DOC022.53.80225

Hydraulic Fracturing Water Analysis Handbook

For use with DR900 Colorimeters

Procedures Manual

03/2021, Edition 10

Table of Contents

Section 1 Introduction

This manual is made up of test procedures and additional explanatory notes for testing of oil and gas field waters. The first part of the manual contains the test procedure documents. Explanatory documents are found in the second part of the manual.

Explanatory documents include information about the purpose of a test, recommended instrumentation, interpreting test results, and information about test interferences and challenges.

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

Alkalinity

DOC316.53.01308

Phenolphthalein and Total Alkalinity

Method 10244

10 to 4000 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 Bromcresol Green-Methyl Red Indicator Powder Pillow, use 4 drops of Bromcresol Green-Methyl Red Indicator Solution.
As an alternative to the Phenolphthalein Indicator Powder Pillow, use 4 drops of Phenolphthalein Indicator Solution.
Color or turbidity in the sample can make it difficult to see the color change at the endpoint. For these samples, use a pH meter to determine the titration endpoint. Refer to Alkalinity pH endpoints on page 4.
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

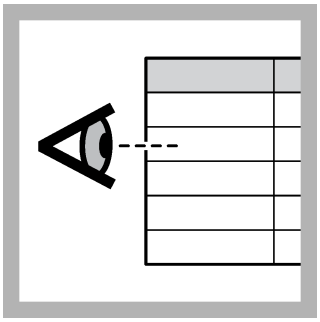
Description	Quantity
Bromcresol Green-Methyl Red Indicator Powder Pillow	1
Phenolphthalein Indicator Powder Pillow	1
Sulfuric Acid Titration Cartridge	1
pH Meter and probe (for samples that have a lot of color or turbidity)	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (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.

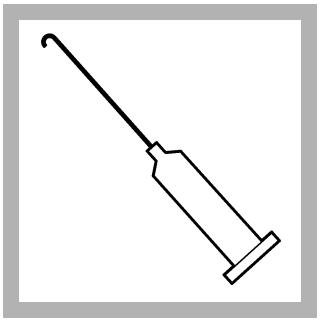
Sample collection

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

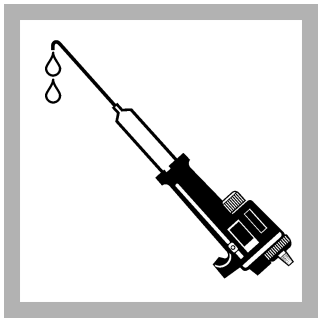
Test procedure



1. Select a sample volume and titration cartridge from Table 1 on page 3. Alkalinity in oil and gas field waters is typically 100–600 mg/L as $CaCO_3$.

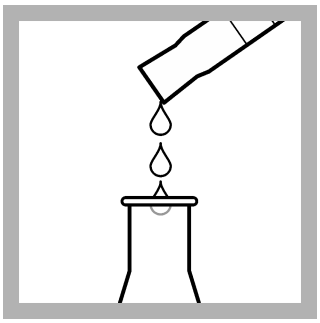


2. Insert a clean delivery tube into the 1.600 N Sulfuric Acid Titration Cartridge. Attach the cartridge to the Digital Titrator.
Note: Other titrant strengths are available.

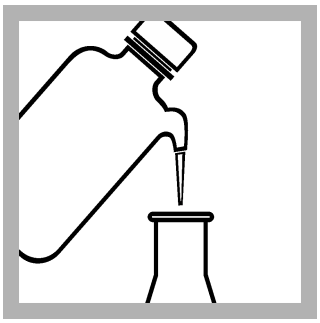


3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.

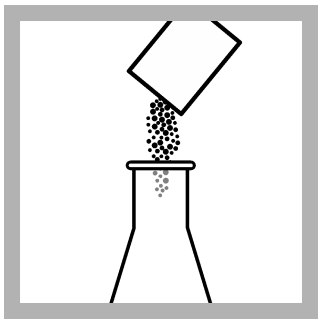
4. Use a graduated cylinder to measure the sample volume from Table 1 on page 3.



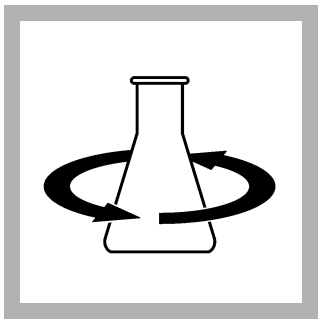
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



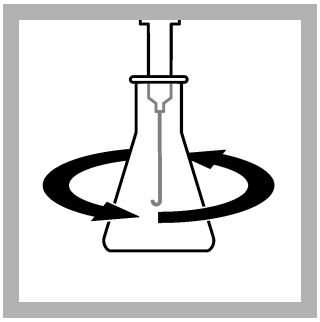
6. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



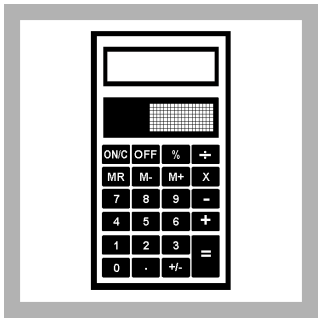
7. Add the contents of one Phenolphthalein Indicator Powder Pillow.
The indicator is not necessary if a pH meter is used. If the solution is colorless or the pH is less than 8.3, the Phenolphthalein alkalinity is zero. Go to step 11.



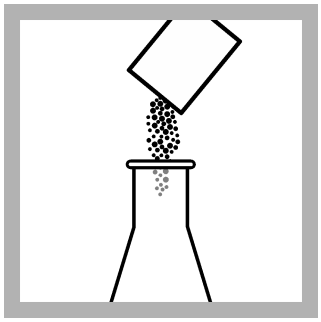
8. Swirl to mix.



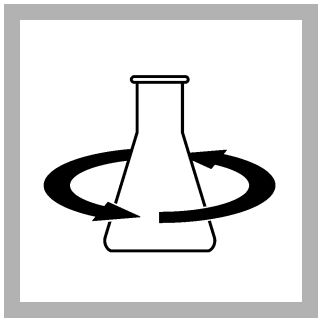
9. Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes from pink to colorless, or until the pH is 8.3. Record the number of digits on the counter.



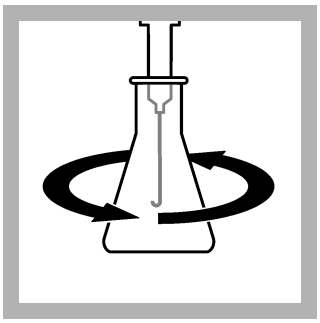
10. Use the multiplier in Table 1 on page 3 to calculate the concentration. Digits used × digit multiplier = mg/L as $CaCO_3$ Phenolphthalein alkalinity.



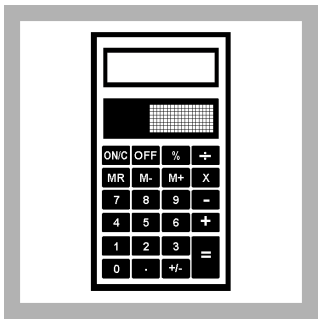
11. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow.
The indicator is not necessary if a pH meter is used.



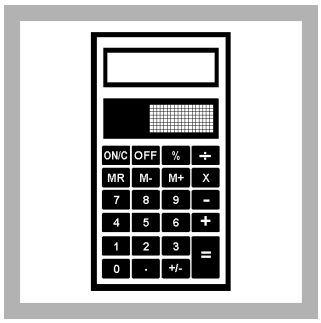
12. Swirl to mix.



13. 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 light pink color, or the pH is 4.5 (refer to Table 2 on page 4 for additional pH endpoints). Record the number of digits on the counter.



14. Use the multiplier in Table 1 on page 3 to calculate the concentration. Total digits used x digit multiplier = mg/L as $CaCO_3$ Total alkalinity.



15. Calculate the bicarbonate, carbonate and hydroxide alkalinities as shown in Determine the alkalinity relationships on page 4.

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 1.600 N Sulfuric Acid Titration Cartridge and the counter showed 250 digits at the first endpoint. The concentration is 250 digits x 2 = 500 mg/L as $CaCO_3$ Phenolphthalein alkalinity.

Table 1 Sample volumes and digit multipliers

Range (mg/L as $CaCO_3$)	Sample volume (mL)	Titration cartridge	Digit multiplier
10–40	100	0.1600 N H_2SO_4	0.1
40–160	25	0.1600 N H_2SO_4	0.4

Table 1 Sample volumes and digit multipliers (continued)

Range (mg/L as $CaCO_3$)	Sample volume (mL)	Titration cartridge	Digit multiplier
100–400	100	1.600 N H_2SO_4	1
200–800	50	1.600 N H_2SO_4	2
500–2000	20	1.600 N H_2SO_4	5
1000–4000	10	1.600 N H_2SO_4	10

Alkalinity pH endpoints

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

Table 2 Alkalinity pH endpoints

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

Determine the alkalinity relationships

The primary forms of alkalinity in water are hydroxide, carbonate and bicarbonate ions. The concentration of these ions in a sample can be determined from the phenolphthalein alkalinity and total alkalinity values. Refer to Table 3 and the steps that follow to determine the hydroxide, carbonate and bicarbonate alkalinities.

1. If the phenolphthalein (P) alkalinity is 0 mg/L, use Row 1.
2. If the phenolphthalein (P) alkalinity is equal to the total alkalinity, use Row 2.
3. Divide the total alkalinity by 2 to calculate one-half of the total alkalinity.
   a. Compare the phenolphthalein (P) alkalinity to one-half of the total alkalinity. Then, use Row 3, 4 or 5.
   b. Do the calculations in the row (if applicable).
4. Make sure that the sum of the three alkalinity types is equal to the total alkalinity.
   Example:

   A sample has 170 mg/L as $CaCO_3$ phenolphthalein alkalinity and 250 mg/L as $CaCO_3$ total alkalinity.

   The phenolphthalein alkalinity of 170 mg/L is more than one-half of the total alkalinity, so use Row 5.

   - Hydroxide alkalinity: 2 x 170 = 340; 340 – 250 = 90 mg/L hydroxide alkalinity
   - Carbonate alkalinity: 250 – 170 = 80; 80 x 2 = 160 mg/L carbonate alkalinity
   - Bicarbonate alkalinity: 0 mg/L

   Sum of the alkalinity types: 90 mg/L hydroxide alkalinity + 160 mg/L carbonate alkalinity + 0 mg/L bicarbonate alkalinity = 250 mg/L total alkalinity.

Table 3 Alkalinity relationships

Row	Titration result	Hydroxide alkalinity	Carbonate alkalinity	Bicarbonate alkalinity
1	P alkalinity = 0	0	0	= Total alkalinity
2	P alkalinity = Total alkalinity	= Total alkalinity	0	0

Table 3 Alkalinity relationships (continued)

Row	Titration result	Hydroxide alkalinity	Carbonate alkalinity	Bicarbonate alkalinity
3	P alkalinity is less than ½ of Total alkalinity	0	= P alkalinity × 2	= Total alkalinity – (P alkalinity × 2)
4	P alkalinity = ½ Total alkalinity	0	= Total alkalinity	0
5	P alkalinity is more than ½ Total alkalinity	= (P alkalinity × 2) – Total alkalinity	= (Total alkalinity – P alkalinity) × 2	0

Conversions

To change the units or chemical form of the test result, multiply the test result by the factor in Table 4.

Table 4 Conversions

mg/L as $CaCO_3$ to...	multiply by...	Example
meq/L as $CaCO_3$	0.02	1000 mg/L alkalinity as $CaCO_3$ x 0.02 = 20 meq/L alkalinity as $CaCO_3$
Grains per gallon (gpg)	0.0584	500 mg/L alkalinity as $CaCO_3$ x 0.0584 = 29.20 gpg alkalinity as $CaCO_3$

Interferences

Interfering substance	Interference level
Chlorine	Chlorine at levels more than 3.5 mg/L can cause a yellow-brown color when the Bromcresol Green-Methyl Red Powder Pillow is added. Add 1 drop of 0.1 N Sodium Thiosulfate to the sample to remove chlorine before the test is started.
Color or turbidity	Color or turbidity can make it difficult to see the color change at the endpoint. Do not filter or dilute samples with color or turbidity. Use a pH meter and titrate the samples to a pH of 8.3 for phenolphthalein alkalinity. For total alkalinity, refer to Table 2 on page 4 for the correct endpoint pH.
Soaps, oily matter, suspended solids and precipitates	Oils or solids can collect on the pH probe and cause a slow response. Clean the probe immediately after use (refer to Clean the pH probes on page 5).

Clean the pH probes

Make sure to clean the pH probes regularly when a pH meter is used to determine the endpoint. Refer to the probe documentation for maintenance instructions. Use the cleaning solution that is specified for the type of contamination that is in the sample. Clean the probe when one or more of the conditions that follow occur:

- Drifting/inaccurate readings
- Slow stabilization times
- Calibration errors

Accuracy check

Validate the endpoint color

Prepare a buffer solution that has the correct pH and color at the endpoint to compare with the titrated sample.

1. Add 50 mL of deionized water to a flask.
2. Add one buffer powder pillow and one indicator powder pillow as follows:
   - Phenolphthalein alkalinity—Add one pH 8.3 Buffer Powder Pillow and one Phenolphthalein Indicator Powder Pillow.
   - Total alkalinity—Add one pH 4.5 Buffer Powder Pillow and one Bromcresol Green-Methyl Red Indicator Powder Pillow.

3. Swirl to mix. The buffer solution will have the correct endpoint color.
4. Compare the color of the buffer solution with the color of the sample during the test procedure. Stop the titration when the titrated sample has the same color as the buffer solution.

Standard additions method (sample spike)

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

Items to collect:

- Alkalinity Voluette Ampule Standard Solution, 25,000-mg/L $CaCO_3$
- 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 25 digits of the 1.600 N Sulfuric Acid Titration Cartridge or 250 digits of the 0.1600 N Sulfuric Acid 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

A phenolphthalein indicator is added to the sample. Then, the sample is titrated with a sulfuric acid solution. The phenolphthalein indicator changes color at the endpoint pH of 8.3. This value indicates the phenolphthalein (P) alkalinity and is a measure of the total hydroxide and one-half of the carbonate in the sample.

A bromcresol green-methyl red indicator is added and the titration continues to the second endpoint at a pH between 4.3 and 4.9. This value indicates the total (T) alkalinity and is a measure of all carbonate, bicarbonate and hydroxide in the sample. The endpoint pH is determined with color indicators or with a pH meter.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Alkalinity Reagent Set (approximately 100 tests)	—	each	2271900
Bromcresol Green-Methyl Red Powder Pillows	1	100/pkg	94399
Phenolphthalein Indicator Powder Pillows	1	100/pkg	94299
Sulfuric Acid Titration Cartridge, 0.1600 N	varies	each	1438801
Sulfuric Acid Titration Cartridge, 1.600 N	varies	each	1438901
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

Recommended standards

Description	Unit	Item no.
Alkalinity Voluette Amp-mLule Standard Solution, 0.500 N (25 g/L as $CaCO_3$), 10 mL	16/pkg	1427810

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette Ampules	each	2196800
Bromcresol Green-Methyl Red Indicator Solution	100 mL MDB	2329232
Buffer Powder Pillows, pH 4.50, 50 mL	25/pkg	89568
Buffer Powder Pillows, pH 8.3	25/pkg	89868
Phenolphthalein Indicator Solution, 5 g/L	100 mL MDB	16232
Pipet, TenSette, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette Pipet, 0.1–1.0 mL	50/pkg	2185696
Stir bar, octagonal	each	2095352
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

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

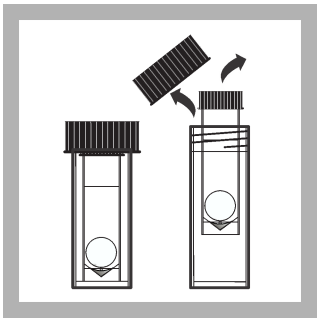
Do not touch the inner surface of the tube or lid. Keep contamination out of the tube and lid. Use the aseptic technique.
Set the caps on a clean surface with the flat surface down.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
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

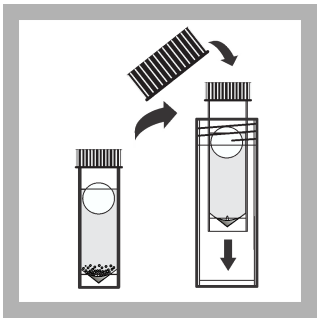


1. Remove the inner tube from the outer tube.

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

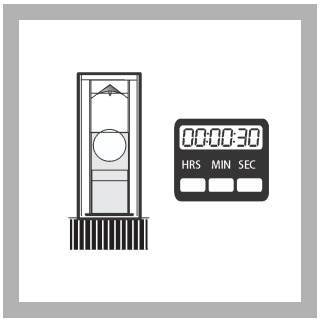
3. Fill the inner tube to the fill line with the sample that is in the outer tube. Tighten the cap on the inner tube.

Discard the unused sample in the outer tube.

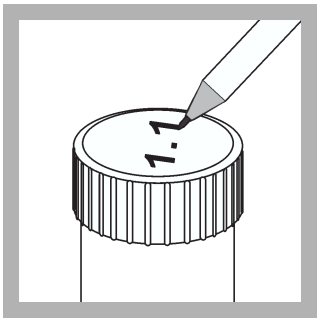


4. Put the inner tube in the empty outer tube. Tighten the cap on the outer tube.

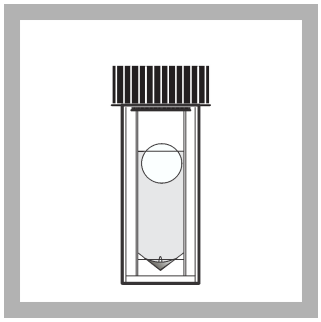
Do not shake or swirl the tubes after the sample is added. Let the ball float to the top with no help.



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

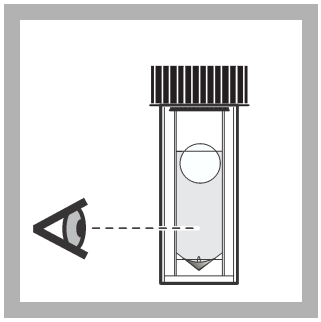


6. Write the date and sample name on the outer tube.



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

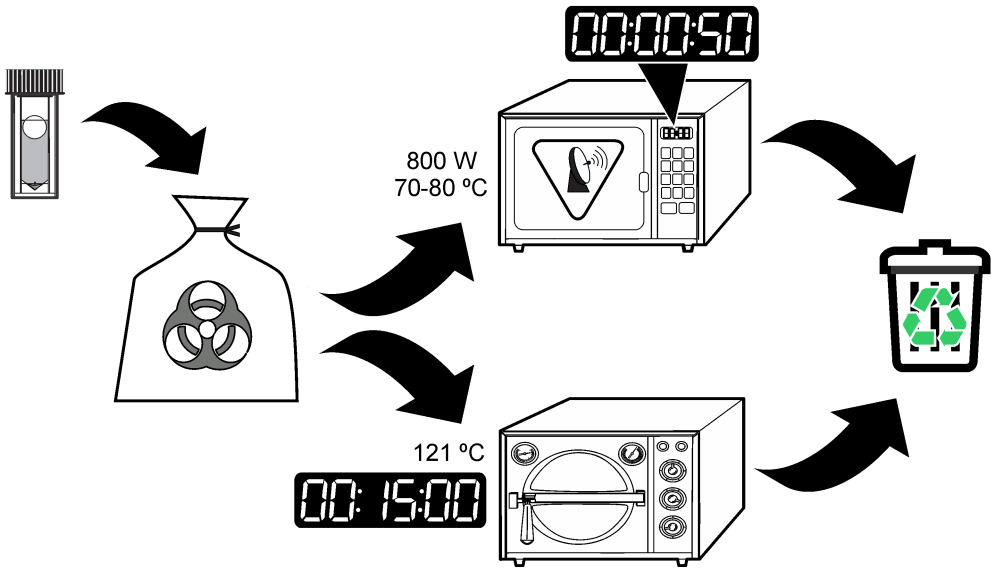
When acid-producing bacteria (APB) are in the sample, the sample becomes acidic (pH 3.5 to 5.5) during incubation. A pH indicator, bromocresol purple, in the APB-BART tube changes from a purple to an orange or yellow color as the pH decreases. This change occurs at a pH of 5.2 to 5.8.

