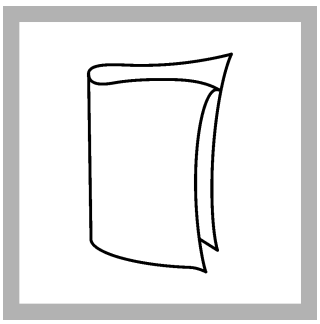
7. Insert the blank into the cell holder.



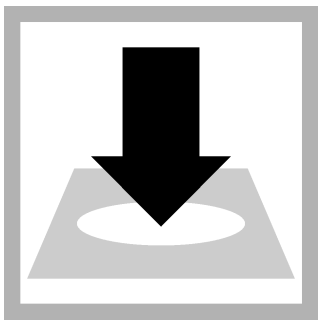
8. Push **ZERO**. The display shows 0 mg/L TSS.



9. Swirl the prepared sample to remove any gas bubbles and uniformly suspend any residue.



10. Clean the prepared sample cell.



11. Insert the prepared sample into the cell holder.

12. Push **READ**. Results show in mg/L TSS.

Interferences

Samples that absorb strongly at the measurement wavelength, such as blue dyes, may give false, high-bias readings. A user-entered calibration is advised for these samples.

Accuracy check

Standard solution method

Calibration for this test is based on the gravimetric technique with parallel sewage samples from a municipal sewage plant. For most samples, this calibration supplies satisfactory results. When higher accuracy is required, run parallel spectrophotometric and gravimetric determinations with portions of the same sample. Make the new calibration on the particular sample using a gravimetric technique as a basis.

Summary of method

This method of determining total suspended solids (TSS) is a simple, direct measurement which does not require the filtration or ignition/weighing steps that gravimetric procedures do. The USEPA specifies the gravimetric method for solids determinations, while this method is often used for checking in-plant processes. The measurement wavelength is 810 nm (DR 1900: 800 nm) for spectrophotometers or 610 nm for colorimeters.

Consumables and replacement items

Required apparatus

Description	Quantity/test	Unit	Item no.
Beaker, polypropylene, 600 mL	1	each	108052
Blender, 2-speed, 120 VAC option	1	each	2616100
Blender, 2-speed, 240 VAC option	1	each	2616102
Cylinder, graduated, 500 mL, polypropylene	1	each	108149

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01/2014, Edition 9

Tannin and Lignin

DOC316.53.01140

Tyrosine Method[1]

Method 8193

0.1 to 9.0 mg/L Tannins (as Tannic Acid)

Reagent Solution

Scope and application: For water, wastewater and boiler water.

[1] Adapted from Kloster, M.B., Journal American Water Works Association, Vol. 66, No. 1, p. 44 (1974).

Test preparation

Instrument-specific information

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

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

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR6000 DR3800 DR2800 DR2700 DR1900	The fill line is to the right.	2495402 
DR5000 DR3900	The fill line is toward the user.	
DR900	The orientation mark is toward the user.	2401906 

Before starting

Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
Measure the volume of the reagent accurately. Use a volumetric or high precision pipet if possible.
Filter samples that are turbid with filter paper and a funnel. The test results are then mg/L soluble tannic acid.
The Pour-Thru Cell can be used (for applicable instruments) if rinsed well with deionized water between the blank and the prepared samples.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

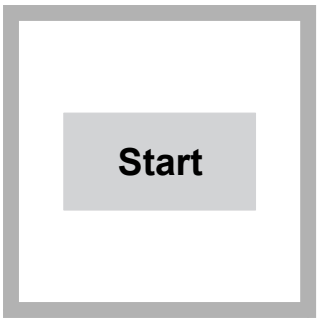
Description	Quantity
Tannin and Lignin Reagent Set:	
Sodium Carbonate Solution	10 mL
TanniVer™ 3 Tannin-Lignin Reagent	1 mL
Cylinder, graduated mixing, 25-mL	2
Pipet Filler	1
Pipet, volumetric Class A, 5.0-mL	1
Pipet, volumetric Class A, 0.5-mL	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2
Water, deionized	25 mL

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

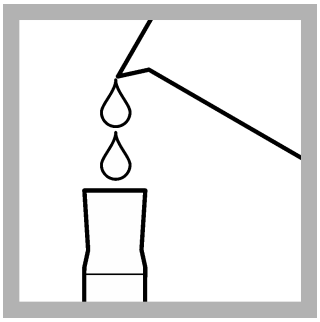
Sample collection

- Collect samples in clean glass or plastic bottles.

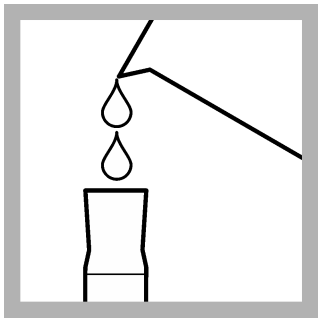
Tyrosine procedure



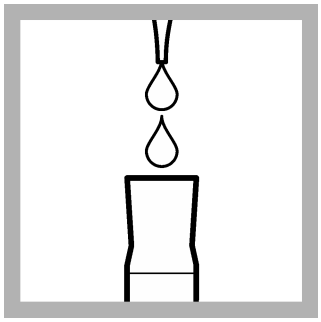
1. Start program **720 Tannin & Lignin**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



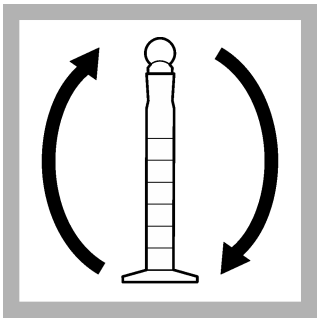
2. Prepare the blank: Fill a 25-mL mixing cylinder to the 25-mL mark with deionized water.



