

Methyl Orange (Total) Acidity¹

Method 8219

0 to 10,000 mg/L as CaCO₃

Buret Titration

Scope and application: For water, wastewater and seawater.

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



Test preparation

Before starting

Prevent agitation of the sample during collection and mixing to prevent the loss of gases such as carbon dioxide, hydrogen sulfide and ammonia.

As an alternative to the Bromphenol Blue Indicator Powder Pillow, use 6 drops of Bromphenol Blue Indicator Solution.

As an alternative to the Bromphenol Blue Indicator Powder Pillow, use 6 drops of Methyl Orange Indicator Solution. When Methyl Orange Indicator Solution is used, the endpoint color change is from red to orange.

Color or turbidity in the sample can make it difficult to see the color change at the endpoint. For these samples, use a pH meter to determine the titration endpoint. The end point for methyl orange acidity is pH 3.7.

The methyl orange and phenolphthalein acidity procedures can be done sequentially as necessary. First, titrate to pH 3.7 and record the mL of titrant used. Then, titrate to pH 8.3.

The optional TitraStir Titration Stand can hold the buret and stir the sample.

Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.

Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Description	Quantity
Bromphenol Blue Indicator Powder Pillow	1
Sodium Hydroxide Standard Solution, 0.020 N	varies
pH meter and probe (for samples that have a lot of color or turbidity)	1
Buret, Class A, 50 mL	1
Graduated cylinder (use a size that is applicable to the selected sample volume), or TenSette pipet with tips	1
Erlenmeyer flask, 250 mL	1
Funnel, micro	1
Support stand with buret clamp	1
Water, deionized	varies

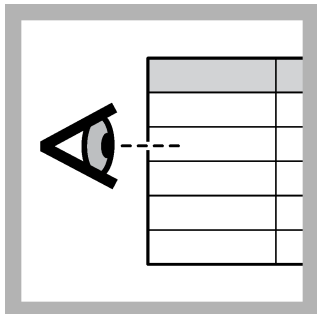
Refer to [Consumables and replacement items](#) on page 4 for order information.

Sample collection

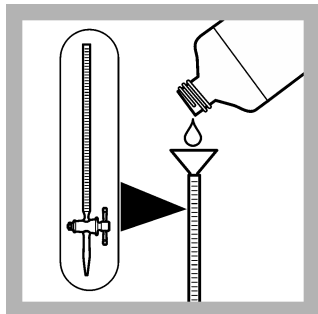
- Collect samples in clean glass or plastic bottles with tight-fitting caps. Completely fill the bottle and immediately tighten the cap.
- Prevent agitation of the sample and exposure to air.
- Analyze the samples as soon as possible for best results.

- If immediate analysis is not possible, keep the samples at or below 6 °C (43 °F) for a maximum of 24 hours.
- Let the sample temperature increase to room temperature before analysis.

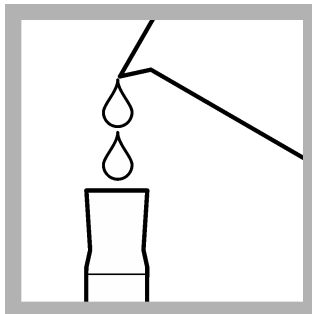
Test procedure



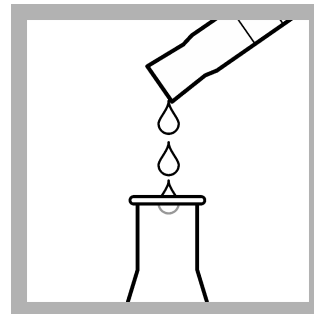
1. Select a sample volume and titrant from [Table 1](#) on page 3.



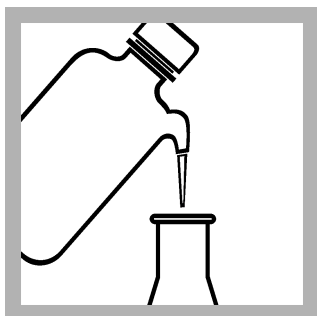
2. Fill a 50-mL buret to the zero mark with the titrant.



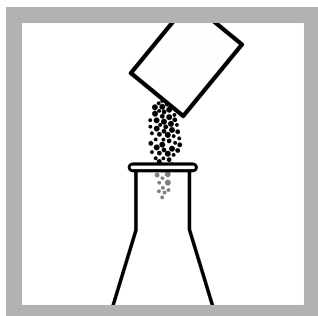
3. Use a graduated cylinder or pipet¹ to measure the sample volume from [Table 1](#) on page 3.



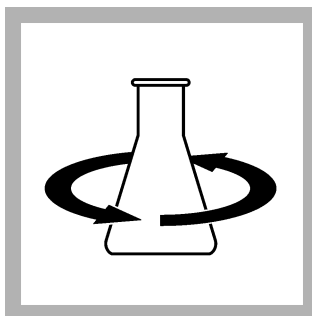
4. Pour the sample into a clean, 250-mL Erlenmeyer flask.



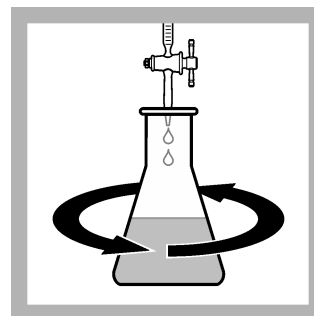
5. If the sample volume is less than 50 mL, dilute to approximately 50 mL with deionized water.