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

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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

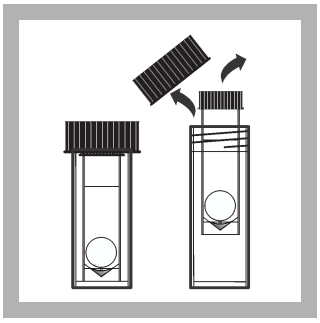
Do not touch the inner surface of the tube or lid. Keep contamination out of the tube and lid. Use the aseptic technique.
Set the caps on a clean surface with the flat surface down.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
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

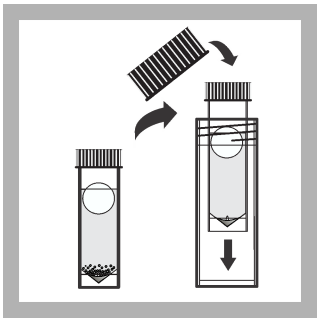


1. Remove the inner tube from the outer tube.

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

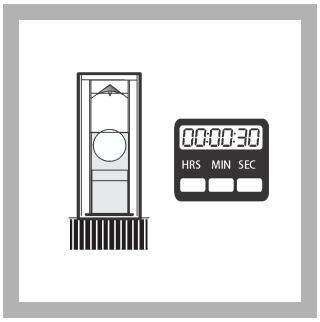
3. Fill the inner tube to the fill line with the sample that is in the outer tube. Tighten the cap on the inner tube.

Discard the unused sample in the outer tube.

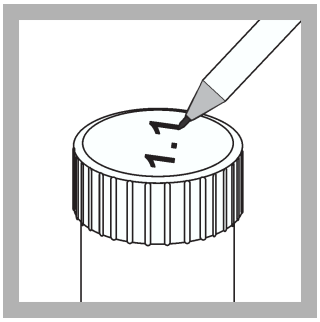


4. Put the inner tube in the empty outer tube. Tighten the cap on the outer tube.

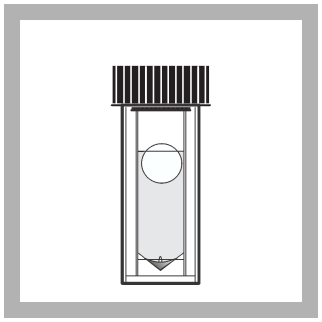
Do not shake or swirl the tubes after the sample is added. Let the ball float to the top with no help.



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

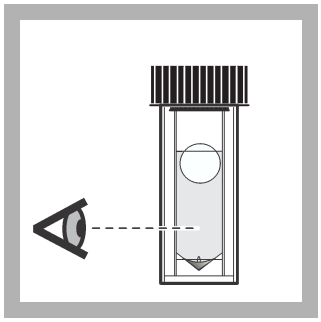


6. Write the date and sample name on the outer tube.



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.

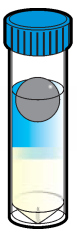
Table 1 Approximate bacteria population

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

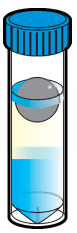
If the test result is positive, examine the tubes for dominant bacteria. Refer to Figure 1.

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

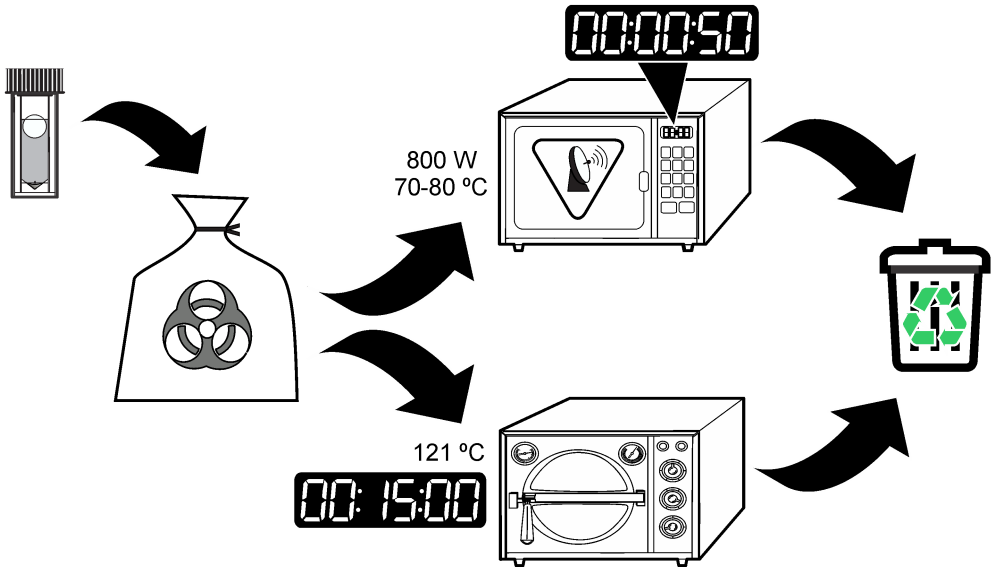
When heterotrophic aerobic bacteria (HAB) are in the sample, the bacteria consume oxygen during incubation. When the oxygen is gone, the bacteria react with the methylene blue dye in the HAB-BART tube and change the dye to the colorless form. The faster the color change, the higher the level of respiration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

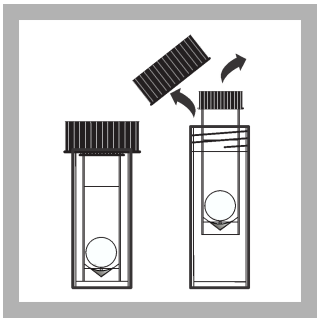
Do not touch the inner surface of the tube or lid. Keep contamination out of the tube and lid. Use the aseptic technique.
Set the caps on a clean surface with the flat surface down.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
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

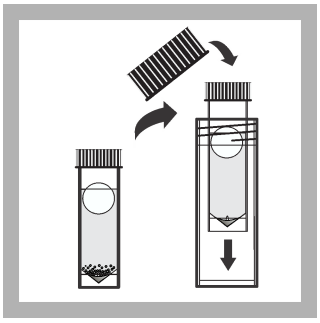


1. Remove the inner tube from the outer tube.

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

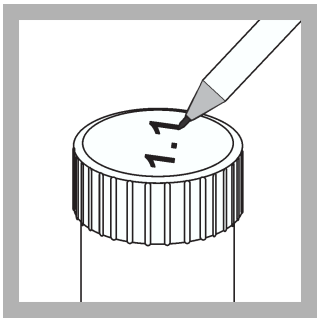
3. Fill the inner tube to the fill line with the sample that is in the outer tube. Tighten the cap on the inner tube.

Discard the unused sample in the outer tube.

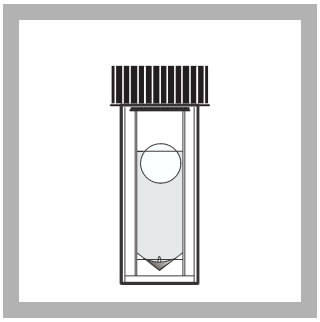


4. Put the inner tube in the empty outer tube. Tighten the cap on the outer tube.

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

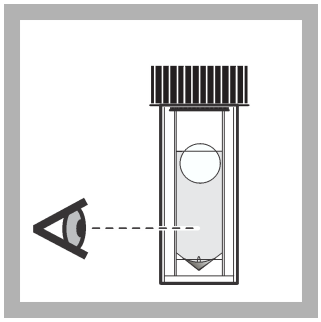


5. Write the date and sample name on the outer tube.



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.

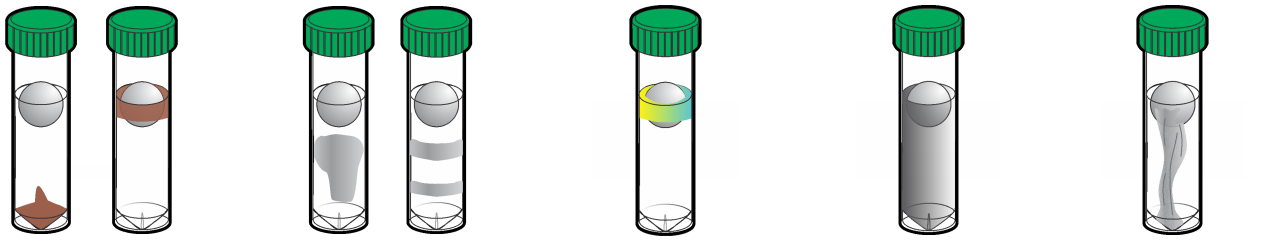
Table 1 Approximate bacteria population

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

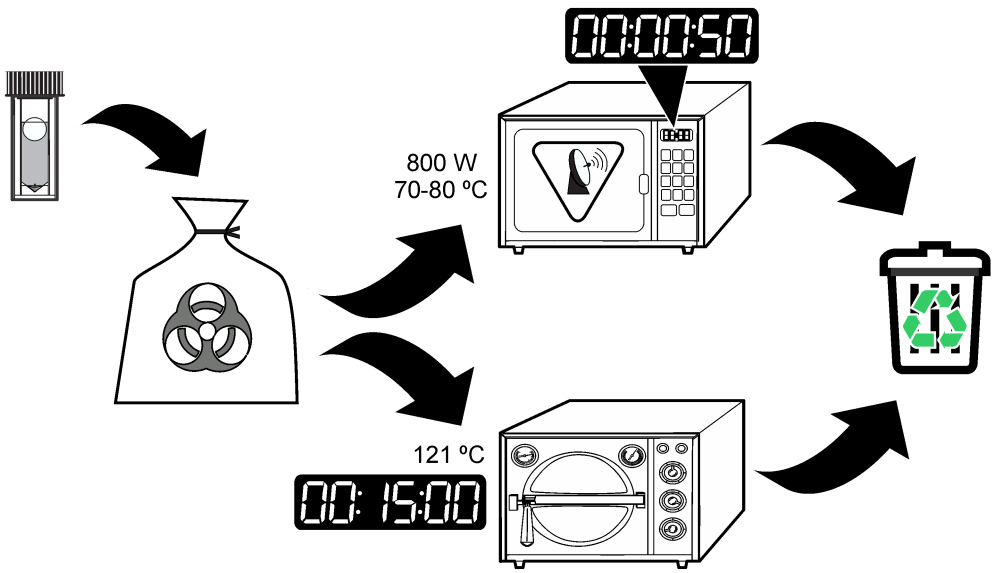
When slime-forming bacteria are in the sample, one or more types of slime grow in the SLYM-BART tube during incubation. The slime is typically seen as a cloudy or gel-like growth, which can be in one location or occur through all the sample. Slime growths are usually white, grey, yellow or beige in color 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

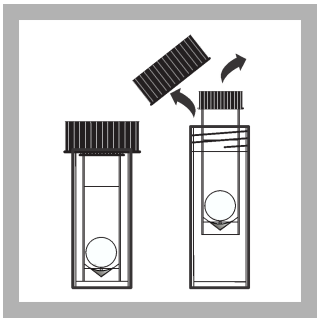
Do not touch the inner surface of the tube or lid. Keep contamination out of the tube and lid. Use the aseptic technique.
Set the caps on a clean surface with the flat surface down.
Sulfate-reducing bacteria (SRB) grow primarily deep within biofilms and not directly in water. Make sure to get a representative 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

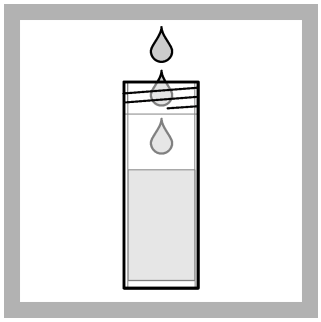
Description	Quantity
BART Test for sulfate-reducing bacteria (SRB)	1

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

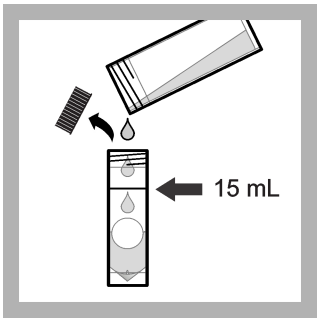
Test procedure



1. Remove the inner tube from the outer tube.

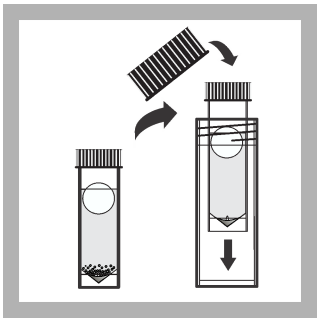


2. Pour at least 20 mL of sample in the outer tube.



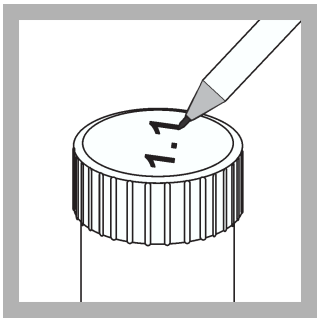
3. Fill the inner tube to the fill line with the sample that is in the outer tube. Tighten the cap on the inner tube.

Discard the unused sample in the outer tube.

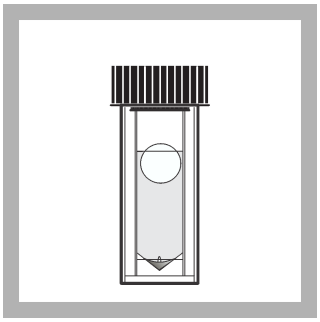


4. Put the inner tube in the empty outer tube. Tighten the cap on the outer tube.

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

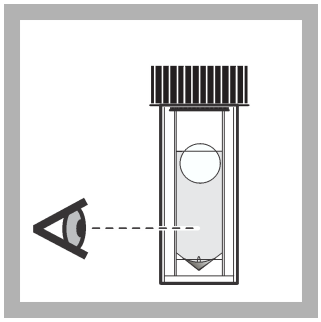


5. Write the date and sample name on the outer tube.



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

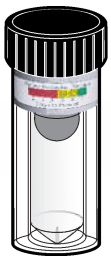
Interfering substance	Interference level
Hydrogen Sulfide (H_2S)	More than 20 ppm can give a false positive. Remove hydrogen gas from the sample as follows: Add 30 mL of sample to the outer tube. Put the outer tube cap on the tube. Shake the tube for 10 seconds. Do not move the tube for 20 seconds. Use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

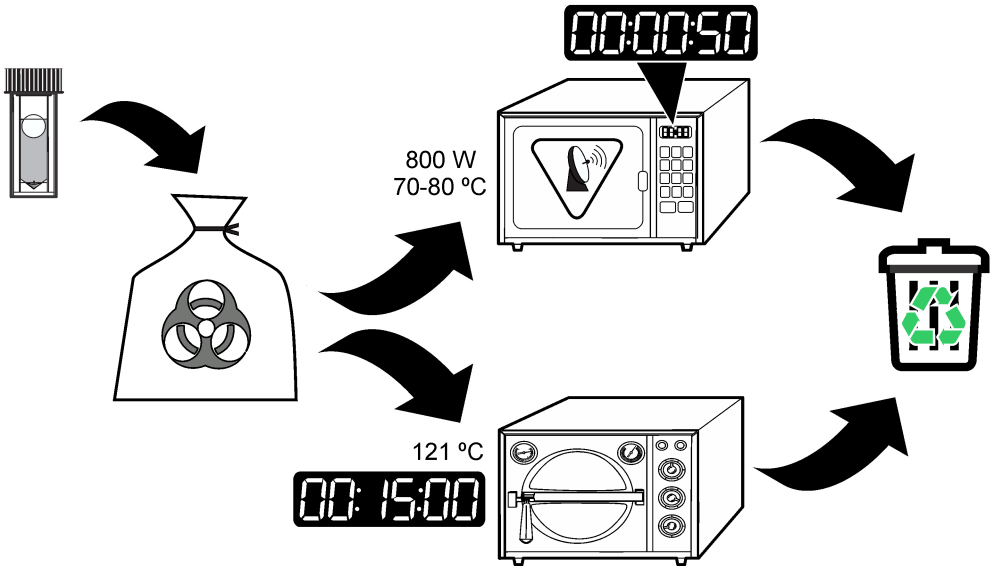
When sulfate-reducing bacteria (SRB) are in the sample, sulfate is reduced to hydrogen sulfide (H_2S) in the SRB-BART tube during incubation. The H_2S reacts with the ferrous iron in the tube to form black iron sulfides. This sulfide commonly forms in the base as a black slime and/or around the ball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

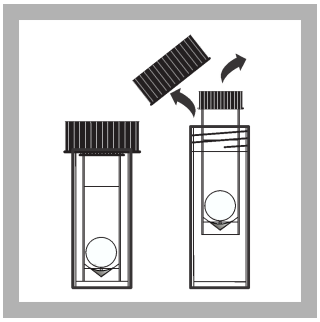
Do not touch the inner surface of the tube or lid. Keep contamination out of the tube and lid. Use the aseptic technique.
Set the caps on a clean surface with the flat surface down.
Iron-related bacteria (IRB) primarily grows on surfaces and not directly in water. Make sure to get a representative sample.
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

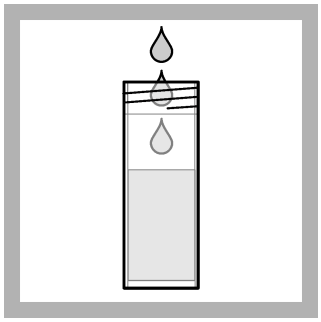
Description	Quantity
BART Test for iron-related bacteria (IRB)	1

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

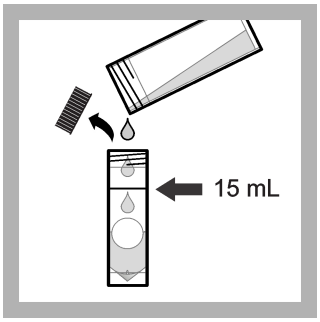
Test procedure



1. Remove the inner tube from the outer tube.

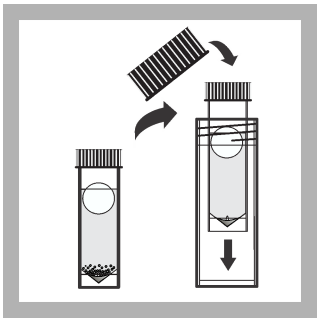


2. Pour at least 20 mL of sample in the outer tube.



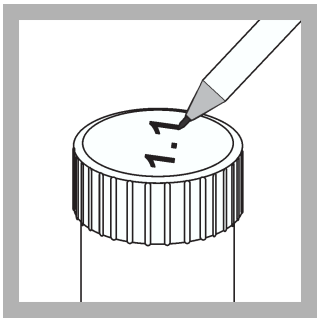
3. Fill the inner tube to the fill line with the sample that is in the outer tube. Tighten the cap on the inner tube.

Discard the unused sample in the outer tube.

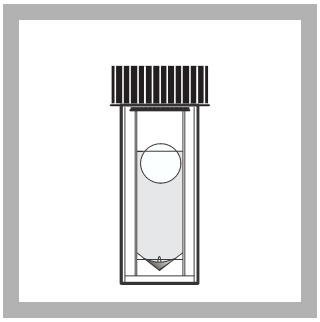


4. Put the inner tube in the empty outer tube. Tighten the cap on the outer tube.

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

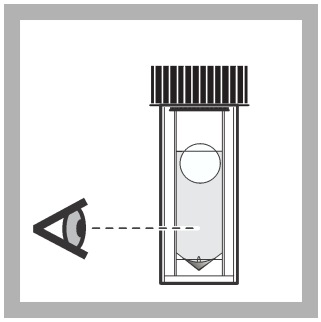


5. Write the date and sample name on the outer tube.



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

Do not move the tube.