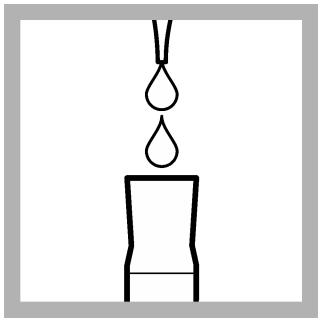
3. Prepare the sample: Fill a second 25-mL mixing cylinder to the 25-mL mark with sample.



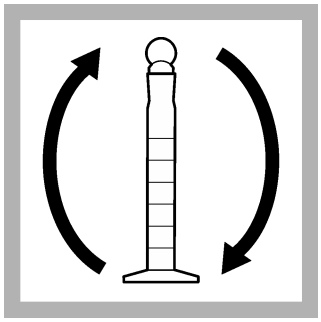
4. Pipet 0.5 mL of TanniVer™ 3 Tannin-Lignin Reagent into each cylinder.



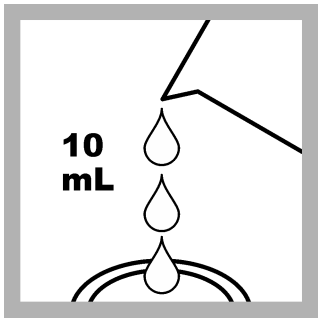
5. Close the two cylinders. Invert both cylinders several times to mix.



6. Add 5.0 mL of Sodium Carbonate Solution into each cylinder.

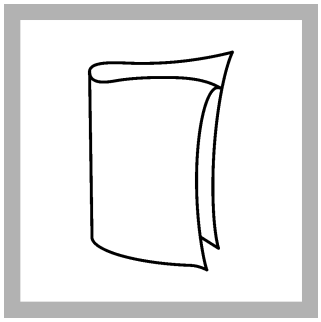


7. Close the two cylinders. Invert both cylinders several times to mix.
A blue color will develop if tannins and/or lignins are present.

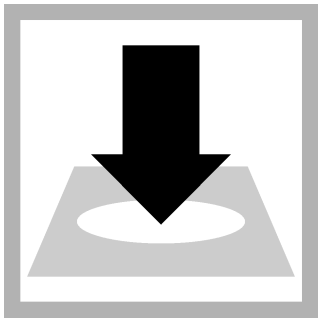


8. Pour 10 mL of each solution into two sample cells.

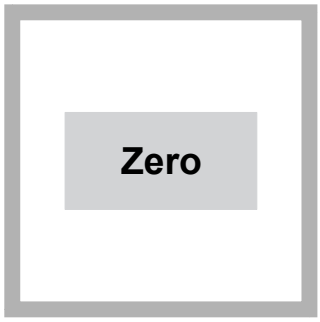
9. Start the instrument timer. A 25-minute reaction time starts.



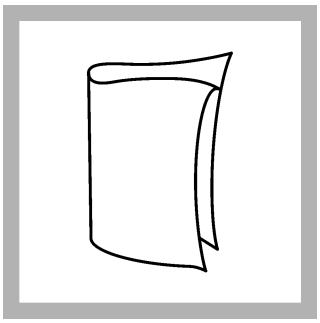
10. When the timer expires, clean the blank sample cell.



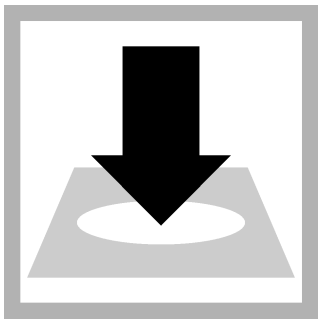
11. Insert the blank into the cell holder.



12. Push **ZERO**. The display shows 0.0 mg/L Tannins (as Tannic Acid).



13. Clean the prepared sample cell.



14. Insert the prepared sample into the cell holder.

15. Push **READ**. Results show in mg/L Tannins (as Tannic Acid).

Interferences

Interfering substance	Interference level
Ferrous iron	Causes a positive interference. (2 mg/L of ferrous iron produces a color equivalent to about 1 mg/L of tannic acid.) To remove interference of ferrous iron up to 20 mg/L, add one 0.2 g scoop of Sodium Pyrophosphate to the sample before the test.
Sulfite	To remove sulfite interference, add 1 mL of formaldehyde[1] to the sample before the sample test.

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

Accuracy check

Standard solution method

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

Items to collect:

- 0.200 g tannic acid, analytical grade
- 1-L volumetric flask, Class A
- 500-mL volumetric flask, Class A
- 15-mL volumetric pipet, Class A and pipet filler safety bulb
- Deionized water

1. Prepare a 200-mg/L tannic acid stock solution as follows:
   a. Add 0.200 g of tannic acid into a 1-L volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare the stock solution each month.
2. Prepare a 6.0 mg/L tannic acid standard solution as follows:
   a. Use a pipet to add 15.00 mL of the 200-mg/L tannic acid stock solution into a 500-mL volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare the standard solution each day.
3. Use the test procedure to measure the concentration of the prepared standard solution.
4. Compare the expected result to the actual result.