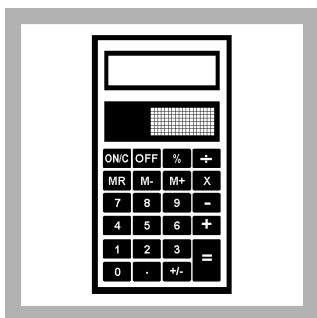
6. Add the contents of one Bromphenol Blue Indicator Powder Pillow. The indicator is not necessary if a pH meter is used.



7. Swirl to mix.



8. Put the flask under the buret. Swirl the flask. Add titrant until the color changes from yellow to pure green (pH 3.7).



9. Use the multiplier in [Table 1](#) on page 3 to calculate the concentration.
 $\text{mL of titrant} \times \text{multiplier} = \text{mg/L as CaCO}_3 \text{ methyl orange acidity.}$

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

Sample volumes and multipliers

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

Example: A 50-mL sample was titrated with 0.020 N titrant and 12 mL of titrant was used at the endpoint. The concentration is $12 \text{ mL} \times 20 = 240 \text{ mg/L}$ as CaCO_3 methyl orange acidity.

Table 1 Sample volumes and multipliers

Range (mg/L)	Sample volume (mL)	Titrant—sodium hydroxide	Multiplier
1–1000	50	0.020 N	20
800–2000	25	0.020 N	40
2000–5000	10	0.020 N	100
4000–10,000	5	0.020 N	100

Interferences

Interfering substance	Interference level
Chlorine	Chlorine can react with the indicators and cause an incorrect result. 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. Use a pH meter and titrate the samples to a pH of 3.7.

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:

- Sulfuric Acid Standard Solution, 0.500 N
 - Pipet, TenSette, 0.1–1.0 mL and pipet tips
1. Use the test procedure to measure the concentration of the sample.
 2. Use a TenSette pipet to add 0.1 mL of the standard solution to the titrated sample.
 3. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
 4. Add one more 0.1-mL addition of the standard solution to the titrated sample.
 5. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
 6. Add one more 0.1-mL addition of the standard solution to the titrated sample.
 7. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
 8. Compare the actual result to the correct result. The correct result for this titration is 2.5 mL of titrant for each 0.1-mL addition of the standard solution. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

Titrant test

Identify the strength of the Sodium Hydroxide Standard Solution each month. Sodium Hydroxide Standard Solution slowly absorbs carbon dioxide from the air, which decreases the strength of the solution.

1. Add 20 mL of Sulfuric Acid Standard Solution, 0.02 N to a 250-mL Erlenmeyer flask.
2. Add one Bromphenol Blue Indicator Powder Pillow to the flask.

3. Titrate the solution to the endpoint. Record the mL of titrant added.
4. Compare the actual result to the correct result. The correct result for this titration is 20 mL of titrant. If more than 21 mL of titrant was added, discard the titrant. Get new titrant.

Summary of method

A bromphenol blue indicator is added to the sample. Then, the sample is titrated with a sodium hydroxide solution until the indicator changes color at the endpoint pH of 3.7. This titration is a measure of strong mineral acidity (also referred to as methyl orange acidity). The bromphenol blue indicator gives a better endpoint than the methyl orange indicator.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Bromphenol Blue Indicator Powder Pillows	1 pillow	100/pkg	1455099
Sodium Hydroxide Standard Solution, 0.020 N	varies	1 L	19353
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity/test	Unit	Item no.
Buret clamp, double	1	each	32800
Buret, Class A, 50 mL	1	each	2636541
Support stand	1	each	56300
Funnel, micro	1	each	2584335
Graduated cylinders—Select one or more for the sample volume:			
Cylinder, graduated, 5 mL	1	each	50837
Cylinder, graduated, 10 mL	1	each	50838
Cylinder, graduated, 25 mL	1	each	50840
Cylinder, graduated, 50 mL	1	each	50841
Cylinder, graduated, 100 mL	1	each	50842
Tensette [®] pipets and pipet tips—Select one or more for the sample volume:			
Pipet, TenSette [®] , 0.1–1.0 mL	1	each	1970001
Pipet tips, TenSette [®] Pipet, 0.1–1.0 mL	varies	50/pkg	2185696
Pipet, TenSette [®] , 1.0–10.0 mL	1	each	1970010
Pipet tips, TenSette [®] Pipet, 1.0–10.0 mL	varies	50/pkg	2199796
Flask, Erlenmeyer, 250 mL	1	each	50546

Recommended standards

Description	Unit	Item no.
Sulfuric Acid Standard Solution, 0.020 N	100 mL	20342
Sulfuric Acid Standard Solution, 0.500 N	100 mL MDB	212132

Optional reagents and apparatus

Description	Unit	Item no.
Bromphenol Blue Indicator Solution	100 mL MDB	1455232
Clippers	each	96800
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL	32332
Stir bar, octagonal	each	2095352
TitraStir® Titration Stand, 115 VAC	each	1940000
TitraStir® Titration Stand, 230 VAC	each	1940010



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