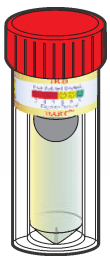
7. Examine the tube each day. Record the date when a reaction is first seen. Refer to Test results on page 2.

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.

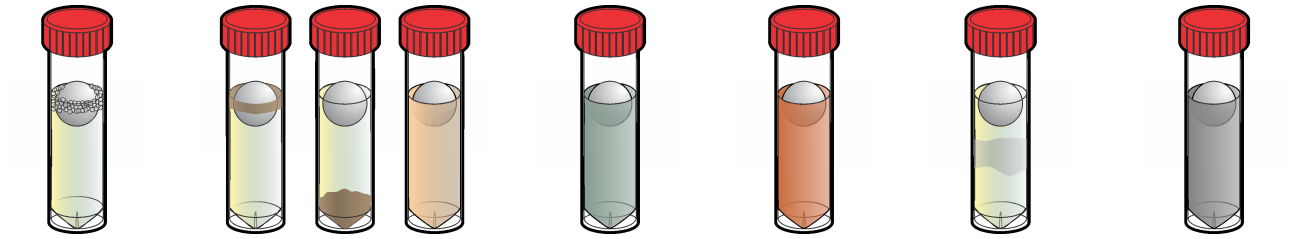
Table 1 Approximate bacteria population

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

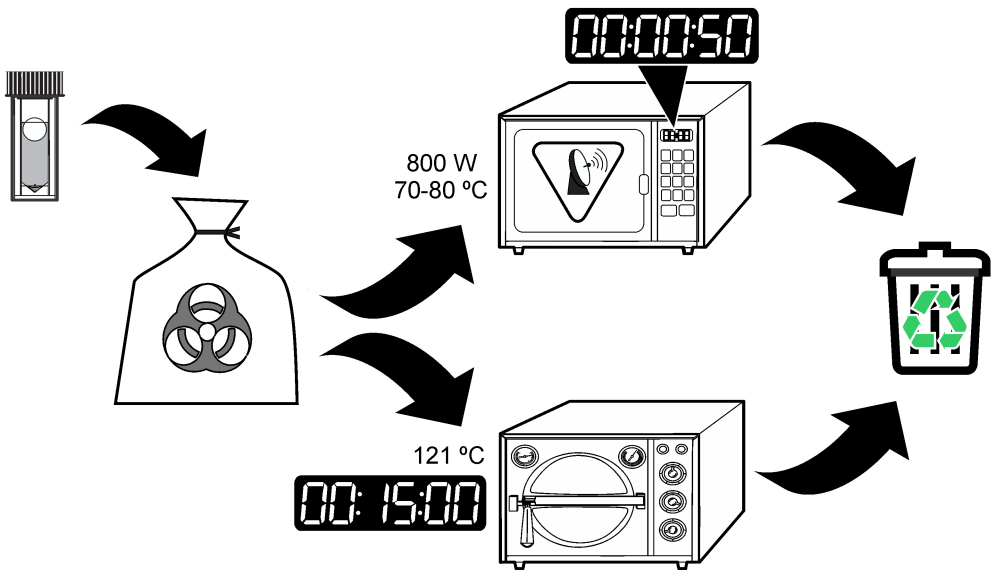
When iron-related bacteria (IRB) are in the sample, a series of reactions occur in the redox and nutrient gradients that develop in the IRB-BART tube during incubation. The iron-related bacteria use the nutrients and ferric iron in the tube to grow. The iron-related bacteria cause foam, clouding, slime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

Barium

DOC316.53.01315

Turbidimetric Method[1]

Method 10251

2 to 100, 20 to 1000, 200 to 10,000 mg/L Ba (spectrophotometers)

Powder Pillows

2 to 80, 20 to 800, 200 to 8000 mg/L Ba (colorimeters)

Scope and application: For oil and gas field waters.

[1] Adapted from Snell and Snell, Colorimetric Methods of Analysis, Vol. II, 769 (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.
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.
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

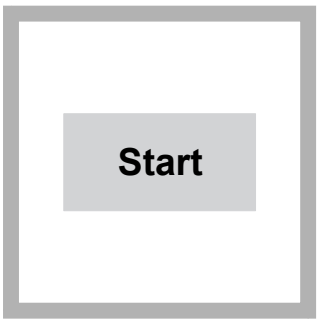
Description	Quantity
BariVer™ 4 Barium Reagent Powder Pillows	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

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

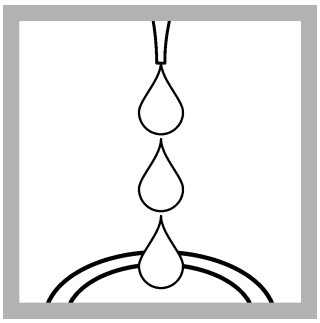
Sample collection and storage

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

Powder pillow procedure



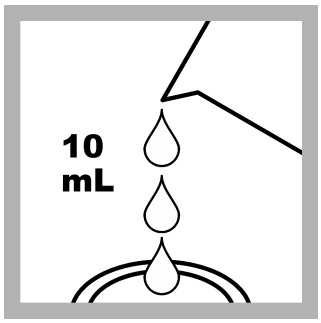
1. Start program **20 Barium**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



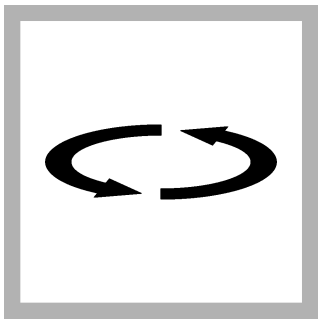
2. Prepare the blank: Add the sample volume that is specified for the test range to a clean sample cell:

- 2–100 mg/L: 10 mL
- 20–1000 mg/L: 1.0 mL
- 200–10,000 mg/L: 0.1 mL

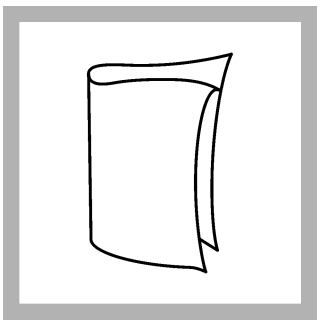
Use a pipet to add the 1.0 mL and 0.1 mL volumes.



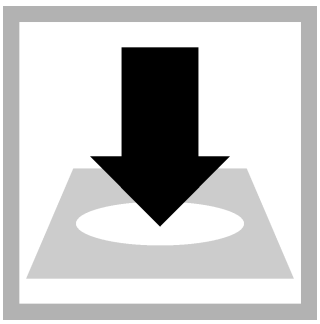
3. If the sample volume is less than 10 mL, add deionized water to the 10-mL line.



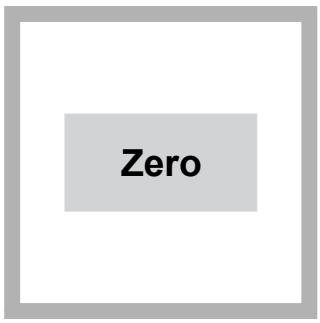
4. Swirl to mix. Refer to Set the dilution factor on page 3. A 10-mL graduated mixing cylinder can be used in steps 2 and 3.



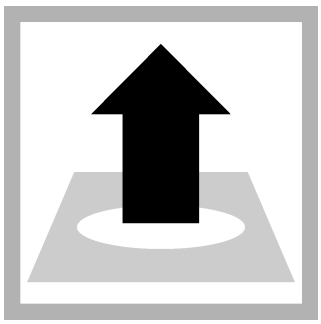
5. Clean the blank sample cell.



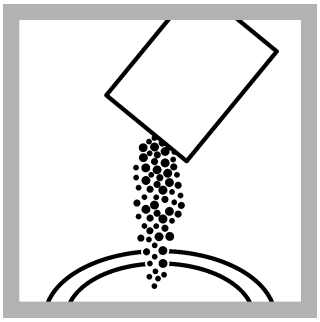
6. Insert the blank into the cell holder.



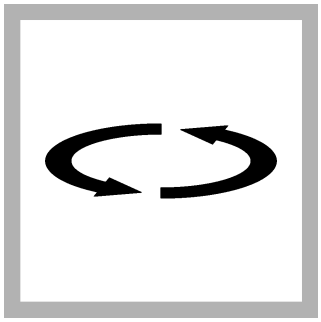
7. Push **ZERO**. The display shows 0 mg/L Ba^{2+}.



8. Remove the sample cell from the cell holder.



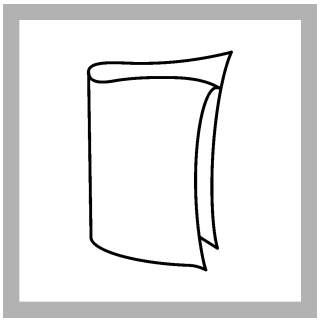
9. Prepare the sample:
Add the contents of one BariVer™ 4 Barium Reagent Powder Pillow to the sample cell.
The solution will get cloudy if barium is in the sample.



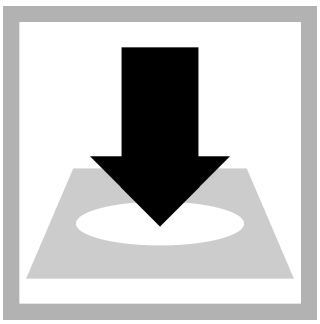
10. Swirl to mix.
The sample will become cloudy if barium is in the sample. Accuracy is not affected by undissolved powder.

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

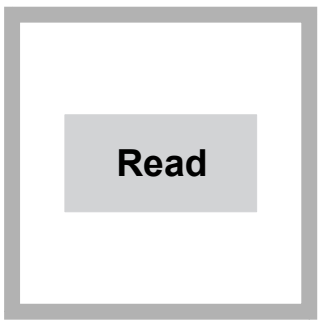
Do not move the sample cell during the reaction period.



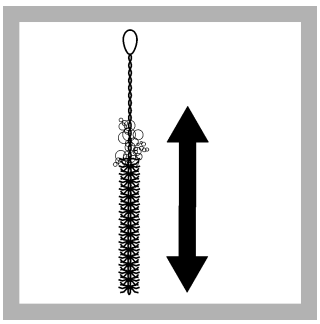
12. Clean the prepared sample cell.



13. Within 5 minutes after the timer expires, insert the prepared sample into the cell holder.



14. Push **READ**. Results show in mg/L Ba^{2+}.



15. Clean the sample cell immediately after each test with soap, water and a brush.

Interferences

Interfering substance	Interference level
Calcium	10,000 mg/L as $CaCO_3$
Magnesium	100,000 mg/L as $CaCO_3$
Silica	500 mg/L
Sodium Chloride	130,000 mg/L as NaCl
Strontium	The interference level is dependent on the sample matrix and the barium concentration. When the barium concentration is zero, there is no interference from strontium. The best results occur when the barium concentration is less than 20 mg/L and when the strontium concentration (as mg/L) is equal to or less than the barium concentration.
Highly buffered samples or extreme sample pH	Can prevent the pH adjustment by the reagent(s) and cause incorrect results.

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:

- Barium Standard Solution, 1000-mg/L Ba
- 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:

- Barium Standard Solution, 1000-mg/L Ba
- 100-mL volumetric flask, Class A
- 5-mL volumetric pipet, Class A and pipet filler
- Deionized water

1. Prepare a 50.0-mg/L barium standard solution as follows:

   a. Use a pipet to add 5.00 mL of 1000-mg/L barium 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
20	30 mg/L Ba	25–35 mg/L Ba	1 mg/L Ba

Summary of method

The BariVer™ 4 Barium Reagent Powder combines with barium to form a barium sulfate precipitate, which is held in suspension by a protective colloid. The amount of precipitate is proportional to the barium concentration. The measurement wavelength is 450 nm for spectrophotometers or 520 for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
BariVer 4 Barium Reagent Powder Pillow	1	100/pkg	1206499

Recommended standards

Description	Unit	Item no.
Barium Standard Solution, 1000-mg/L Ba	100 mL	1461142
Water, deionized	4 L	27256

Optional reagents and apparatus

Description	Unit	Item no.
Brush, test tube	each	69000
Filter paper, 2–3-micron, pleated, 12.5 cm	100/pkg	189457
Flask, volumetric, Class A, 100 mL, glass	each	1457442
Funnel, poly, 65 mm	each	108367
Liqui-Nox Phosphate-free detergent	946 mL	2088153
Nitric Acid Solution, 1:1	500 mL	254049
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
Pipet, volumetric 5.00 mL	each	1451537
Pipet filler, safety bulb	each	1465100
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	245032

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01/2014, Edition 9

Boron

DOC316.53.01313

Carmine Method **Method 10252**

2 to 50 mg/L B **Powder Pillows**

Scope and application: For oil and gas field waters

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 Test 'N Tube 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 Test 'N Tube vials

Instrument	Adapters	Light shield
DR6000, DR5000	—	—
DR3900	—	LZV849
DR3800, DR2800, DR2700	—	LZV646
DR1900	9609900 (D[1])	—
DR900	4846400	Cover supplied with the instrument

Before starting

Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
DR3900, DR3800, DR2800 and DR2700: Install the light shield in Cell Compartment #2 before this test is started.
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
BoroVer 3 Reagent Powder Pillow	1
Sufuric Acid, Concentrated	75 mL
Water, deionized	2 mL
Tubes, glass, 16 mm x 100 mm	2
Caps, white Teflon	2
Flask, poly, screw-on cap, 250-mL	1
Cylinder, graduated, poly, 100-mL	1

[1] The D adapter is not available with all instrument versions.

Items to collect (continued)

Description	Quantity
Light shield or adapter (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	1
Select:	
Pipet, 0.2 - 1.0 mL , BBP078	1
Pipet Tip, for BBP078	2
Pipet, 1.0 - 1.0 mL, BBP065	1
Pipet Tip for BBP065	2
OR	
Pipet, TenSette, 0.1- to 1.0-mL	1
Pipet tips for 0.1- to 1.0-mL TenSette	2
Pipet, TenSette, 1.0- to 10.0-mL	1
Pipet tips for 1.0- to 10.0-mL TenSette	2

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

Sample collection

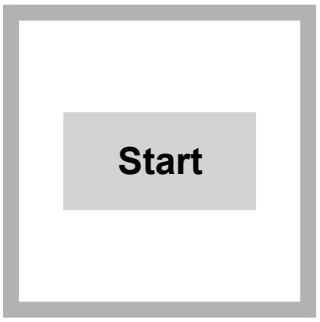
Collect samples in clean polyethylene or polypropylene bottles.

Prepare the glass tubes for first use

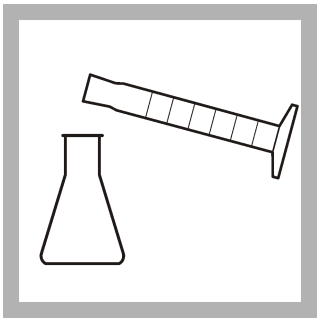
New glass tubes can contain residual amounts of reactive boron from the glass manufacturing process. For best results, precondition the tubes before the first use. Previously used tubes do not need to be preconditioned.

1. Prepare the BoroVer 3/Sulfuric Acid Solution.
2. Add 3 to 4 mL of the prepared BoroVer 3/Sulfuric Acid Solution into the tubes.
3. After 30 minutes, discard the solution.
4. Rinse and dry the tubes before use.

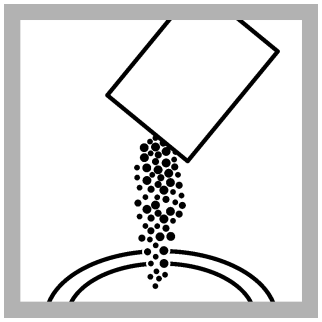
Powder pillow procedure



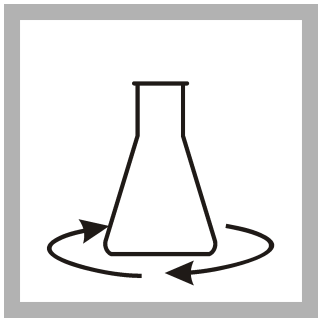
1. Start program **41 Boron HR**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



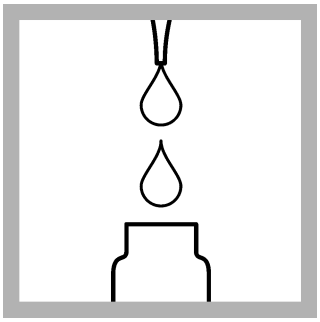
2. Use a 100-mL graduated cylinder to measure 75 mL of concentrated sulfuric acid. Pour the acid into a plastic 250-mL Erlenmeyer flask.



3. In a well-ventilated area or fume hood, add the contents of one BoroVer 3 Reagent Powder Pillow to the flask.

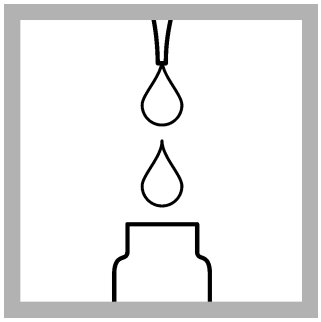


4. Swirl the flask immediately to mix. Swirl for up to 5 minutes to dissolve the powder completely.



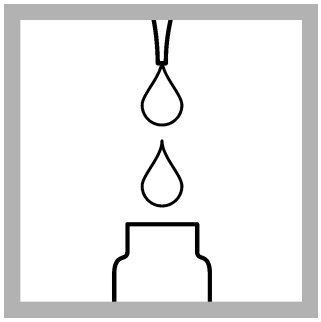
5. Prepare the blank: Remove the cap from a clean 16-mm tube. Add 0.2 mL of deionized water. Refer to Prepare the glass tubes for first use on page 2 and Clean the glass tubes after use on page 4.

Note: *If a 3.5-mL pipet is not available, 0.4 mL of DI water can be used.*



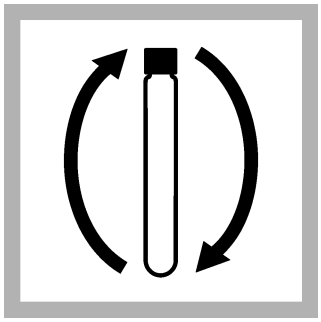
6. Prepare the sample: Remove the cap from a clean 16-mm tube. Add 0.2 mL of sample.

Note: *If a 3.5-mL pipet is not available, 0.4 mL of sample can be used.*

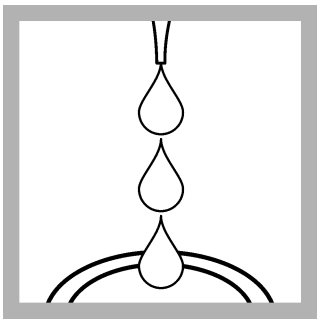


7. Add 3.5 mL of the BoroVer 3 Solution from step 4 to the **prepared** sample tube.

Note: *If a 3.5-mL pipet is not available, 7.0 mL of BoroVer 3 Solution can be used with 0.4 mL of sample.*

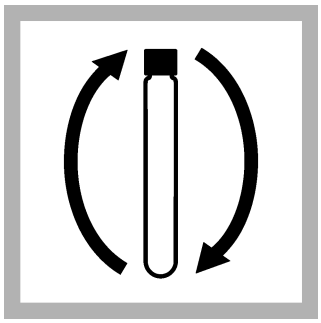


8. Put the cap on the prepared sample and invert to mix.
The solution in the tube will get warm.



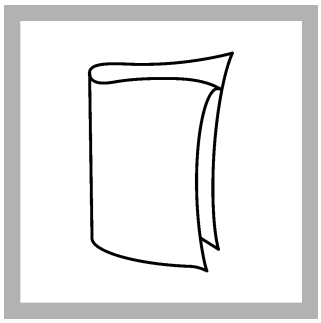
9. Add 3.5 mL of the BoroVer 3 Solution from step 4 to the **blank** sample tube.