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

Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
720	6.0 mg/L tannic acid	5.8–6.2 mg/L tannic acid	0.1 mg/L tannic acid

Summary of method

This test measures all hydroxylated aromatic compounds, including tannin, lignin, phenol and cresol. This method produces a blue color proportional to the amount of these compounds in the sample. The results are reported as total tannin and lignin and expressed as mg/L tannic acid. The measurement wavelength is 700 nm for spectrophotometers or 610 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Water, deionized	varies	4 L	27256
Tannin and Lignin Reagent Set	1	Up to 100 tests	2244600

Consumables and replacement items (continued)

Description	Quantity/test	Unit	Item no.
Includes:			
Sodium Carbonate Solution	10 mL	500 mL	67549
TanniVer 3 Tannin-Lignin Reagent	1 mL	100 mL	256032

Required apparatus

Description	Quantity/test	Unit	Item no.
Mixing cylinder, graduated, 25 mL with stopper	2	each	2088640
Pipet filler, safety bulb	1	each	1465100
Pipet, volumetric, Class A, 5.00 mL	1	each	1451537
Pipet, volumetric, Class A, 0.5 mL	1	each	1451534

Recommended standards

Description	Unit	Item no.
Tannic Acid, Analytical Grade	113 g	79114

Optional reagents and apparatus

Description	Unit	Item no.
Flask, volumetric, Class A, 1000 mL glass	each	1457453
Flask, volumetric, Class A, 500 mL, glass	each	1457449
Formaldehyde, ACS	100 mL MDB	205932
Pipet, volumetric Class A, 15 mL	each	1451539
Sodium Pyrophosphate	50 g	1429525
Pipet, TenSette, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette Pipet, 0.1–1.0 mL	1000/pkg	2185628
Balance, analytical, 80 g x 0.1 mg 100–240 VAC	each	2936701
Paper, for weighing, 100 x 100 mm	500/pkg	1473885
Spatula, micro	each	1225600

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01/2014, Edition 9

TPH (Total Petroleum Hydrocarbons)

DOC316.53.01142

Immunoassay[1]

Method 10050

Scope and application: For soil, water, produced waters and hydraulic fracturing waters.

[1] This test is semi-quantitative. Results are shown as more or less than the threshold value used.

Test preparation

Instrument specific information

Table 1 shows all of the instruments that can be used for this test. The table also shows adapter requirements for the instruments that use them.

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

Table 1 Instrument-specific information

Instrument	Adapter	Light shield
DR 6000, DR 5000	—	—
DR 3900	—	LZV849
DR 3800, DR 2800, DR 2700	—	LZV646

Before starting

This method analyzes for TPH in soil or water samples. For soil analysis, do the Soil Extraction procedure before the Immunoassay procedure. For water analysis, start with the Immunoassay procedure. The test requires about 20 to 30 minutes for complete analysis.
Before the procedure starts, read the full procedure. Identify and prepare all the necessary reagents, cuvettes and other apparatus, then start the procedure.
Timing is very important in this procedure. Follow the instructions carefully.
It is very important to use a consistent technique to mix the solution in the cuvettes. Refer to Use of the 12-mm MicroCuvette rack on page 7. If the cuvettes are individually mixed, the results can be less consistent.
DR 3900, DR 3800, DR 2800 and DR 2700: Install the light shield in Cell Compartment #2 before this test is started.
Be careful with the cuvettes. A scratch on the inner or outer cuvette surfaces can cause incorrect results. Carefully clean the outer surfaces with a clean, absorbent cloth or tissue before use.
Antibody cuvettes and enzyme conjugate are made in matched lots. Do not mix reagent lots.
Keep the color developing solution out of direct sunlight to prevent deterioration.
The cuvette rack can be inverted with the cuvettes in the rack. This lets the user prepare many samples at the same time. The cuvettes stay in the rack until the results are read in the instrument.
The recommended temperature for reagent storage is 4 °C (39.2 °F). Let the reagent temperature increase to room temperature before analysis.
The Soil Extractant contains methyl alcohol, which is poisonous and flammable. Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Each reagent set has 20 antibody cuvettes. Use one antibody cuvette for each calibrator and each sample. Cuvettes are not reusable.
Use protective nitrile gloves for this procedure.

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

Items to collect

Description	Quantity
TPH Reagent Set	1
Caps, flip spout	1
Cylinder, graduated 10-mL	1
Light shield (refer to Instrument specific information on page 1)	1
Marker, laboratory	1
Pipet, TenSette, 0.1–1.0 mL	1
Pipet tips, for TenSette Pipet, 0.1–1.0-mL	1
Rack, for 12-mm Micro Cuvettes	1
Scoop, 5 g	1
Soil extraction kit	varies
Water, deionized	varies
Wipes, disposable	1
Wiretrol pipet	1

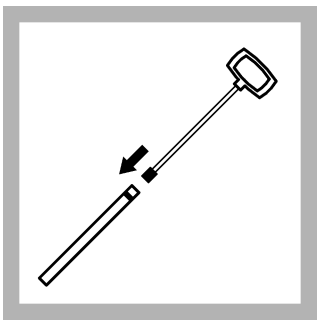
Refer to Consumables and replacement items on page 10 for order information.

Sample collection and storage

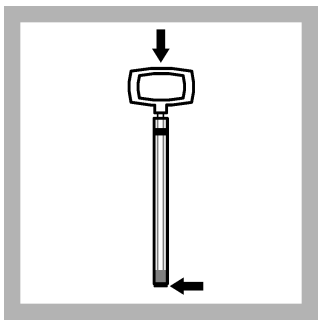
- Analyze the samples as soon as possible for best results.
- If sample storage is necessary, collect the samples in glass or PTFE containers. Clean the containers with soap and water, then rinse the containers with methanol. Use PTFE-lined caps for the containers. If PTFE-lined caps are not available, use aluminum foil as a substitute cap liner. Rinse the aluminum foil with methanol before use.
- For water samples, completely fill the container (no head space) and immediately tighten the cap.
- Keep soil samples in storage at 6 °C (43 °F) for a maximum of 14 days.
- Keep water samples in storage for a maximum of 24 hours. Put the sample in an ice bath or a refrigerator to limit the loss of volatile compounds.