Note: *If a 3.5-mL pipet is not available, 7.0 mL of BoroVer 3 Solution can be used with 0.4 mL of deionized water.*

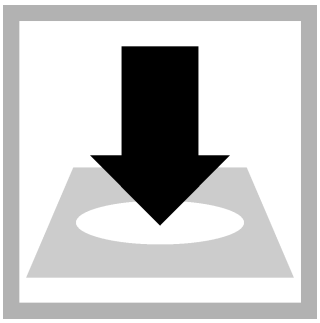


10. Put the cap on the blank. Iinvert to mix.
The solution in the tube will get warm.

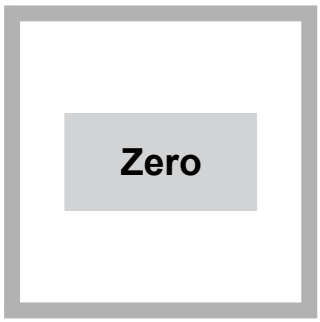
11. Start the instrument timer. A 30-minute reaction time starts.



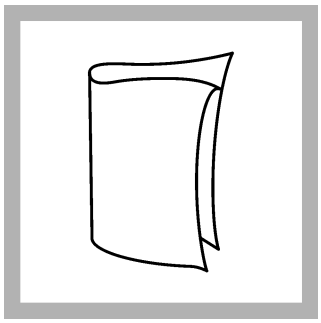
12. When the timer expires, clean the blank sample cell.



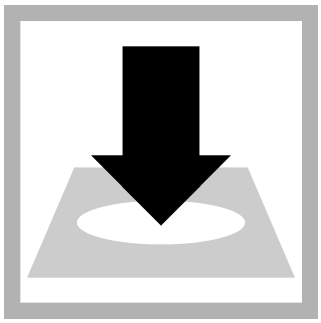
13. Insert the blank into the cell holder.



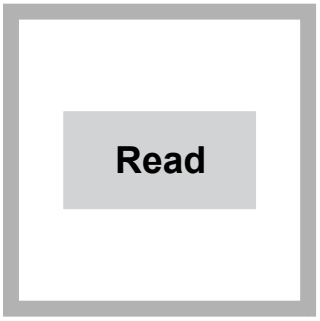
14. Push **ZERO**. The display shows 0.0 mg/L B HR.



15. Clean the prepared sample cell.



16. Insert the prepared sample into the cell holder.



17. Push **READ**. Results show in mg/L B.

Reagent preparation

More than 75 mL of the BoroVer 3/Sulfuric Acid Solution can be prepared for use in multiple analyses.

Preparation notes

- Gaseous hydrochloric acid (HCl) forms when the powder pillow is added to sulfuric acid. Always mix under a fume hood.
- The solution is stable for a maximum of 48 hours when kept in plastic containers.
- To prevent boron contamination from the glassware, do not keep the solution in borosilicate glassware (Pyrex® or Kimax®) for more than 1 hour.
- The BoroVer 3/Sulfuric Acid Solution is highly acidic. Refer to the current MSDS/SDS for safe handling and disposal instructions.

1. Determine the amount of sulfuric acid and powder pillows that are necessary for the number of samples to be analyzed. Use 75 mL of sulfuric acid for each analysis. Use one BoroVer 3 Reagent Powder Pillow for each 75 mL of sulfuric acid.
2. Under a fume hood, measure the concentrated sulfuric acid with a graduated cylinder.
3. Pour the acid into a Erlenmeyer flask.
4. Stir the acid and add the contents of one BoroVer 3 Reagent Powder Pillow to the flask. Swirl to mix. Wait for the powder to completely dissolve. Continue to add one powder pillow at a time. Stir to dissolve after each powder pillow is added.
5. Pour this solution into plastic containers and use within 48 hours.

Clean the glass tubes after use

NOTICE

The BoroVer 3/Sulfuric Acid solution is highly acidic. Neutralize the solution to pH 6–9 before disposal. Refer to a current SDS (Safety Data Sheet) for safe handling and disposal instructions of reacted boron.

Glass tubes and caps can be reused.

1. Thoroughly drain the boron solution.
2. Rinse the vials several times with deionized water.
3. Let the vials dry completely before the next use.

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 Boron Standard Solution
- 100-mL volumetric flask, Class A
- 3-mL volumetric pipet, Class A and pipet filler
- Deionized water

1. Prepare a 30.0 mg/L boron standard solution as follows:
   a. Use a pipet to add 3.0 mL of 1000 mg/L boron 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
41	25 mg/L B	24.2–25.8 mg/L B	2.2 mg/L B

Summary of method

Boron is determined by its reaction with carminic acid in the presence of sulfuric acid to produce a reddish to bluish color. The amount of color is directly proportional to the boron concentration. The measurement wavelength is 605 nm for spectrophotometers or 610 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
BoroVer 3 Boron Reagent Powder Pillow	1 pillow/1 tests	100/pkg	1417099
Sulfuric Acid, concentrated, ACS	varies	500 mL	97949
Water, deionized	varies	100 mL	27242

Required apparatus

Description	Quantity/test	Unit	Item no.
Tubes, glass, 16-mm x 100-mm	1	6/pkg	2275806
Caps, white, Teflon lining, for 16-mm vials	2	6/pkg	2241106
Cylinder, graduated, polypropylene, 100 mL	1	each	108142
Flask, Polymethylpentene, screw cap, 250 mL	1	each	2089846
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

Required apparatus (continued)

Description	Quantity/test	Unit	Item no.
Pipet tips, for 1.0–5.0 mL pipet	1	75/pkg	BBP068
OR			
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
Tubes, glass, 16-mm x 100-mm	1	6/pkg	2275806

Optional reagents

Description	Unit	Item no.
Boron Standard Solution, 1000 mg/L as B	100 mL	191442

Optional apparatus

Description	Unit	Item no.
Gloves, chemical resistant, size 10	pair	2410105
Goggles, safety, standard	each	2927902
Pipet tips for TenSette Pipet, 0.1–1.0 mL	1000/pkg	2185628
Pipet tips for TenSette Pipet, 1.0–10.0 mL	250/pkg	2199725
Test tube rack, stainless steel	each	1864100
Pipets, adjustable volume, includes one 0.2–1.0 mL and one 1.0–5.0 mL pipet plus tips	each	LZP320

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01/2014, Edition 10

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

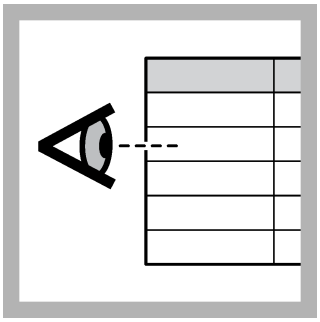
Use the steps that follow to make an estimate of the sample volume to use in the test procedure.

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.

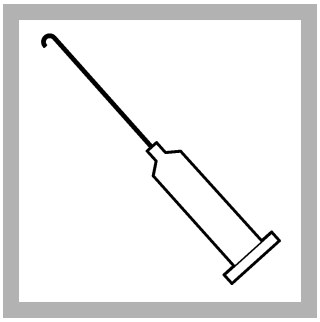
Table 1 Determine the sample volume

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

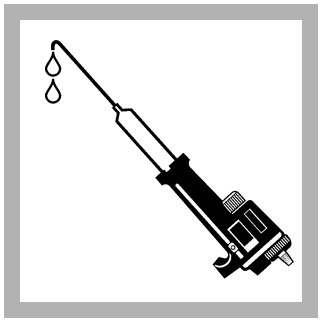
Test procedure



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

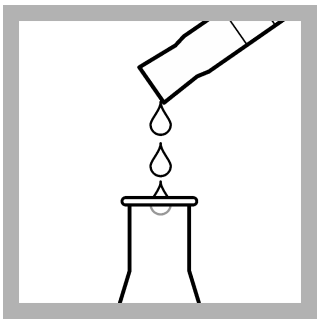


2. Insert a clean delivery tube into the Silver Nitrate Titration Cartridge. Attach the cartridge to the Digital Titrator.
Keep the silver nitrate cartridge in a dark area when not in use.

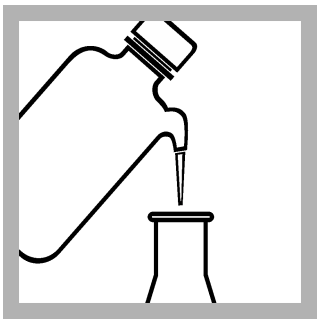


3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.

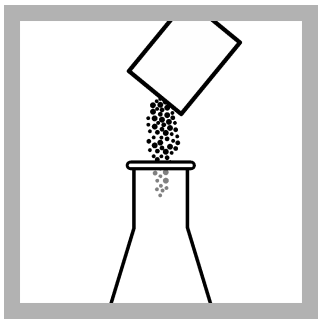
4. Use a graduated cylinder or TenSette pipet to measure the sample volume from Table 2 on page 3.



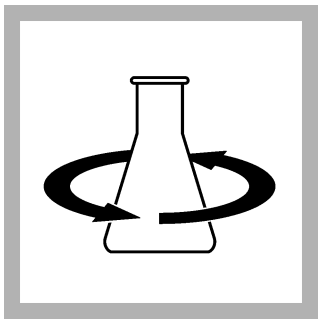
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



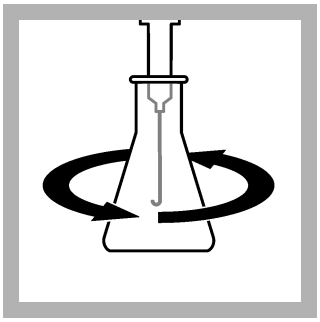
6. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



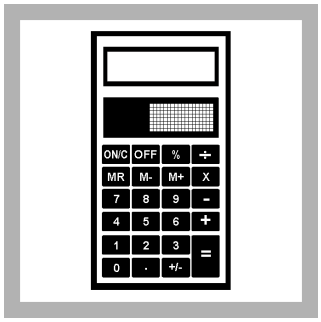
7. Add the contents of one Chloride 2 Indicator Powder Pillow.



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

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.

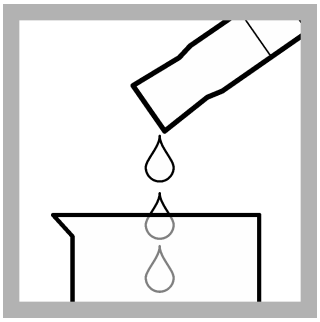
Sample collection

- 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.

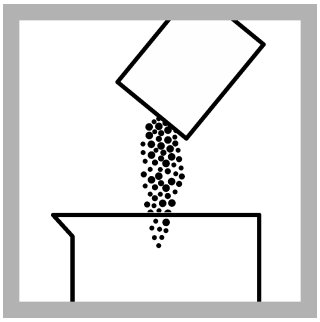
Configure the meter

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

Procedure

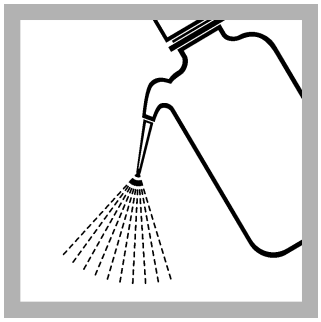


1. Add 25 mL of sample to a beaker.

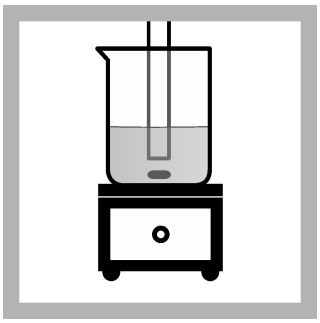


2. Add the contents of one chloride ISA powder pillow.

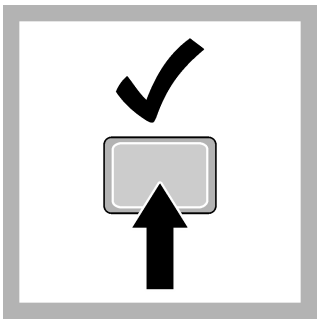
3. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



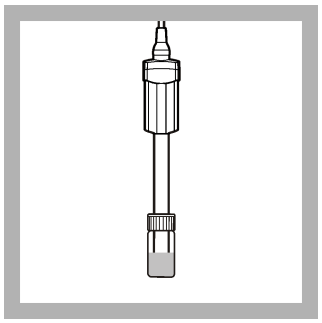
4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



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

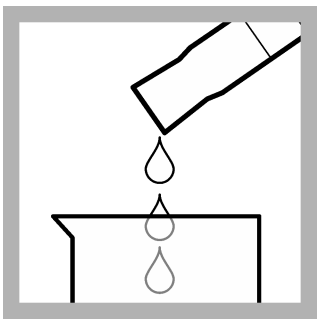
Prepare the standard solutions for calibration as follows.

Items to collect:

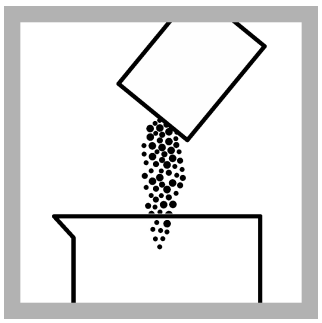
- Sodium chloride (NaCl)
- 200-mL volumetric flasks (3), Class A
- Laboratory balance
- Deionized water

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

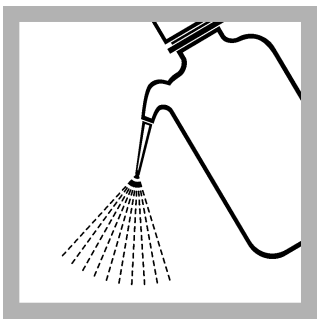


1. Add 25 mL of the lowest concentration standard solution to a beaker.

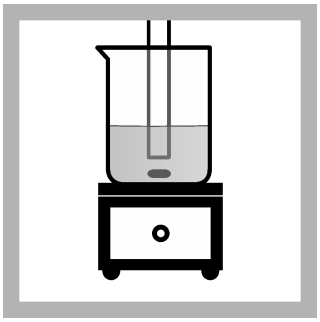


2. Add the contents of one chloride ISA powder pillow.

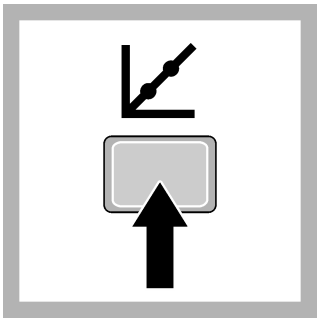
3. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



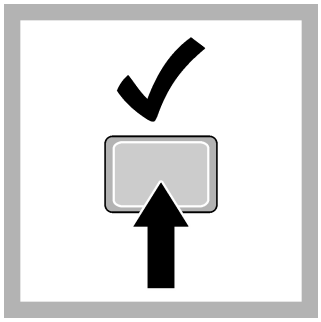
4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



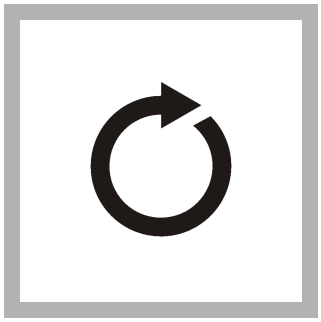
5. Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.



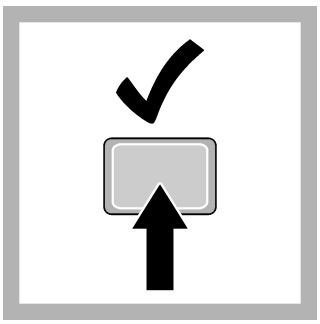
6. Push **Calibrate**. The standard solution value is shown.



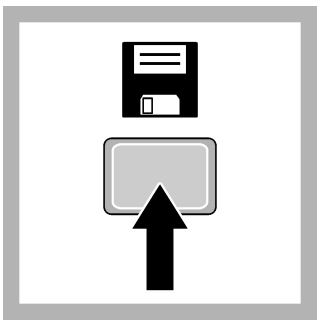
7. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.



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

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

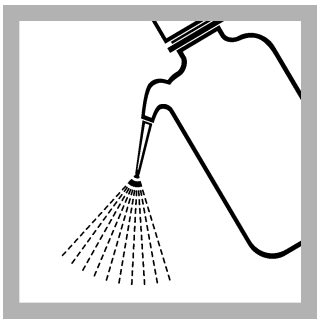
Description	Quantity
Beaker, 100 mL, polypropylene	1
Wash bottle with deionized water	1
Conductivity standard solution (refer to Recommended standards on page 4)	1

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

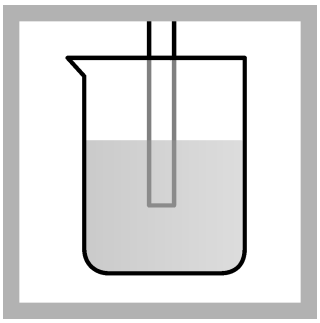
Sample collection and storage

- 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

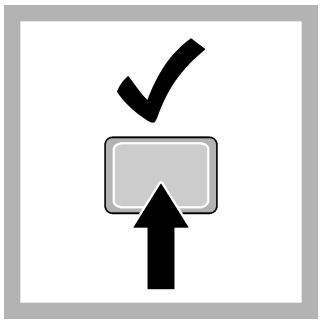


1. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

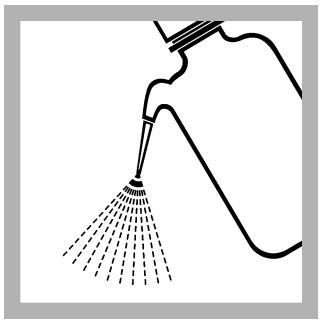


2. Laboratory test: Put the probe in a beaker that contains the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip. Stir the sample at a slow to moderate rate.
Field test: Put the probe in the sample. Move the probe up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

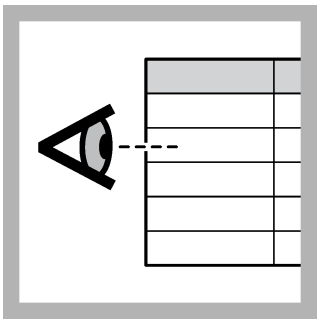
Use the steps that follow to make an estimate of the sample volume to use in the test procedure.

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.

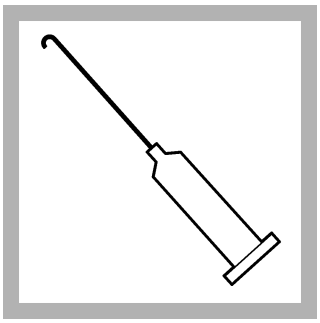
Table 1 Determine the sample volume

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

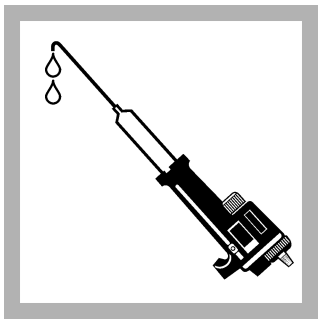
Test procedure



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

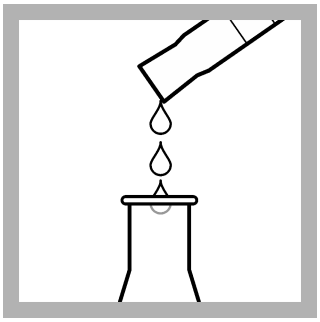


2. Insert a clean delivery tube into the 0.800 M EDTA Titration Cartridge. Attach the cartridge to the Digital Titrator.

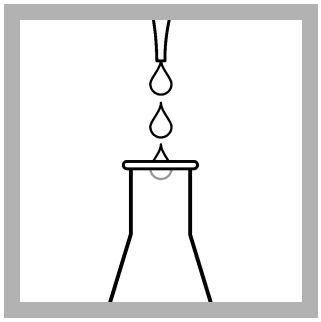


3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.

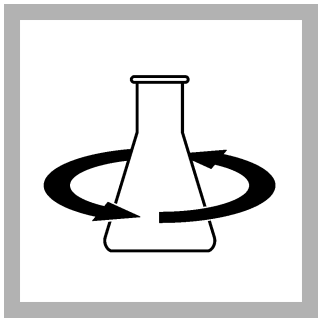
4. Use a graduated cylinder to measure the sample volume from Table 2 on page 3.



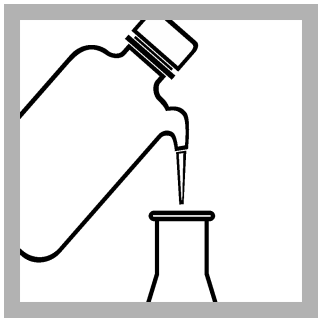
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



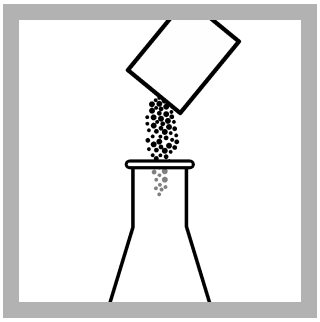
6. If the sample volume is 100 mL, add 2 mL of 8 N Potassium Hydroxide Standard Solution. If the sample volume is 50 mL or less, add 1 mL of 8 N Potassium Hydroxide Standard Solution.



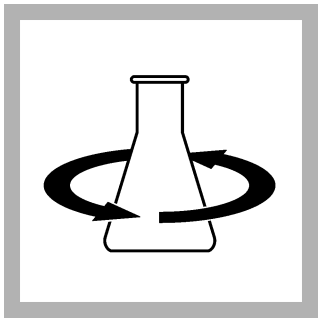
7. Swirl to mix.



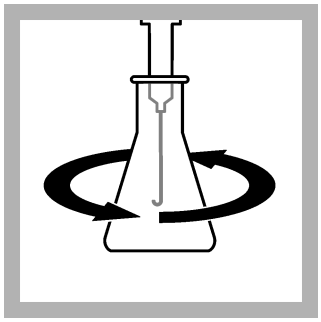
8. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



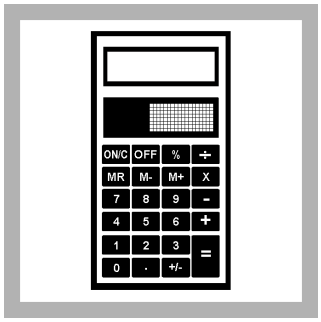
9. Add the contents of one CalVer 2 Calcium Indicator Powder Pillow.



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

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.

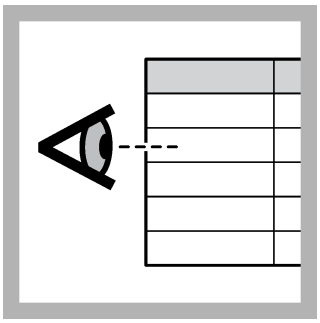
1. Add approximately 75–100 mL of deionized water to a clean titration flask.
2. Use a TenSette pipet to add 0.2 mL of the sample to the titration flask. Swirl to mix.

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.

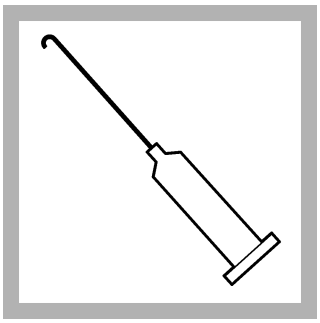
Table 1 Determine the sample volume

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

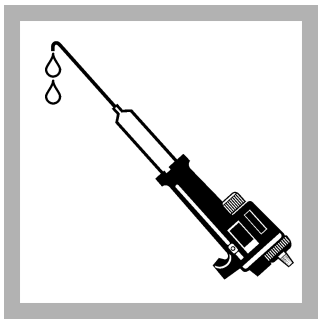
Test procedure



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

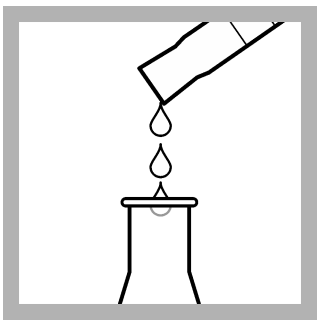


2. Insert a clean delivery tube into the 0.800 M EDTA Titration Cartridge. Attach the cartridge to the Digital Titrator.

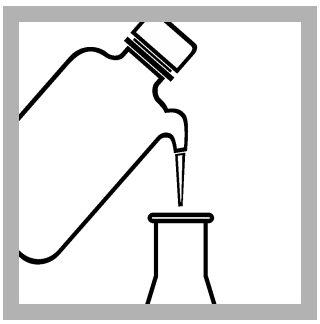


3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.

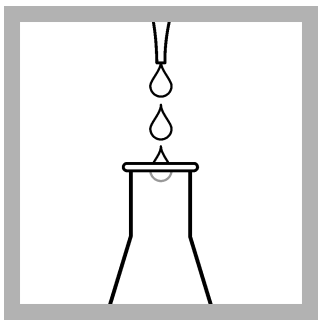
4. Use a graduated cylinder to measure the sample volume from Table 2 on page 3.



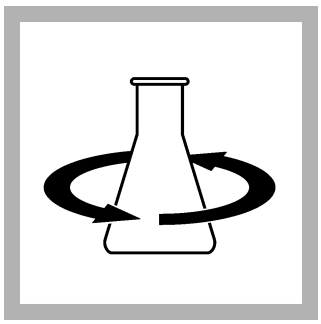
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



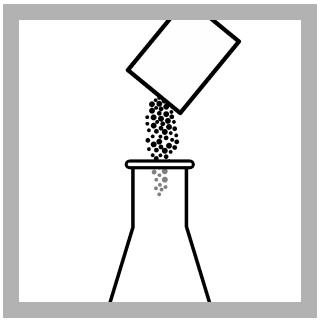
6. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



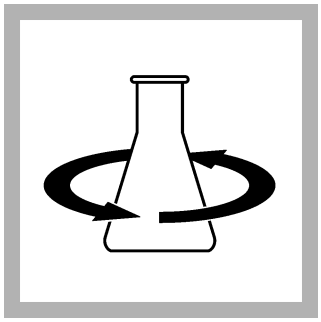
7. Add 1 mL of Hardness 1 Buffer Solution.



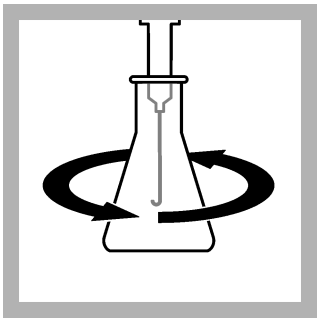
8. Swirl to mix.



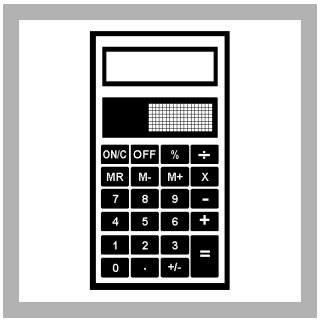
9. Add the contents of one ManVer 2 Hardness Indicator Powder Pillow.



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

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

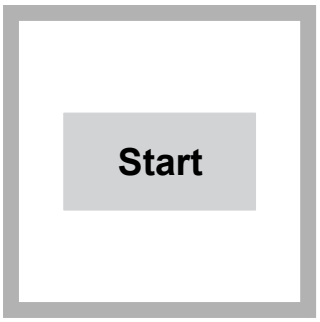
Description	Quantity
FerroVer® Iron Reagent Powder Pillow, 10-mL	1
EDTA solution, 1M	2 drops
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	1

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

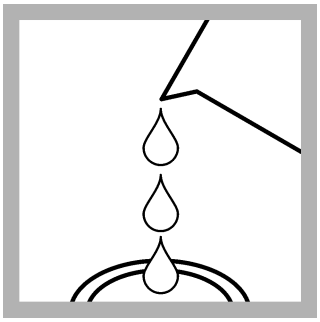
Sample collection and storage

- 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



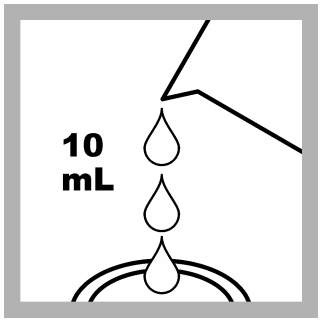
1. Start program **265 Iron, FerroVer**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



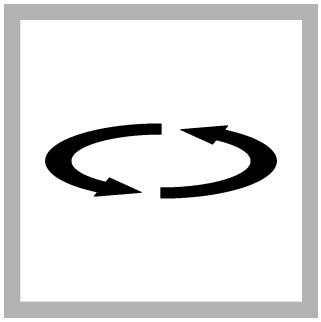
2. Fill a clean sample cell with sample:

- 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.*

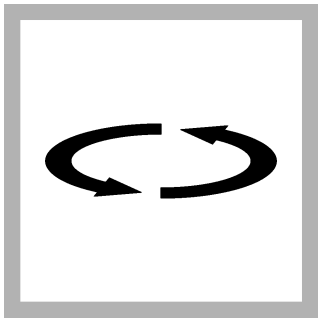


3. If the sample volume is less than 10 mL, add deionized water to the 10-mL line.

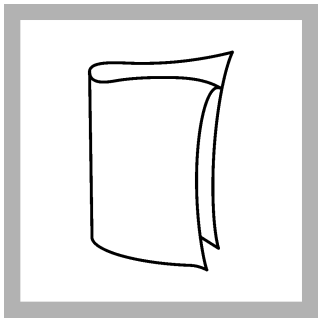


4. Swirl to mix.

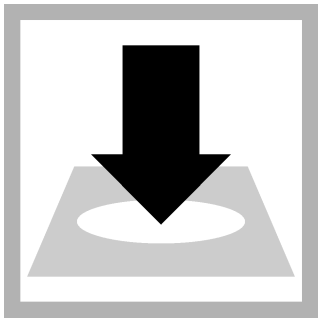
5. Add 2 drops of 1 M EDTA Solution to the sample.



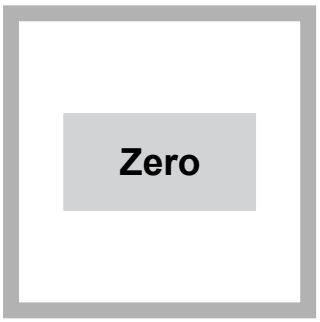
6. Swirl to mix.



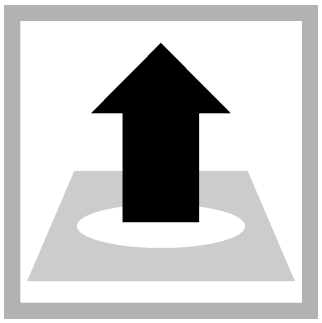
7. Clean the sample cell.



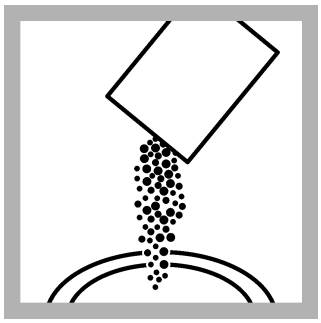
8. Insert the sample cell into the cell holder.



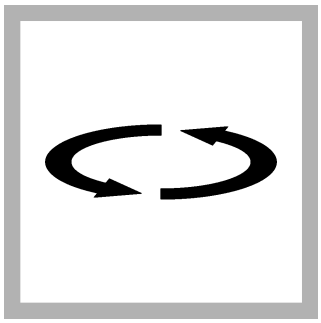
9. Push **ZERO**. The display shows 0.0 mg/L Fe.



10. Remove the sample cell from the cell holder.



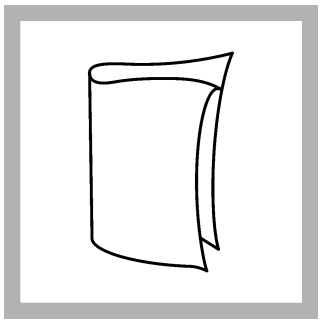
11. Add the contents of one FerroVer Iron Reagent Powder Pillow to the sample cell.



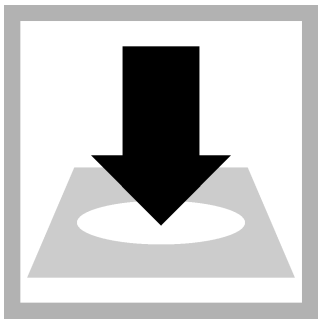
12. Swirl to mix. Accuracy is not affected by undissolved powder.

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

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

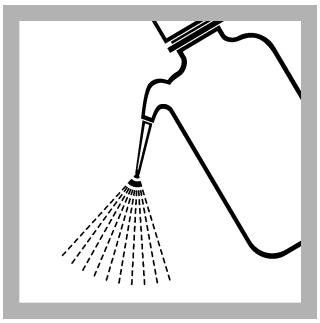
Description	Quantity
Beaker or sample containers	3
Wash bottle with deionized water	1
pH buffers (4.0, 7.0, 10.0)	3

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

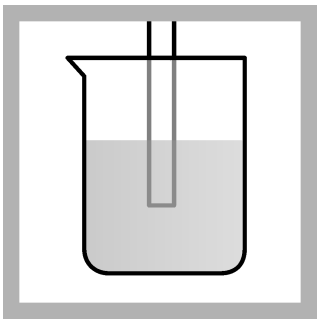
Sample collection

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Collect samples in clean glass or plastic bottles.

Test procedure

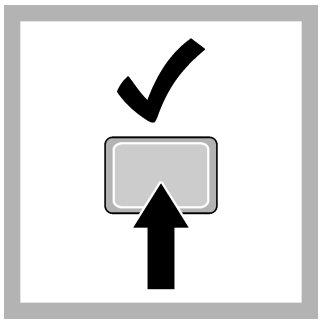


1. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

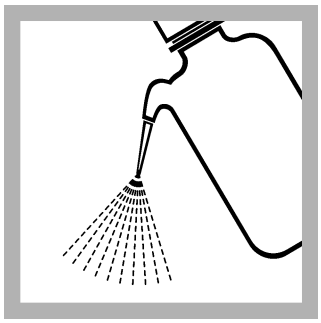


2. Laboratory test: Put the probe in a beaker that contains the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip. Stir the sample at a slow to moderate rate.
Field test: Put the probe in the sample. Move the probe up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

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

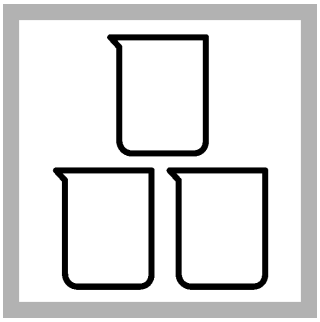


3. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.



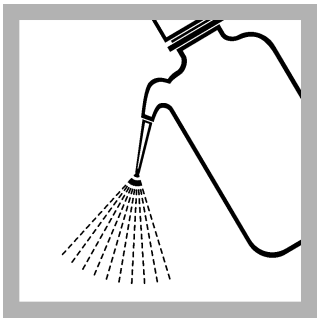
4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

Calibration procedure

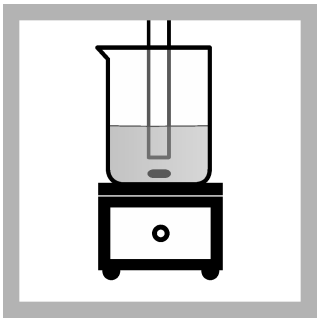


1. Prepare two or three fresh buffer solutions in separate beakers. If two buffers are used, use a 7.0 and a 4.0 or a 7.0 and a 10.0 pH buffer solution.

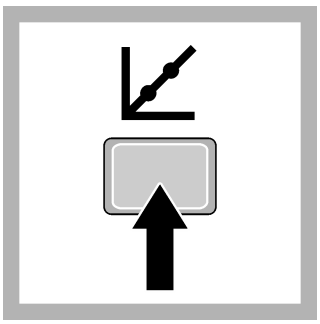
2. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



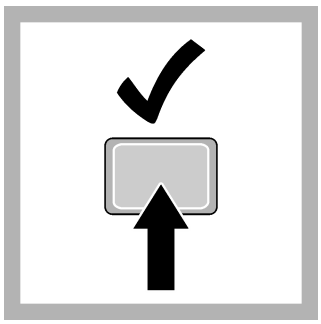
3. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



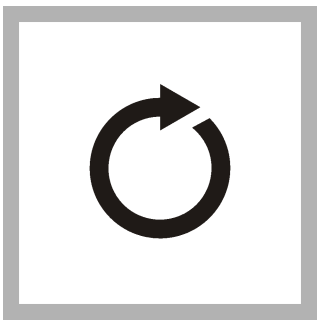
4. Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.



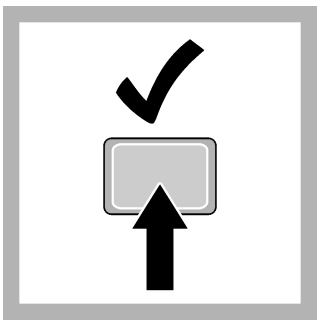
5. Push **Calibrate**. The standard solution value is shown.



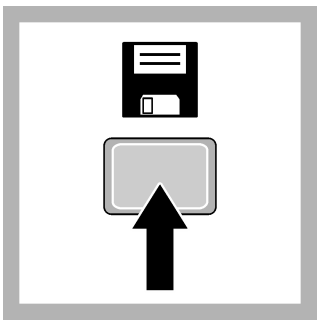
6. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.



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

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

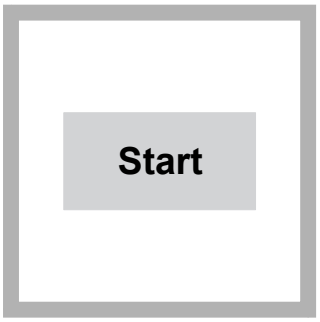
Description	Quantity
SulfaVer® 4 Reagent Powder Pillows, 10-mL	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	1

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

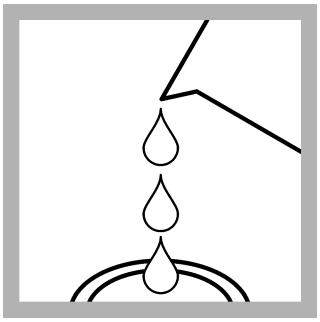
Sample collection and storage

- 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



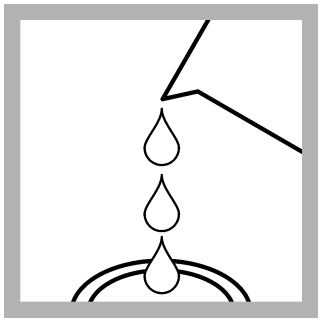
1. Start program **680 Sulfate**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



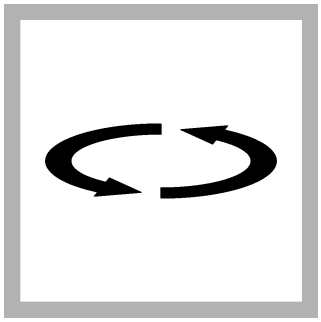
2. Add the sample volume that is specified for the test range to a sample cell:

- 2–70 mg/L: 10 mL
- 20–700 mg/L: 1.0 mL
- 200–7,000 mg/L: 0.1 mL

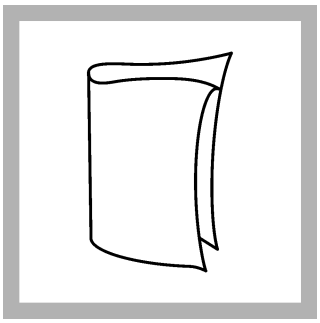
Use a TenSette Pipet or glass pipet to measure 0.1 mL or 1.0 mL.



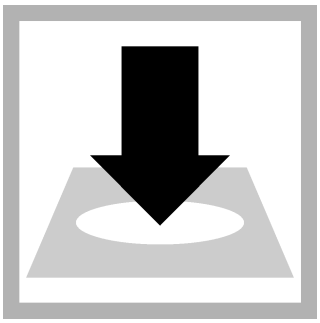
3. If the sample volume is less than 10-mL add deionized water to the 10-mL line.
For the dilution factor, refer to Set the dilution factor on page 3.



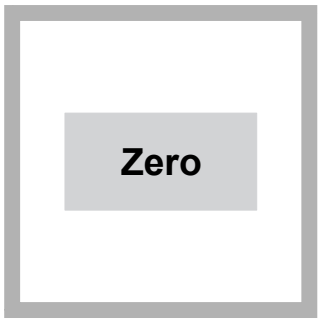
4. Swirl to mix.