Use of the Wiretrol Pipet

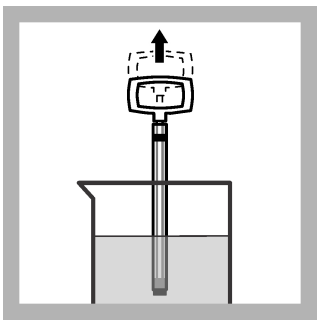
The Wiretrol Pipet accurately measures small quantities of liquids. The Wiretrol Pipet has two parts: a PTFE-tipped plunger and a calibrated capillary tube. The plunger can be used many times. Discard the capillary tubes after one use.



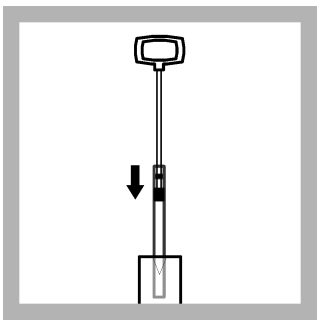
1. Make sure that the plunger tip is wet with the liquid. Carefully insert the plunger tip into the end of the capillary tube with the colored band.



2. Push the plunger tip to the other end of the capillary tube. Stop when the plunger tip barely extends beyond the end of the capillary tube.

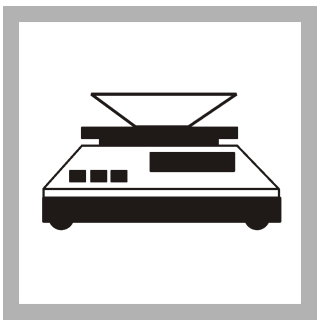


3. Insert the capillary tube below the surface of the liquid. Slowly and smoothly, pull the plunger up until the bottom of the plunger tip reaches the applicable volume line. Touch the end of the tube to the side of the vessel to release drops that remain on the capillary tube tip.

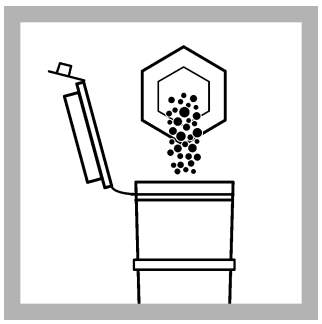


4. To release the liquid, insert the tip of the capillary tube **below the surface of the receiving solution**, and push the plunger downward in one smooth motion. Change capillary tubes for each calibrator and sample.

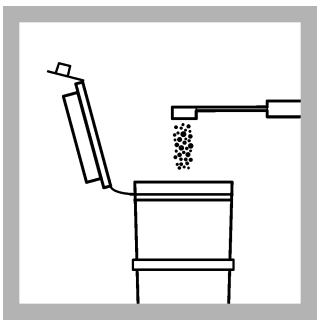
Soil extraction procedure



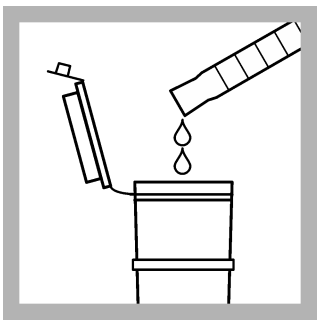
1. Weigh 10 g of soil in the plastic weighing boat.



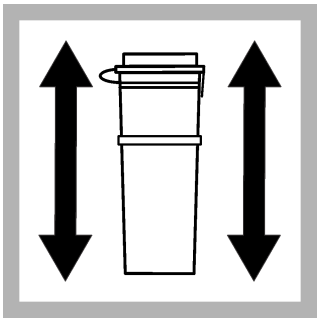
2. Carefully pour the soil into an extraction vial.



3. Use the 5-gram scoop to add one scoop of sodium sulfate to the extraction vial.

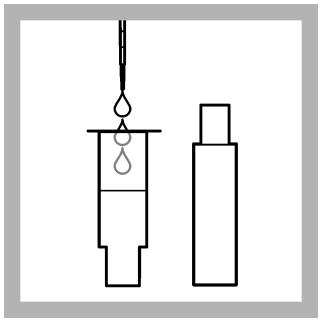


4. Use the graduated cylinder to add 10 mL of Soil Extractant into the extraction vial.

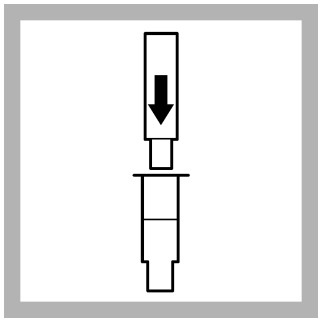


5. Put the cap on the extraction vial tightly. Shake vigorously for 1 minute.

6. Let the particles settle for a minimum of 1 minute. Carefully open the extraction vial.

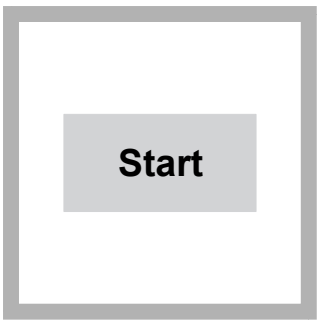


7. Use the disposable pipet to remove 1.0 to 1.5 mL from the top of the liquid layer. Add the removed liquid to the filtration barrel. Do not use more than 1.5 mL. The pipet can measure in 0.25-mL increments.

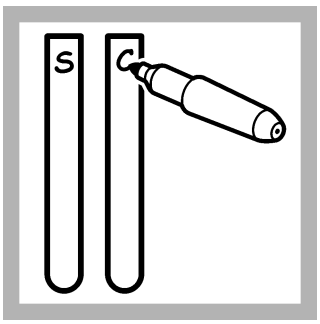


8. Put the filtration plunger into the filtration barrel. Set the filtration assembly on a table or flat surface. Push firmly on the plunger until the sample extract is forced upward into the center of the plunger.
Use the resulting filtrate for the immunoassay procedure.