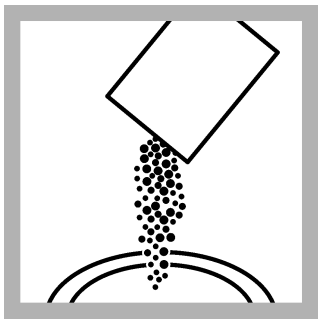
5. Clean the blank sample cell.



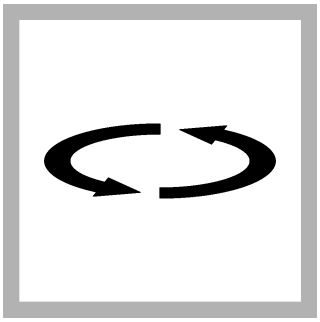
6. Insert the blank into the cell holder.



7. Push **ZERO**. The display shows 0 mg/L SO_4^{2-}.



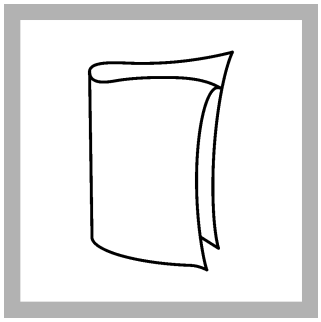
8. Add the contents of one SulfaVer 4 Reagent Powder Pillow to the sample cell. The sample will get cloudy if sulfate is present in the sample.



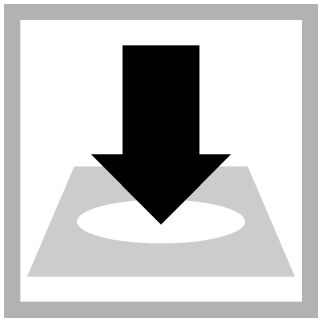
9. Swirl the sample cell to mix. Undissolved powder will not affect accuracy.

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

Do not move the sample cell during the reaction period.

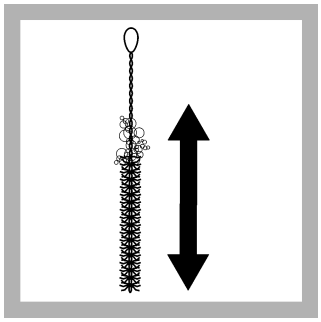


11. Clean the prepared sample cell.



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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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)

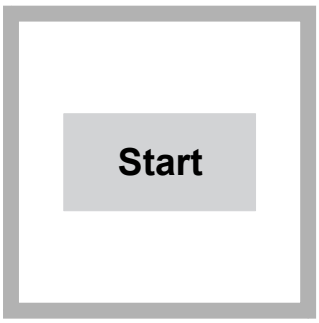
Description	Quantity
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2
Stoppers	2
Water, deionized	10 mL

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

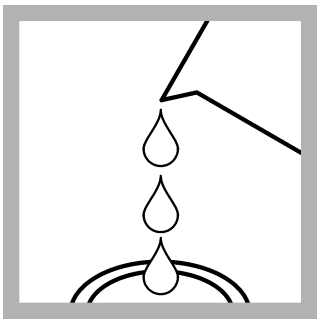
Sample collection

- 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.

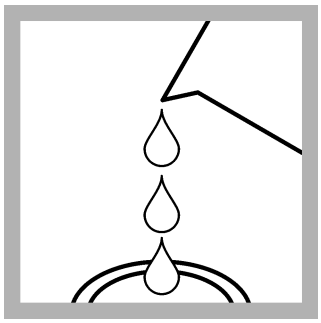
Methylene Blue method



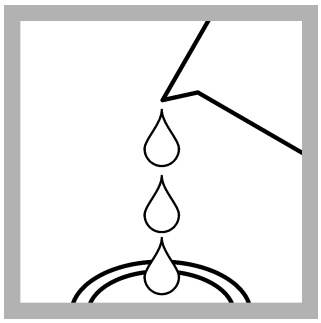
1. Start program **691 Sulfide HR**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



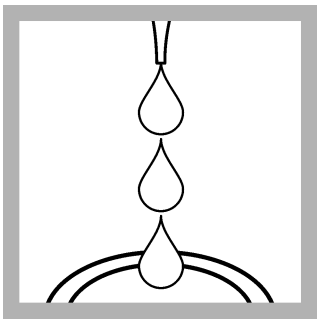
2. Prepare the blank: Fill a sample cell with deionized water. Use 10 mL for spectrophotometers and 25 mL for colorimeters.



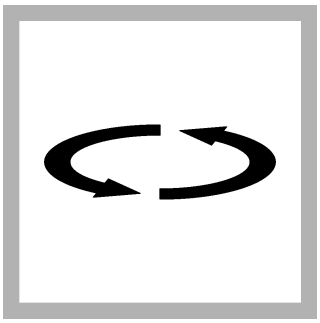
3. Prepare the sample: Add the sample volume that is specified for the test range to a clean sample cell. Refer to Table 2 on page 3.
Use a pipet to measure small volumes.



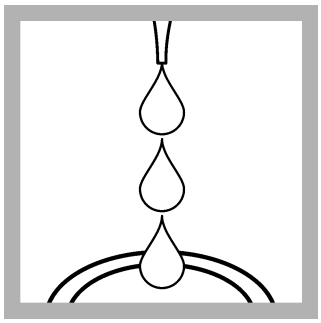
4. Spectrophotometers: Add deionized water to the 10-mL line. **Colorimeters:** Add deionized water to the 25-mL line.
To prevent sulfide loss, do not mix the sample more than necessary.



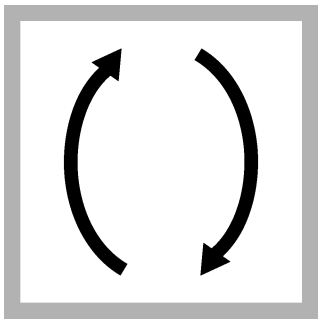
5. Add Sulfide 1 Reagent to each sample cell. Use 0.5 mL of reagent for spectrophotometers. Use 1.0 mL of reagent for colorimeters.



6. Swirl to mix.

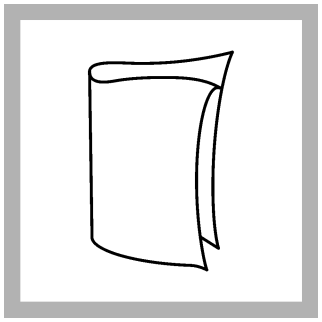


7. Add Sulfide 2 Reagent to each sample cell. Use 0.5 mL of reagent for spectrophotometers. Use 1.0 mL of reagent for colorimeters.

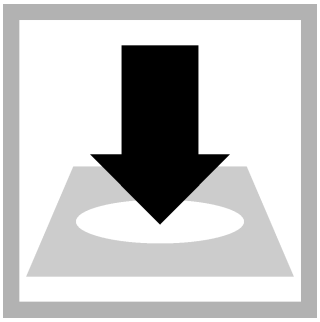


8. Put the stopper on both sample cells with a stopper. Invert to mix. The solution shows pink and then blue if sulfide is in the sample.

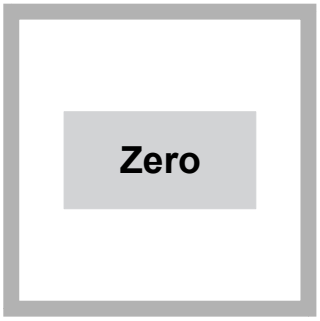
9. Start the instrument timer. A 5-minute reaction time starts.



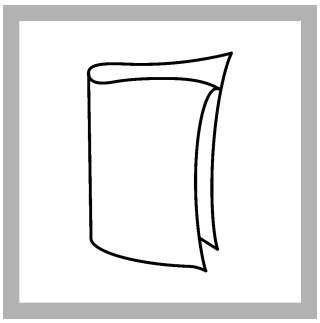
10. When the timer expires, clean the blank sample cell.



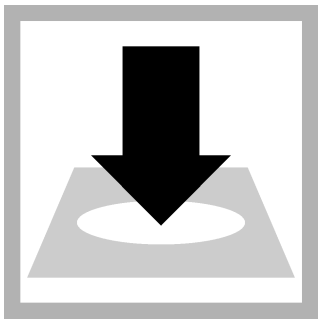
11. Insert the blank into the cell holder.



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

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

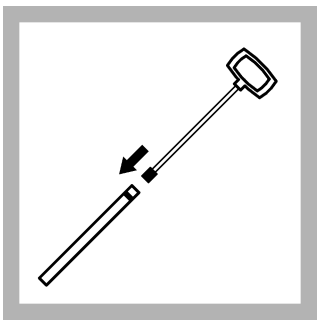
Refer to Consumables and replacement items on page 10 for order information.

Sample collection and storage

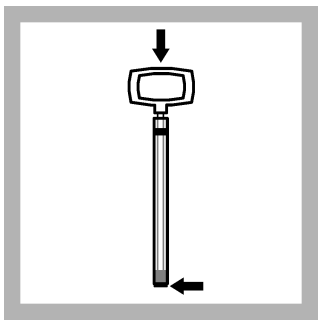
- Analyze the samples as soon as possible for best results.
- If sample storage is necessary, collect the samples in glass or PTFE containers. Clean the containers with soap and water, then rinse the containers with methanol. Use PTFE-lined caps for the containers. If PTFE-lined caps are not available, 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

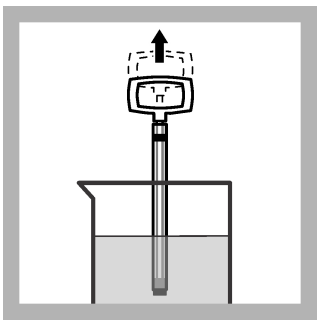
The Wiretrol Pipet accurately measures small quantities of liquids. The Wiretrol Pipet has two parts: a PTFE-tipped plunger and a calibrated capillary tube. The plunger can be used many times. Discard the capillary tubes after one use.



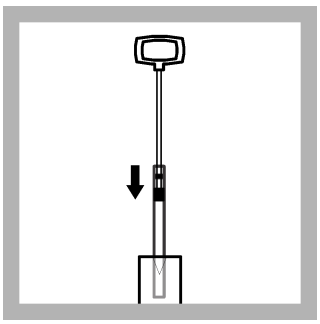
1. Make sure that the plunger tip is wet with the liquid. Carefully insert the plunger tip into the end of the capillary tube with the colored band.



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.

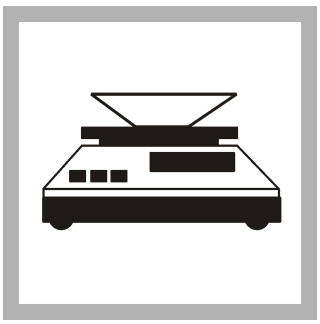


3. Insert the capillary tube below the surface of the liquid. Slowly and smoothly, pull the plunger up until the bottom of the plunger tip reaches the applicable volume line. Touch the end of the tube to the side of the vessel to release drops that remain on the capillary tube tip.

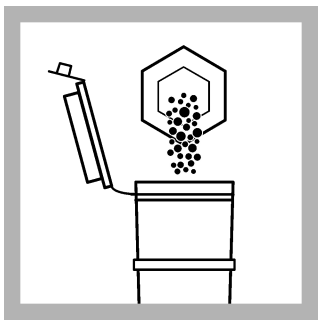


4. To release the liquid, insert the tip of the capillary tube **below the surface of the receiving solution**, and push the plunger downward in one smooth motion. Change capillary tubes for each calibrator and sample.

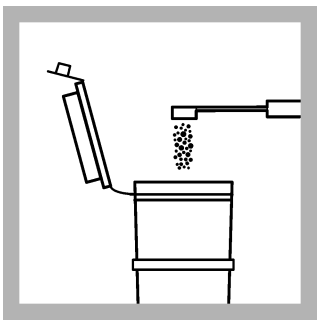
Soil extraction procedure



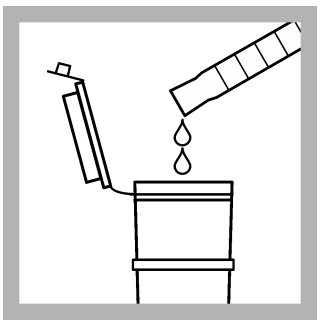
1. Weigh 10 g of soil in the plastic weighing boat.



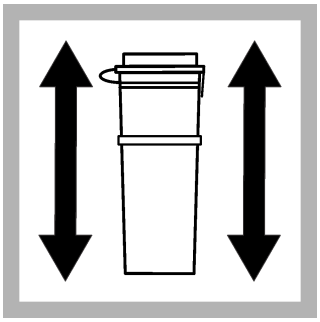
2. Carefully pour the soil into an extraction vial.



3. Use the 5-gram scoop to add one scoop of sodium sulfate to the extraction vial.

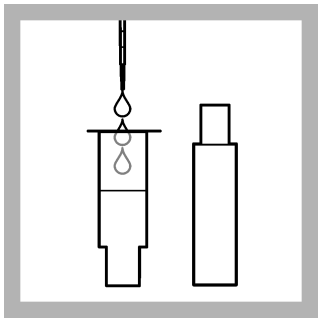


4. Use the graduated cylinder to add 10 mL of Soil Extractant into the extraction vial.

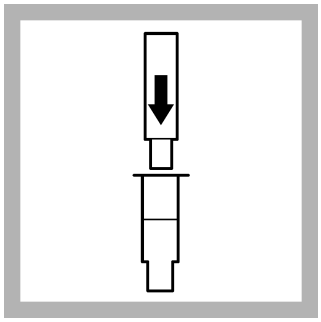


5. Put the cap on the extraction vial tightly. Shake vigorously for 1 minute.

6. Let the particles settle for a minimum of 1 minute. Carefully open the extraction vial.

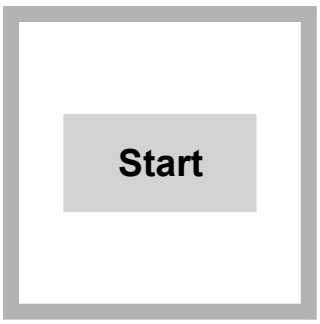


7. Use the disposable pipet to remove 1.0 to 1.5 mL from the top of the liquid layer. Add the removed liquid to the filtration barrel. Do not use more than 1.5 mL. The pipet can measure in 0.25-mL increments.

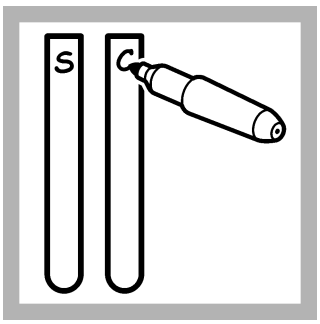


8. Put the filtration plunger into the filtration barrel. Set the filtration assembly on a table or flat surface. Push firmly on the plunger until the sample extract is forced upward into the center of the plunger.
Use the resulting filtrate for the immunoassay procedure.

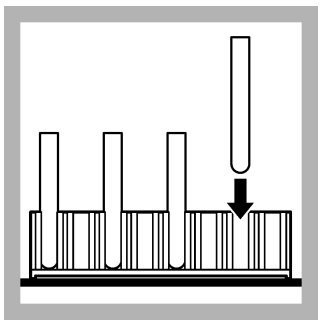
Immunoassay procedure



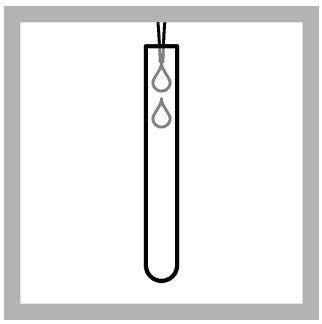
1. Push **SINGLE WAVELENGTH**>**OPTIONS**, then the **λ** key. Enter **450 nm** and push OK. For information about adapters, refer to Instrument specific information on page 1.



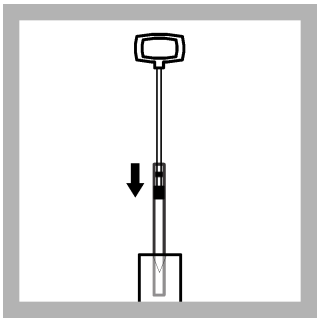
2. Put marks on the cuvettes to identify the samples and calibrators.



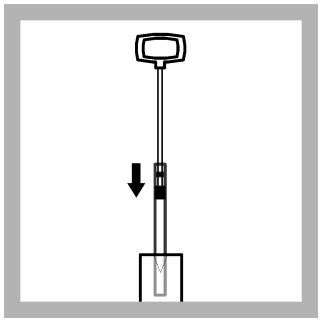
3. Insert the cuvettes into the rack. Make sure that the cuvettes are secure. Do not use force to put them into position because the cuvettes can spill or can be difficult to remove.



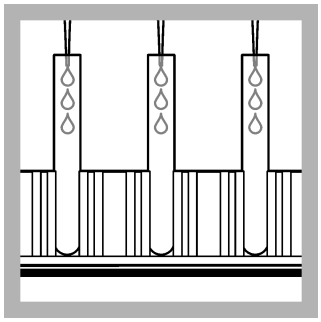
4. Soil samples: Use a pipet to add 0.5 mL of Diluent Solution into each calibrator and sample cuvette. The same pipette tip can be used for this step.
Water samples: Use a pipet to add 0.5 mL of each water sample into a sample cuvette. Use a new pipet for each sample.



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.**

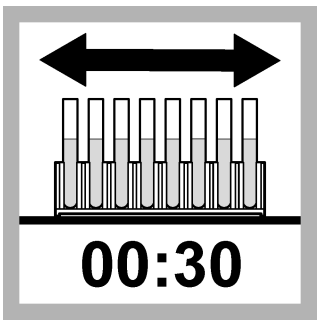


6. Soil samples: Use a Wiretrol pipet to add 50 µL of the filtered extract from the soil extraction procedure. Refer to Soil extraction procedure on page 3. Use a separate capillary tube for each solution. Mix the contents of the cuvettes after each addition.
Water samples: Use a Wiretrol pipet to add 50 µL of methanol into each sample cuvette. Mix the contents of the cuvettes after each addition.

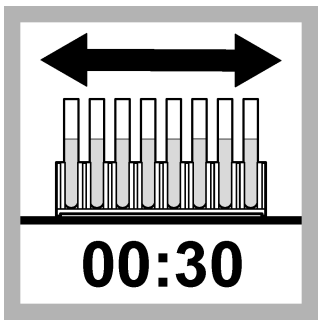


7. Immediately use a pipet to add 0.5 mL of TPH Enzyme Conjugate into each calibrator and sample cuvette. The same pipette tip can be used for this step.

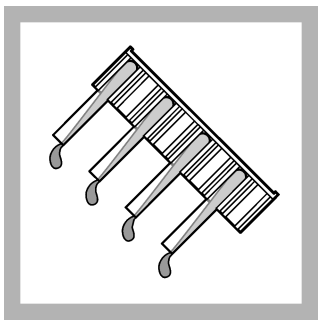
8. Start the instrument timer. The reaction time starts.



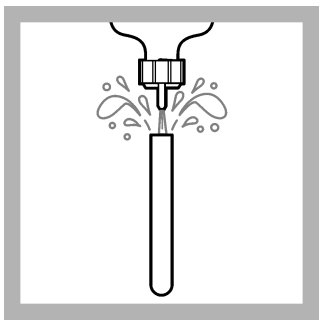
9. Immediately mix the cuvettes for 30 seconds. Refer to Use of the 12-mm MicroCuvette rack on page 7 for the correct mixing procedure.



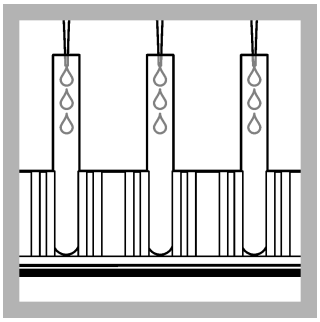
10. After 5 minutes, mix the contents of the rack a second time for 30 seconds.



11. At the end of the 10-minute reaction period, discard the contents of all the cuvettes into a waste container for disposal.

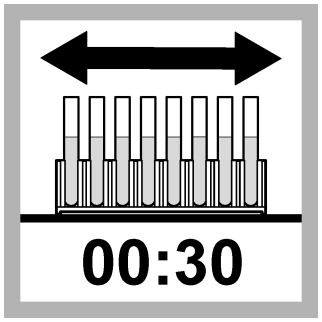


12. Fully rinse each cuvette with deionized water four times. Discard the contents into the waste container for disposal. Turn the cuvettes and rack upside down on a paper towel to dry. Carefully tap the cuvettes on the towel to remove the liquid.

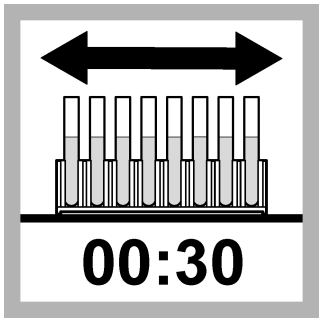


13. Start color development: Timing is very important. Make sure that the cuvettes are still in position in the rack. Use the pipet to add 0.5 mL of Color Developing Solution into each Antibody Cuvette. Use a new pipette tip for each cuvette.

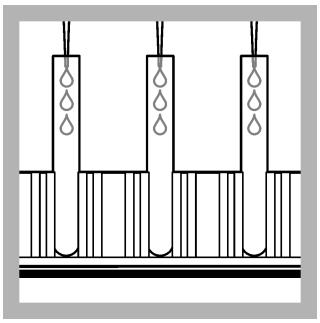
14. Start the instrument timer. The reaction time starts.



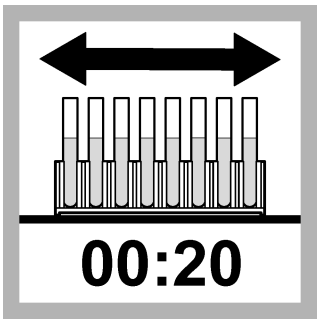
15. Immediately mix the cuvettes for 30 seconds.



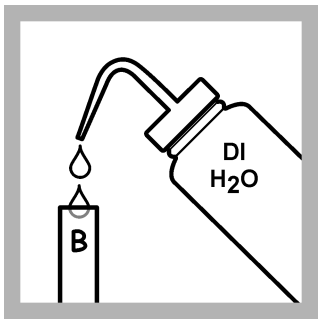
16. After 5 minutes, mix the contents of the rack a second time for 30 seconds.



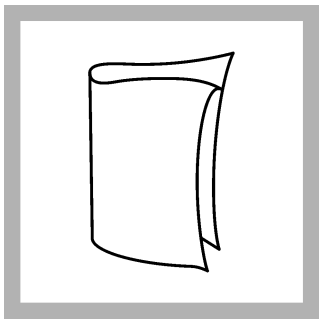
17. When the timer expires, use a pipette to add 0.5 mL of Stop Solution into each cuvette with the same pipette tip. Consistent technique is very important. Add the solution in the same sequence that was used for the Color Developing Solution addition.



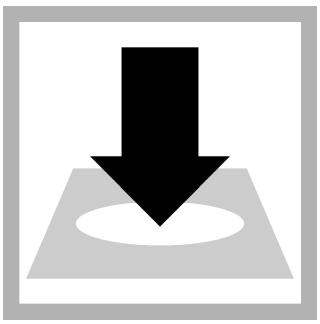
18. Slide the rack back and forth for 20 seconds. The blue solution color changes to yellow.



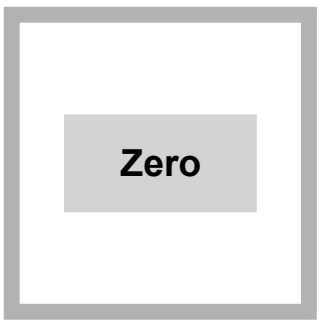
19. Put a mark on a zeroing cuvette to identify it as the blank. Fill the cuvette with deionized water.



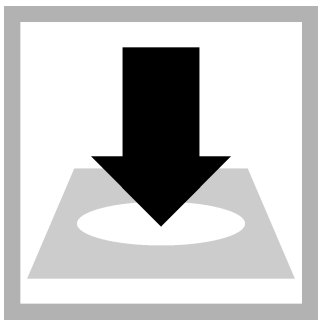
20. Clean all of the cuvettes.



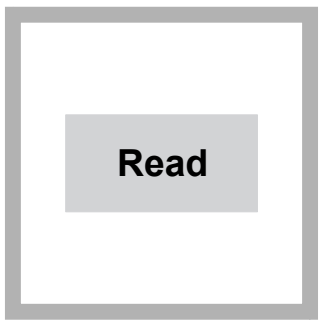
21. Insert the blank into the circular cell holder.



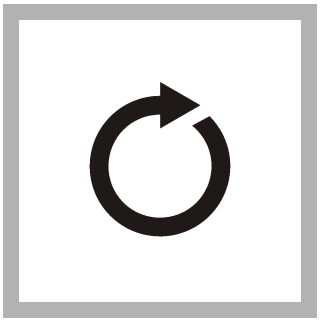
22. Push **ZERO**. The display shows 0.000 Abs.



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.

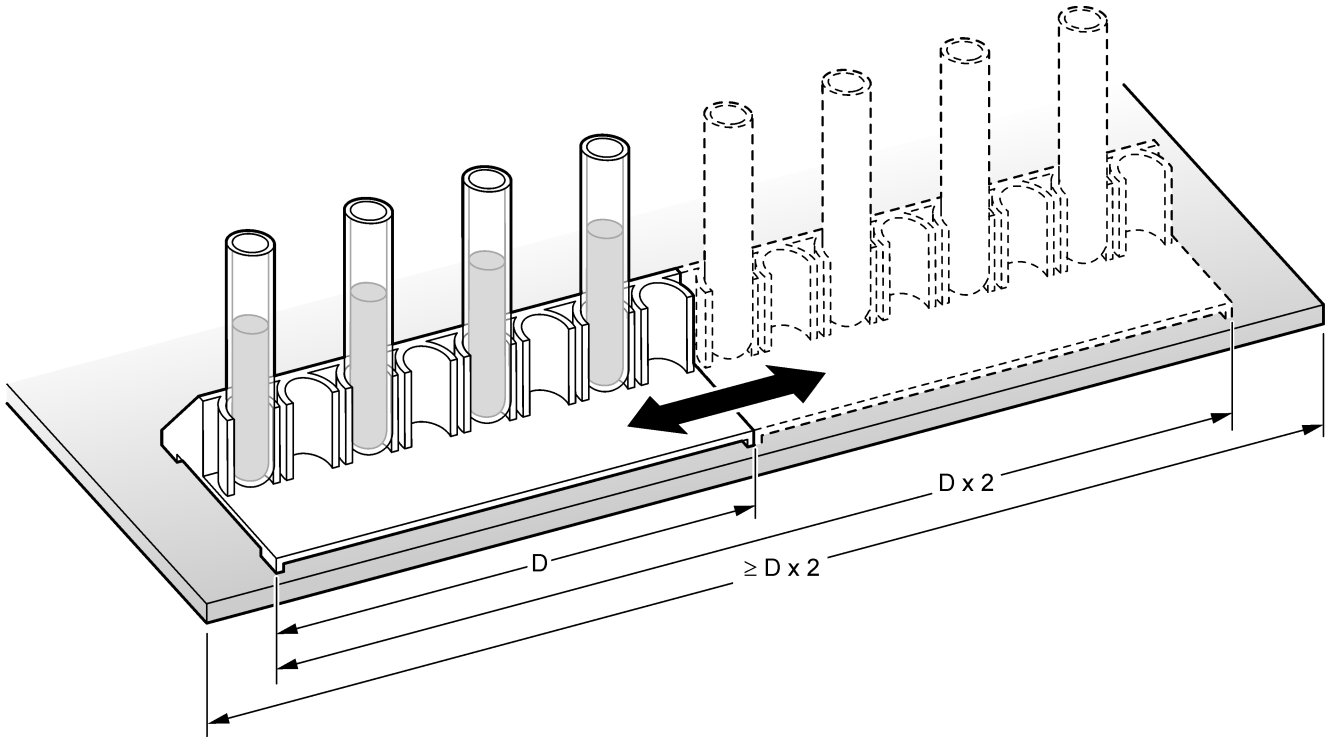
Use of the 12-mm MicroCuvette rack

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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FAX: (970) 669-2932

 01/2017, Edition 11

Chemical Procedures Explained

Barium

Introduction

Barium is a naturally-occurring byproduct of the drilling process. Barium with strontium, calcium and bicarbonate can cause scale deposits to form in flow line pipes when fracturing water with high sulfate concentrations is in the flow line pipes. Barium and strontium react with sulfate to form a white precipitate, which causes scaling inside the pipes.

Recommended instrumentation

- BariVer 4 Reagent Powder Pillows for 10-mL samples
- Hach DR spectrophotometer/colorimeter for use with Method 8014 or Method 10251. Method 8014 and Method 10251 are specifically for oil and gas produced and flowback waters.

Matrix challenges

Strontium interferes with barium at concentration of 20 mg/L stronium (Sr) and 20 mg/L barium (Ba). If the sample concentration of Ba and Sr are diluted to a concentration 20 mg/L or less, the interference from Sr becomes almost zero. When Sr is in the sample without Ba, Sr is not detectable with the BariVer 4 reagent. A 100-mg Sr/L spike in a sample without Ba gave a concentration of 2-mg Ba/L, which is the lowest detectable concentration for the method.

Figure 1 and Table 1 show the effect that Sr has on the Ba concentration when both Ba and Sr are in the sample at the same concentrations.

If the Ba and the Sr concentrations are approximately the same concentration, the analyst can dilute them within the applicable concentration range for the Ba method (2–100 mg/L). Dilute the Ba and Sr concentrations so they are both 20 mg/L or less to prevent the Sr interference.

Figure 1 Ba spike versus a combination of Ba and Sr at the same concentration levels

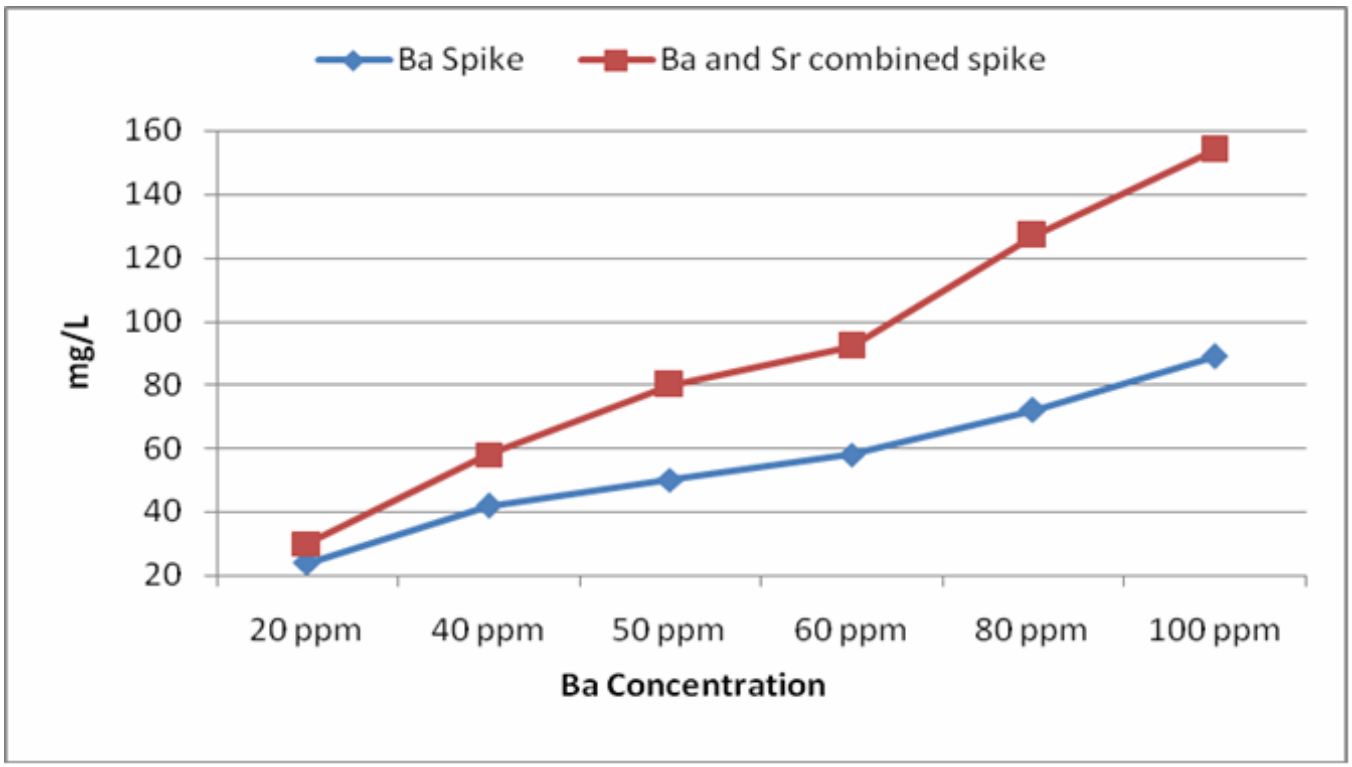


Table 1 Corresponding data for Figure 1

Ba spike concentration (mg Ba/L)	Ba spike recovery	Sr spike recovery at the same concentration as the Ba spike (mg Ba/L)[1]	% difference
20	24	30	20
40	42	58	28
50	50	80	38
60	58	92	37
80	72	127	43
100	89	154	42

[1] Both Ba and Sr are spiked at the same concentration. For example, the first combined standard set was spiked with 20 mg/L Ba and Sr, the second set was spiked with both 40 mg/L of Ba and Sr, and so on. As the concentration of both analytes in the combination spike increases, the % difference between the Ba spike and the combination spike of Ba and Sr increases based on the nature of the Sr interference with the BariVer 4 chemistry.

Hardness, Total and Calcium

Introduction

Total hardness in water is caused by dissolved minerals, mostly divalent cations. In natural water systems, calcium and magnesium are the primary contributing ions for total hardness. However, produced and flowback waters have high quantities of barium, strontium and iron, along with elevated concentrations of calcium and magnesium, which titrate out directly with the EDTA titrant. Elevated quantities of calcium can prevent the borate and zirconate crosslinking.

The calcium hardness titration is done at a different pH than the total hardness titration. The pH is elevated to a minimum of 13 to precipitate magnesium so only the calcium ion is titrated.

Recommended_instrumentation

- Digital Titrator Kit
- Total Hardness Reagents, 4000 mg/L
- Calcium Hardness Reagents, 4000 mg/L
- CDTA Magnesium Salt Powder Pillows to remove iron interference

Matrix challenges

Total hardness

Produced and flowback water can have elevated levels of barium, strontium and iron. Iron interference in the sample causes a red-orange to green endpoint. Add a CDTA powder pillow when the iron concentrations are more than 100 mg/L to remove the iron interference. The hardness concentrations in these matrices are very high, so use a smaller sample volume to decrease the iron interference. If the iron concentration in the sample is at a concentration of more than 100 mg/L after a smaller sample volume is used, add a CDTA powder pillow to decrease the iron interference.

CDTA does not have an effect on barium or strontium interference, which are titrated directly along with calcium and magnesium. So, the total hardness value includes the divalent cations of barium, strontium, calcium and magnesium. If the barium and strontium concentrations (interfering cations) of the sample are known, do a molecular weight conversion of barium and strontium to $CaCO_3$ to subtract the barium and strontium concentrations from the total hardness value.

The hardness equivalence factor for barium is 0.729 and strontium is 1.142. Multiply the barium and strontium concentrations by the hardness equivalence factors to convert their concentrations to $CaCO_3$. Then, subtract the $CaCO_3$ values from the total hardness concentration to get a more accurate hardness value for only magnesium and calcium hardness. Refer to the Hardness equivalence factors table in Use CDTA to remove metal interferences for other metal hardness equivalence factors. To report the actual total hardness of the sample, do not subtract the barium and strontium concentrations.

Calcium hardness

For the calcium hardness titration, laboratory studies have shown that a sample that contains barium and strontium will not precipitate at pH 13 and barium and strontium are titrated with the calcium in the sample. If strontium and calcium are not in the sample, the barium precipitates at pH 13.

Most produced and flowback water samples have strontium, calcium and barium at high concentrations. If the concentrations of barium and strontium are known, barium and strontium can be subtracted from the calcium hardness titration in the same manner as the total hardness titration. Convert the barium and strontium to $CaCO_3$ with the equivalence factors given for total hardness. After the barium and strontium are subtracted, the value is the calcium hardness as $CaCO_3$. To convert calcium as $CaCO_3$ to the elemental of only calcium, multiply the Ca hardness value by 0.4.

Iron

Introduction

Iron is a byproduct of the drilling process. Ferrous (Fe+2) is destructive to the fracing fluid. The fracing fluids have chemicals added to prevent the precipitation of metal oxides. Iron is one of the most important metals. When the fracing fluid is prepared, make sure that the ferrous iron concentration is less than 10 mg/L to prevent fluid degradation. The FerroVer chemistry identifies ferrous and ferric (Fe+3) iron. Iron in ground water is typically in the ferrous form, which oxidizes quickly to ferric iron with exposure to air.

Recommended instrumentation

- FerroVer Iron Reagent Powder Pillows for 10-mL samples
- EDTA Solution (1 M), 50 mL
- Hach DR spectrophotometer/colorimeter applicable to the FerroVer 8008 method or Method 10249, which is written for oil and gas produced and flowback waters.

Determination of iron

Test results are dependent on the sample pretreatment steps and the iron reagent reaction conditions. The FerroVer Iron Reagent contains strong reducing agents and 110 phenanthroline indicator. The reducing agents change the ferric iron in the sample to ferrous iron. The phenanthroline indicator then reacts with the ferrous iron to form an orange color in proportion to the iron concentration. The strong reducing agents in FerroVer change most insoluble iron forms to soluble ferrous iron and can be included in the test results.

A total iron test to determine soluble and insoluble iron includes a mild acid digestion followed by analysis with FerroVer Iron Reagent. Samples that are filtered before analysis to remove particulates (or analyzed with iron reagents that contain ascorbic acid as the reducing agent) usually give much lower test results. So, it is important to record the sample pretreatment steps when the test results are compared with previous analysis or with other outside laboratories that use other colorimetric or instrumental methods of analysis.

Matrix challenges

Barium and strontium can be at high concentrations in fracing fluids. Barium and stronium concentrations of more than 50 mg/L interfere with the iron analysis by the formation of a precipitate. Strontium by itself does not interfere with the iron analysis. When strontium and barium are in the solution together, which is usual in fracing fluids, the strontium is a catalyst that increases the barium interference.

The precipitate/turbidity interference is removed with the addition of a 1 M EDTA solution. The EDTA does not chelate the iron, but removes barium and strontium from the sample. The amount of EDTA necessary to overcome the interference is dependant on the concentration of the barium (Ba) and strontium (Sr) in the sample. Laboratory studies have shown that 1 to 2 drops of a 1 M EDTA solution added to a 10-mL sample volume is sufficient to remove the barium interference of approximately 50 to 200-mg/L Ba/Sr. Concentrations of 200 to 1000 mg/L Ba/Sr, use a maximum of 5 drops of 1 M EDTA to remove the interference. If there is precipitate in the sample after the addition of the FerroVer Reagent Powder Pillow, add more EDTA or dilute the sample to decrease the barium/strontium interference. Use 5 drops of EDTA or less with a 10-mL sample volume.

Add no more than 10 drops to a 10-mL sample. If too much EDTA is added to the sample, the color development of the FerroVer reagent is slowed. It was seen in the laboratory that 10 drops of EDTA in a 10-mL sample caused the colorimetric reaction to take as much as 30 minutes to develop. The addition of EDTA ties up the barium, strontium and the iron, because they are all cations. However, the phenanthroline indicator in the FerroVer reagent has a stronger affinity to the iron than the EDTA does and will complete the colorimetric reaction.