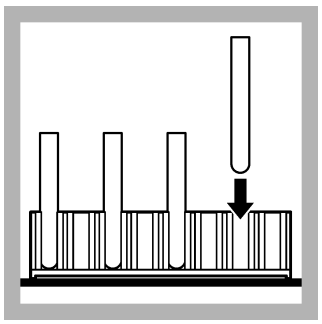
Immunoassay procedure



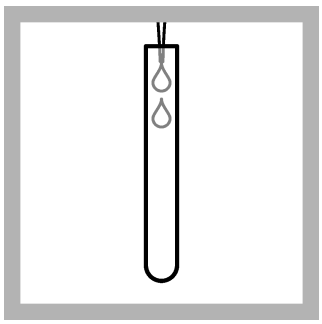
1. Push **SINGLE WAVELENGTH**>**OPTIONS**, then the **λ** key. Enter **450 nm** and push OK. For information about adapters, refer to Instrument specific information on page 1.



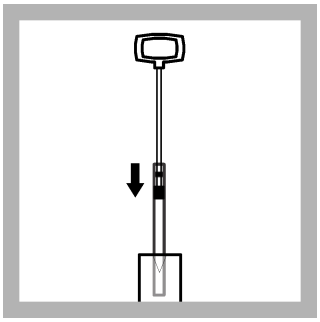
2. Put marks on the cuvettes to identify the samples and calibrators.



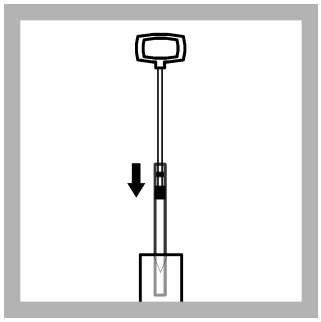
3. Insert the cuvettes into the rack. Make sure that the cuvettes are secure. Do not use force to put them into position because the cuvettes can spill or can be difficult to remove.



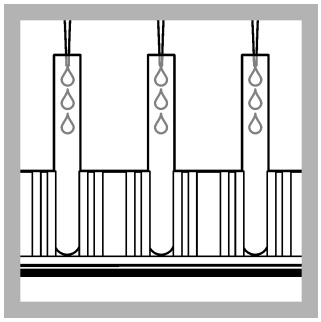
4. Soil samples: Use a pipet to add 0.5 mL of Diluent Solution into each calibrator and sample cuvette. The same pipette tip can be used for this step.
Water samples: Use a pipet to add 0.5 mL of each water sample into a sample cuvette. Use a new pipet for each sample.



5. Use the Wiretrol pipet to add 50 µL of each **calibrator** to the applicable calibrator cuvette. Mix the cuvettes after each addition. Use a separate capillary tube for each solution. **Have the necessary apparatus ready for this step and the next four steps. Do not wait—do these steps quickly.**

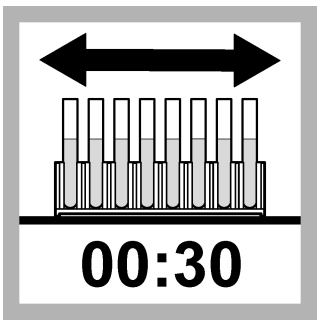


6. Soil samples: Use a Wiretrol pipet to add 50 µL of the filtered extract from the soil extraction procedure. Refer to Soil extraction procedure on page 3. Use a separate capillary tube for each solution. Mix the contents of the cuvettes after each addition.
Water samples: Use a Wiretrol pipet to add 50 µL of methanol into each sample cuvette. Mix the contents of the cuvettes after each addition.

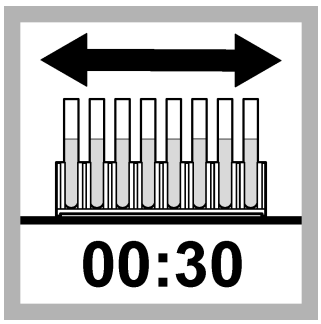


7. Immediately use a pipet to add 0.5 mL of TPH Enzyme Conjugate into each calibrator and sample cuvette. The same pipette tip can be used for this step.

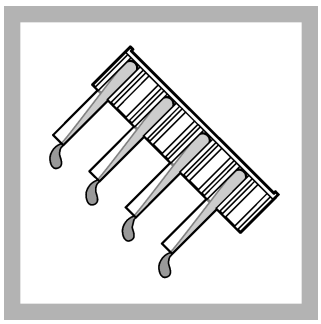
8. Start the instrument timer. The reaction time starts.



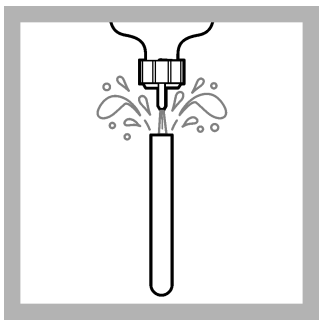
9. Immediately mix the cuvettes for 30 seconds. Refer to Use of the 12-mm MicroCuvette rack on page 7 for the correct mixing procedure.



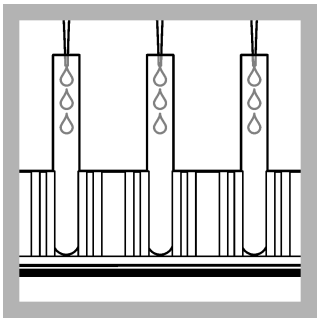
10. After 5 minutes, mix the contents of the rack a second time for 30 seconds.



11. At the end of the 10-minute reaction period, discard the contents of all the cuvettes into a waste container for disposal.

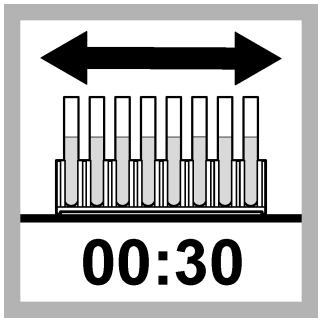


12. Fully rinse each cuvette with deionized water four times. Discard the contents into the waste container for disposal. Turn the cuvettes and rack upside down on a paper towel to dry. Carefully tap the cuvettes on the towel to remove the liquid.

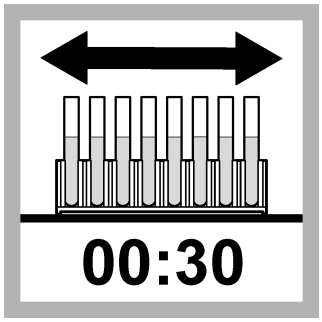


13. Start color development: Timing is very important. Make sure that the cuvettes are still in position in the rack. Use the pipet to add 0.5 mL of Color Developing Solution into each Antibody Cuvette. Use a new pipette tip for each cuvette.

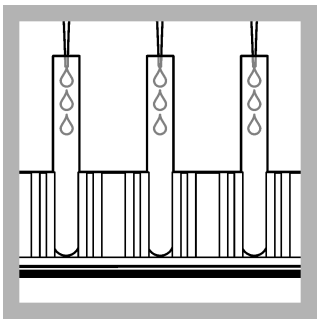
14. Start the instrument timer. The reaction time starts.



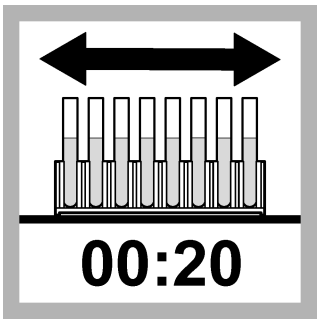
15. Immediately mix the cuvettes for 30 seconds.



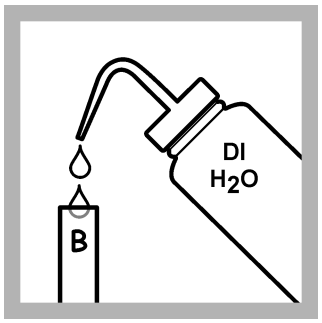
16. After 5 minutes, mix the contents of the rack a second time for 30 seconds.



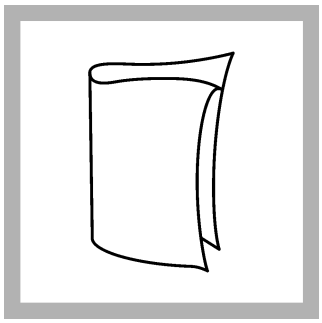
17. When the timer expires, use a pipette to add 0.5 mL of Stop Solution into each cuvette with the same pipette tip. Consistent technique is very important. Add the solution in the same sequence that was used for the Color Developing Solution addition.



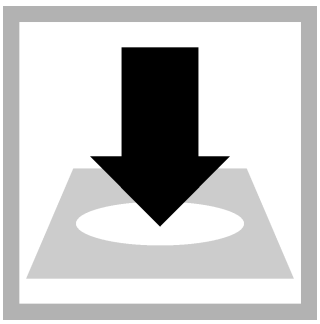
18. Slide the rack back and forth for 20 seconds. The blue solution color changes to yellow.



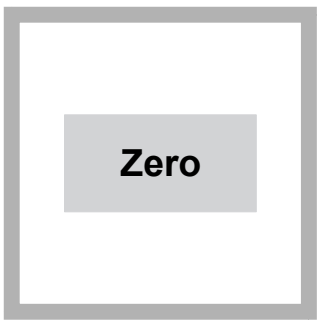
19. Put a mark on a zeroing cuvette to identify it as the blank. Fill the cuvette with deionized water.



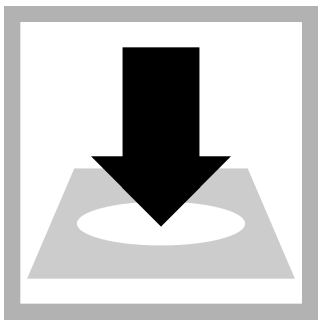
20. Clean all of the cuvettes.



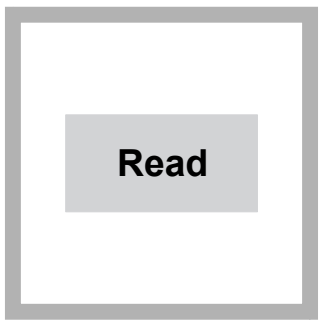
21. Insert the blank into the circular cell holder.



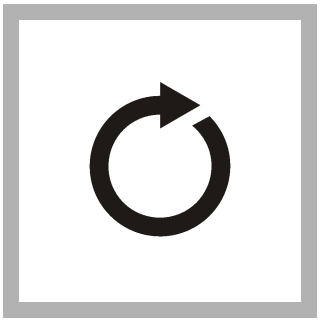
22. Push **ZERO**. The display shows 0.000 Abs.



23. Insert the first calibrator into the circular cell holder.



24. Push **READ**. Results show in Abs. Record the result.



25. Read the absorbance values of the remaining calibrators and samples. Record the results. Refer to Interpret and report the results on page 8.

Interferences

Interfering substance	Interference level
Chlorine (water samples only)	Interferes above 2 ppm. To remove chlorine from the sample, add 1 drop of 0.1 N sodium thiosulfate per 100 mL of sample.