At very high concentrations of Ba and Sr in the sample (more than 500 mg/L of Ba and Sr together), laboratory studies have shown that with the addition of EDTA at the upper-end of the FerroVer concentration range (2.5 to 3.0 mg/L iron) the color formation is still slower. Complete color development can take as much as 10 minutes.

For the most accurate results, dilute the sample to an iron concentration of approximately 1 mg/L and the barium/strontium combination to approximately 50 to 200 mg/L. Then the 2 to 5 drops of EDTA added to the sample will work the most effectively to remove the barium/strontium interference.

Conductivity and Total Dissolved Solids

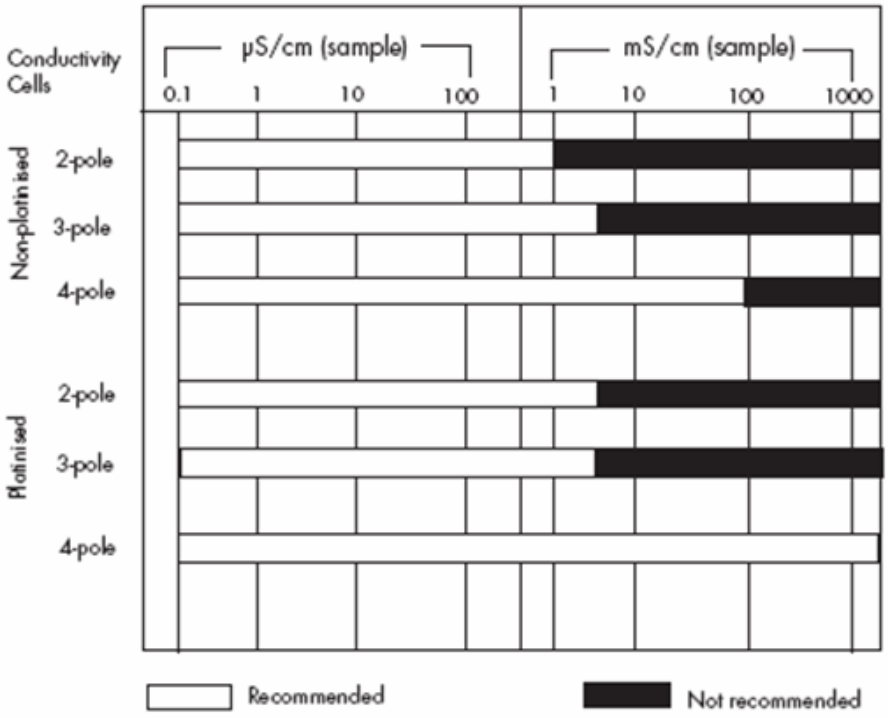
Introduction

Conductivity is an important parameter for very saline industrial water samples. Through the use of a conversion factor, the conductivity value is used to identify an estimate of the TDS value for the sample. Users can then use this TDS value (and past sample results) to identify an estimate of the applicable dilution factor necessary to analyze other parameters to identify trends in the treatment process efficiencies and to identify water quality changes.

Recommended instrumentation

Produced and flowback water have conductivity values that are in the mS/cm range, approximately 10 200+ mS/cm (approximately 10 150 g/L as TDS). As Figure 1. Figure x shows, to accurately measure conductivity values at this elevated level, it is necessary to use a 4-pole conductivity cell with an enhancement from graphite, stainless steel, or platinum[1].

Figure 1 Conductivity guidelines



Matrix challenges

Due to the high ranges of conductivity in the sample matrices, use a metal enhanced 4-pole cell. If a metal enhanced 4-pole cell is not available, dilute the sample to get the sample within the applicable range for the specifications of the available cell.

Note: *Laboratory studies have shown it is possible to get a 30% increase in conductivity values when the sample is diluted compared to samples that are not diluted. It is recommended that the samples for conductivity measurements are not diluted to prevent errors.*

Figure 2 and Table 1 show some of the effects of an increase in conductivity on diluted samples. Higher sample conductivities give larger positive errors when the sample is diluted.

[1] The enhanced 4-poled cells have a layer of metal (graphite, stainless steel or platinum) on the poles to decrease the effects of polarization and increase the concentration range. Refer to *Conductivity Theory and Practice* on the manufacturer's website for more information on conductivity theory.

The conductivity cells were calibrated with a single-point calibration and three different standards: 1408 µS/cm, 12.85 mS/cm and 111.3 mS/cm. None of the three calibrations decreased the difference between the undiluted and diluted samples. However, it is always recommended to calibrate with a calibration standard that applicable to the range of conductivity values of the sample. Figure 3 gives guidance on how to select the correct standard concentration.

Figure 2 Effects of increased conductivity on diluted samples

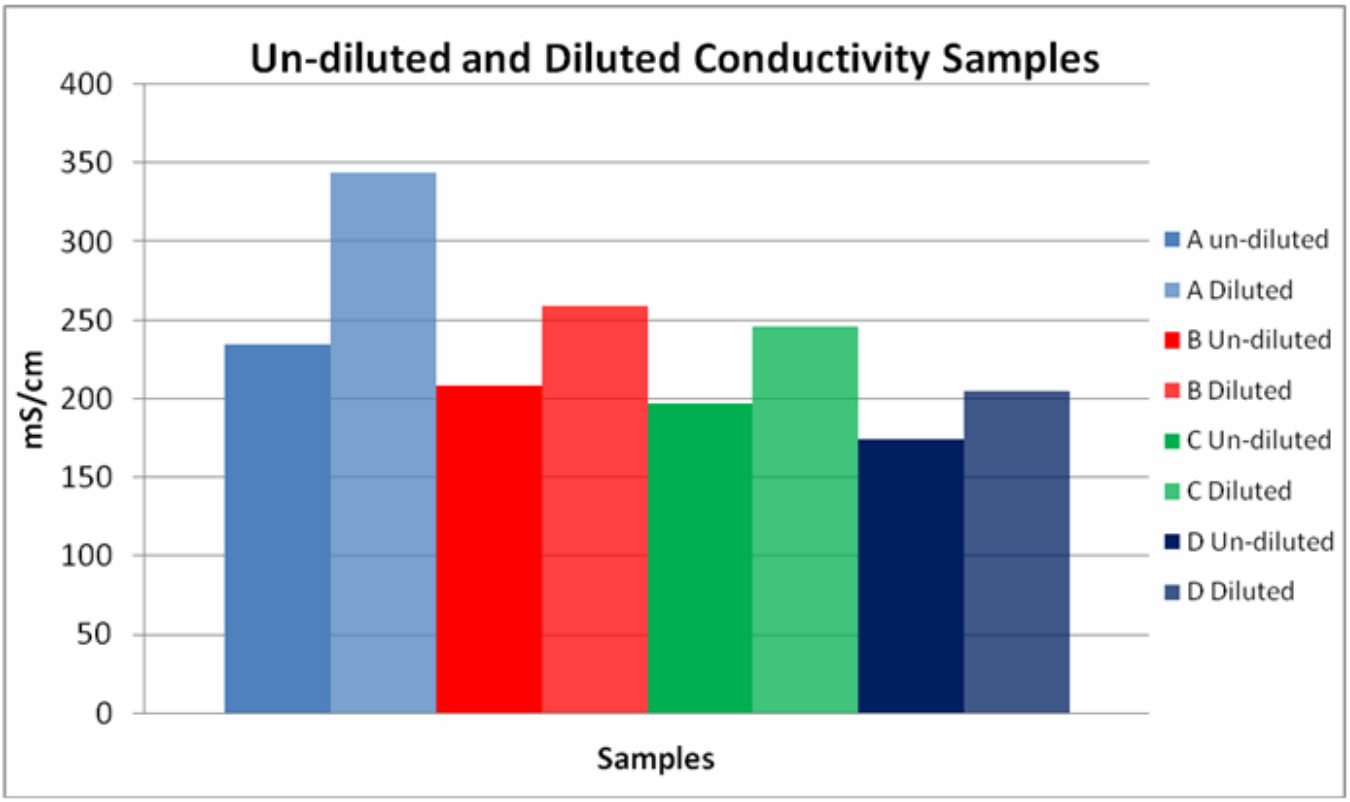
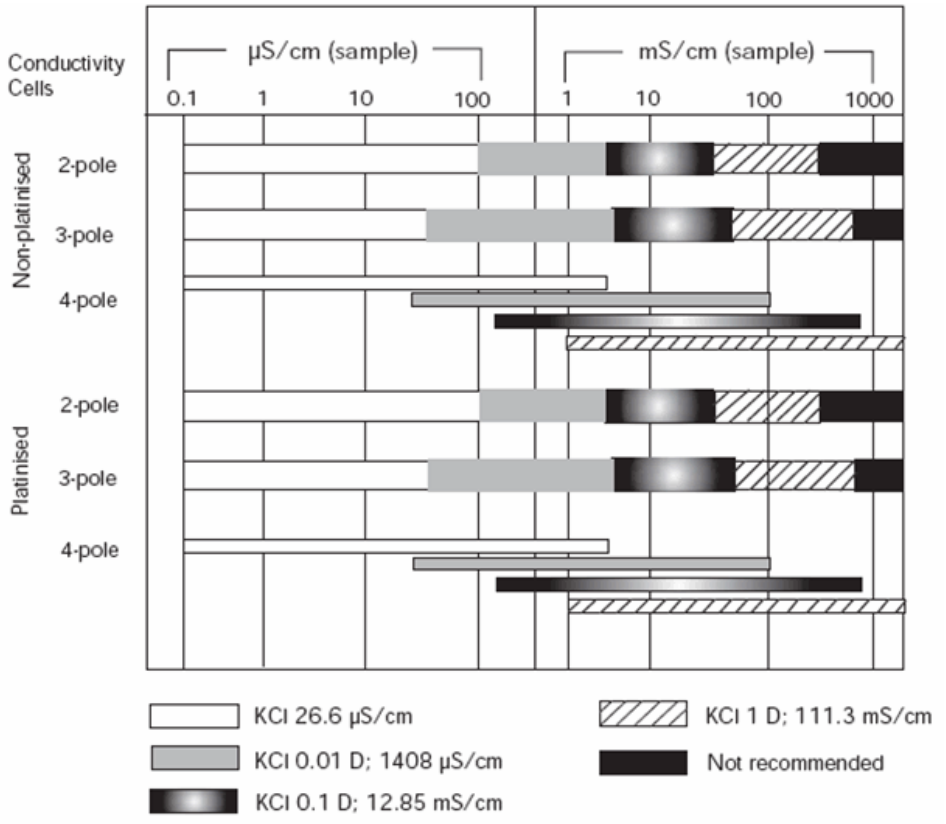


Table 1 Effects of increased conductivity on diluted samples

Sample[2]	Undiluted	Diluted	% difference
A	235	344	31.7
B	208	258.8	19.6
C	197.1	245.8	19.8
D	174.5	205.2	15.0

[2] Samples were diluted 1:1 and the conductivity measured. The result was multiplied by 2 to get the final diluted result.

Figure 3 Guidelines for choosing a conductivity cell and standard



Conductivity standards provided by Hach

- 111.3 mS/cm KCl Standard (1 D)
- 12.85 mS/cm KCl Standard (0.1D)
- 1408 µS/cm KCl Standard (0.01 D)

TDS factors

The different Hach meter platforms offer direct measurements for TDS. The user selects the type of conversion factor that is the nearest to the actual TDS value. The TDS is typically used to estimate the quantity of total dissolved solids in the sample. The standard method used to determine TDS is to filter and evaporate the sample to dryness at 180 °C (356 °F), then weigh the residue.

Hach Method 8163 is available to determine the total dissolved solids with the standard method. If necessary, Method 8163 can be used to determine the conversion factor for a specific solution or sample matrix.

To determine the conversion factor for a specific solution of a known TDS value, measure the conductivity of the solution and divide the mg/L TDS value by the conductivity value reported. For example, a solution of a known TDS value of 64 g/L and the measured conductivity value of 100 mS/cm has a conversion factor of 64 ÷ 100 or 0.64. It is important to know the conversion factor used, especially when the TDS results are compared with results from another lab, another test site or previously published or referenced data.

The different TDS concentration conversion options for the HQd meters are as sodium chloride (NaCl) (a generic default factor of 0.5) or a user-entered custom value. The operator selects a factor within the custom field. A common factor for high-salinity samples is 0.64.

For the MP6 meter, the TDS factor options are as NaCl, as potassium chloride (KCl), 442 and user-entered custom value. The MP6 meter default is the:

- KCl for conductivity
- NaCl for resistivity (mineral/salt)
- 442 factor (an algorithm) for the estimation of TDS in natural waters
- User-entered factor option

Maintenance

Due to the nature of the produced and flowback water, make sure to rinse the conductivity cell off with clean water. Do not let the cell sit in water. Do not keep the cell in the samples. After the cell is rinsed off, dry the cell and keep the cell dry.

Turbidity and Total Suspended Solids

Introduction

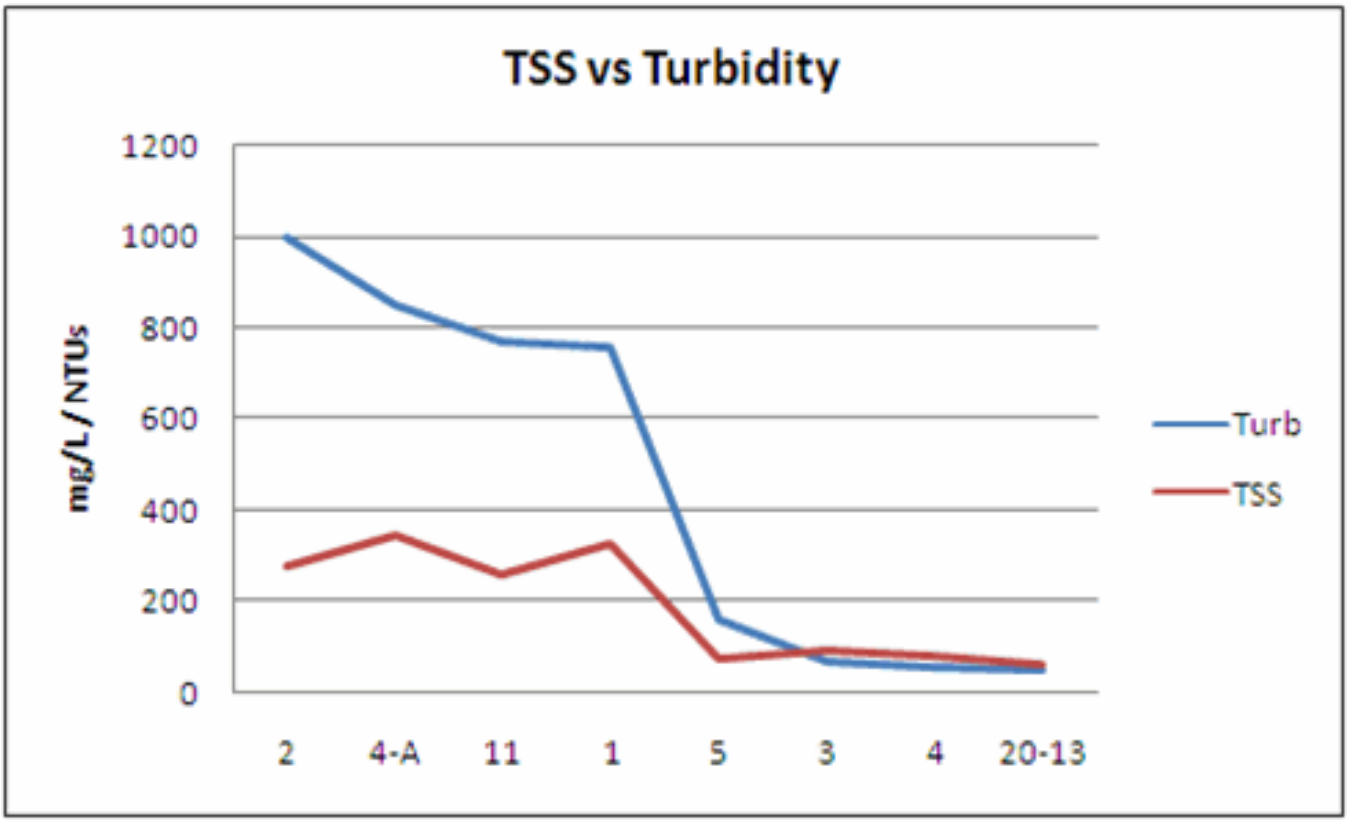
Turbidity is a measurement of water clarity where solids in the water stop the transmittance of light through the sample. Turbidity is an important water quality parameter that can show dispersed suspended solids, algae and other microorganisms, organic material and other minute particles in the water.

Total suspended solids (TSS) is a laboratory gravimetric procedure where the solids from the water sample are filtered through a 47-mm glass fiber filter, dried and weighed to determine the total non-filterable residue (TNR) of the sample reported as mg/L.

Turbidity and total suspended solids can be measured together with a TSS probe. The probe, which uses a modified absorbance measurement, gives a qualitative analysis for TSS. For the turbidity function, the probe uses a 2-channel, 90° scattered light measurement. The units of measure for turbidity are NTU, FNU and EBC. The units of measure for suspended solids are ppm, mg/L, g/L and %.

Turbidity and TSS can be used for process control in the treatment of the produced and flowback water. At different stages in the treatment process, the sample can be analyzed to determine and trend the effectiveness of the treatment to remove the solids from the water. Figure 1 shows the trend of TSS and turbidity measurements with the same samples. The data from the two methodologies give the operator process management information.

Figure 1 TSS versus Turbidity



Recommended instrumentation

- Turbidity measurement: Portable Turbidimeter 2100Q
- Laboratory turbidimeter: 2100N or 2100AN
- Total Suspended Solids: TSS portable probe
- Laboratory method: Gravimetric method (Hach method 8158) for non-filterable total suspended solids

Measuring turbidity and total suspended solids

Turbidity

The 2100Q is a portable turbidimeter that has a measurement range of 0 to 1000 NTUs. When a sample is over the 1000 NTU range, use a 1:1 dilution to lower the NTU concentration to less than 1000 NTU.

For laboratory turbidity measurements, use a 2100N or 2100AN. The measurement range of the 2100N is 0 to 4000 NTUs. The measurement range of the 2100AN is 0 to 10,000 NTUs.

The turbidity measurement range of the TSS portable probe is 0 to 4000 NTUs.

Suspended solids

The laboratory total suspended solids method is the gravimetric procedure where the sample is filtered, dried and weighed to determine the true quantitative TSS.

The TSS probe has an operating concentration range of 0.001 to 400 g/L.

Matrix challenges

The laboratory turbidimeters, 2100A and 2100AN, measure above 1000 NTUs because of the ratio measurement feature that corrects for color interference. The laboratory turbidimeters are not portable for field analysis, but they can be used in an onsite mobile lab.

For a smaller footprint, the 2100Q is sufficient for most produced and flowback water samples. If the sample turbidity is more than the measurement range of the 2100Q (0 to 1000 NTU), use a simple 1:1 dilution to lower the turbidity. High levels of color in the sample can cause high results.

The challenge for the gravimetric TSS procedure is that this application is a laboratory test. It is possible to do the analysis in a mobile lab, but an abundance of lab equipment is necessary for this procedure (e.g., oven, analytical balance, vacuum pump and desiccators). Moderate laboratory skills are necessary for the method. Test results are not available for 3 to 4 hours. Sample size adjustments can be necessary for samples that have a high TSS load or high oil residual levels.

The TSS portable probe is ideal for measurement of suspended solids in the field. The 10 m cable of the TSS portable probe lets the probe be lowered into the storage container to spot check the suspended solids or turbidity of the produced or flowback water. The probe is best used after calibration or correlation to the gravimetric TSS procedure. The TSS probe gives immediate results for process control and decreases the necessity of the time-consuming suspended solids lab analysis. Samples that have high levels of oil or hydrocarbon residuals can coat the probe. Routine cleaning is necessary. Samples that have variable color or particulate size can cause variable test results.

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