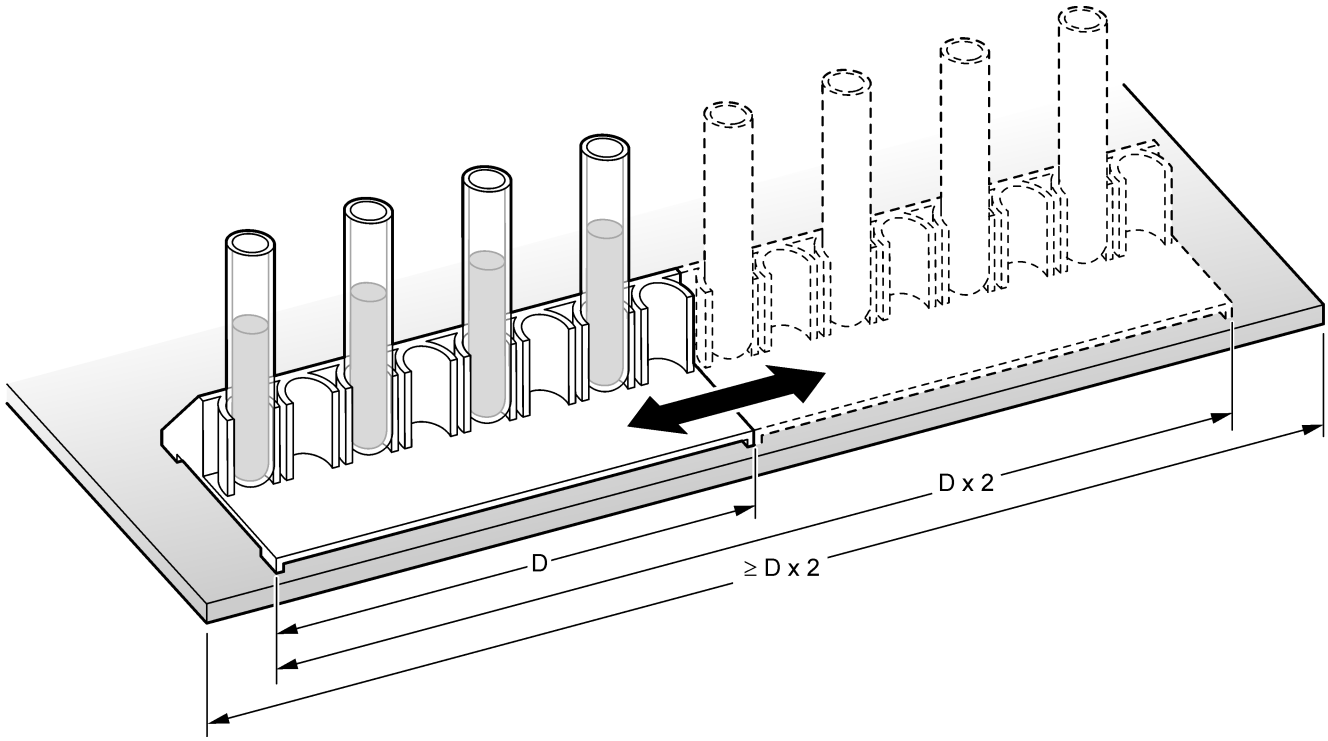
Use of the 12-mm MicroCuvette rack

Use the MicroCuvette rack to get accurate and precise results for the immunoassay procedure during the analysis of several samples at a time. Refer to Figure 1.

Insert the cuvettes in the rack—Use the MicroCuvette rack to securely hold cuvettes that are set in the rack. Before the procedure starts, identify each cuvette with a sample or a calibrator number. Correctly insert the cuvettes in the rack. Do not force the cuvettes into the rack because the sample can spill or the cuvettes can be difficult to remove. The cuvettes must stay in position if the rack is inverted and carefully tapped.

Mix the sample—Put the rack on a hard, flat surface that is at least twice the length of the rack. Refer to Figure 1. Hold one end of the rack, then vigorously slide the rack back and forth along its axis for 30 seconds. The rack moves through a distance equal to its own length in each direction.

Figure 1 MicroCuvette rack



Interpret and report the results

There is an inverse relationship between the concentration of TPH and the absorbance reading. In other words, the higher the reading, the lower the concentration of TPH. Refer to Table 2.

Table 2 Relative TPH concentration

If the sample absorbance reading is...	then the sample concentration is...
Smaller than the calibrator reading	Larger than the calibrator reading
Larger than the calibrator reading	Smaller than the calibrator reading

For example, if the readings are:

- TPH Calibrator 1 (20 ppm as diesel fuel): 0.480 Abs
- TPH Calibrator 2 (50 ppm as diesel fuel): 0.360 Abs
    - Sample 1: 0.200 Abs
    - Sample 2: 0.400 Abs
    - Sample 3: 0.550 Abs

The interpretation for a soil sample:

- Sample 1: The sample reading is smaller than the readings for both calibrators. The sample concentration of TPH is larger than 50 ppm diesel fuel.
- Sample 2: The sample reading is between the readings for the calibrators. The sample concentration of TPH is between 20 ppm and 50 ppm diesel fuel.
- Sample 3: The sample reading is larger than the readings for both calibrators. The sample concentration of TPH is smaller than 20 ppm diesel fuel.

The interpretation for a water sample:

- Sample 1: The sample reading is smaller than the readings for both calibrators. The sample concentration of in the sample is larger than 5 ppm diesel fuel.
- Sample 2: The sample reading is between the readings for the calibrators. The sample concentration of TPH is between 2 and 5 ppm diesel fuel.

- Sample 3: The sample reading is larger than the readings for both calibrators. The sample concentration of TPH is smaller than 2 ppm diesel fuel.

Reagent storage and handling

1. Always wear gloves and eyewear for protection.
2. For long-term storage, make sure that the reagents are not in direct sunlight. Keep the reagent set at 4 °C (39.2 °F) when not in use. Warm the reagents to room temperature before use.
3. When not in use, seal the foil pouch that contains the antibody cuvettes.
4. If the Stop Solution is in contact with the eyes, rinse fully for 15 minutes with cold water and get immediate medical help.

Sensitivity

The antibodies used in the TPH Test Kit react with a variety of compounds found in petroleum fuels. Each TPH calibrator is formulated to show a known concentration of diesel fuel. Refer to Table 3 and Table 4 to use calibrators for other TPH compounds.

For example, to use the TPH calibrators for gasoline, find "Gasoline" in the correct table column. Then, read across the row to find the ppm of that hydrocarbon for each calibrator. For gasoline, TPH calibrator 1 = 15 ppm, TPH calibrator 2 = 35 ppm, etc.

Table 3 TPH compounds in soil

Compound	TPH calibrator 1 (ppm)	TPH calibrator 2 (ppm)	TPH calibrator 3 (ppm)	TPH calibrator 4 (ppm)
Diesel fuel	20	50	100	200
Gasoline	15	35	70	140
Kerosene	35	75	140	250
Benzene	20	45	85	160
Toluene	15	30	50	90
Ethylbenzene	5	15	35	75
m-Xylene	9	20	35	70
o-Xylene	10	20	40	80
p-Xylene	3	5	9	16
BTEX	5	15	25	45

Table 4 TPH compounds in water

Compound	TPH calibrator 1 (ppm)	TPH calibrator 2 (ppm)	TPH calibrator 3 (ppm)	TPH calibrator 4 (ppm)
Diesel fuel	2	5	10	20
Gasoline	1.5	3.5	4	14
Kerosene	3.5	7.5	14	24
Benzene	2	4.5	8.5	16
Toluene	1.5	3	5	9
Ethylbenzene	0.5	1.5	3.5	7.5
m-Xylene	0.9	2	3.5	7
o-Xylene	1	2	4	8
p-Xylene	0.3	0.5	0.9	16
BTEX	0.5	1.5	2.5	4.5

Dilute a water sample

For higher levels of TPH in water than those shown in Table 4 on page 9, dilute the sample with deionized water. To dilute a sample, refer to Table 5, then add that sample volume to a graduated cylinder and dilute to 50 mL with deionized water. Do the test. Refer to Table 4 on page 9 again to multiply the calibrator levels by the dilution multiplier.

For example, if a 0.5 mL water sample is diluted to 50 mL, the calibrator levels in Table 4 on page 9 for diesel fuel are approximately 200, 500, 1000 and 2000 ppm.

Table 5 Dilution multipliers

mL sample	Dilution multiplier
0.5	100
1.0	50
2.0	25
5.0	10
10.0	5
25.0	2

Summary of method

This method is the semi-quantitative screening for TPH based on thresholds as diesel fuel in the concentrations that follow:

- Soil—20, 50, 100, 200 ppm as diesel fuel
- Water—2, 5, 10, 20 ppm as diesel fuel

Immunoassay tests use antigen/antibody reactions to detect specific organic compounds in water and soil. The walls of plastic cuvettes are layered with antibodies that are specific for TPH. The antibodies selectively remove TPH from complex sample matrices. A prepared sample and a reagent with enzyme-conjugate molecules (analyte molecules attached to molecules of an enzyme) are added to the Antibody Cuvettes. During incubation, enzyme-conjugate molecules and TPH compete for binding sites on the antibodies. Samples with higher levels of analyte have more antibody sites occupied by the analyte and fewer antibody sites occupied by the enzyme-conjugate molecules.

After incubation, the sample and unbound enzyme conjugate are rinsed from the cuvette and a color-development reagent is added. The enzyme in the conjugate catalyzes the development of color. Thus, there is an inverse relationship between color intensity and the amount of TPH in the sample. The resulting color is then compared with a calibrator to determine if the analyte concentration in the sample is larger or smaller than the threshold levels. The TPH concentration is inversely proportional to the color development—the lighter the color, the higher the TPH concentration. The test results are measured at 450 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Soil Extraction Kit	1	each	2775100
TPH Reagent Set	1	20 cuvettes	2774300
Water, deionized	varies	500 mL	27248

Required apparatus

Description	Quantity/test	Unit	Item no.
Balance, portable, 300 g capacity	1	each	2796900
Caps, flip spout (for 500-mL deionized water bottle)	1	2/pkg	2581802
Marker, laboratory	1	each	2092000
Gloves, nitrile, medium	1	100/pkg	2550502
Pipet, TenSette, 0.1–1.0 mL	1	each	1970001
Pipet tips, for TenSette Pipet, 0.1–1.0 mL	2	50/pkg	2185696
Pipet, Wiretrol®, 10–50 µL	1	each	2852200
Pipet, Wiretrol®, 50–1000 µL	1	each	2568905
Rack, for 12-mm Micro Cuvettes	1	each	4879910
Safety goggles, vented	1	each	2550700
Soil scoop, 5-g, 4.25-cc	1	20/pkg	2657205
Timer, talking	1	each	2764400
Wipes, disposable	1	280/pkg	2097000
Soil extraction refill kit, for 2775100, includes:	1	each	2775200
Dropper, LDPE, 0.5 and 1.0-mL	1	20/pkg	2124720
Filter and barrel assembly	1	20/pkg	2567620
Sodium sulfate, anhydrous	1	250 g	709929
Soil extraction solution	1	200 mL	2567729
Soil sample container	1	20/pkg	2592920
Weighing boat, 8.9-cm square	1	20/pkg	2179020
Spatula, disposable	1	2/pkg	2569320

Optional reagents and apparatus

Description	Unit	Item no.
Graduated cylinder, 10-mL	each	108138
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL MDB	32332

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 01/2017, Edition 11

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