

## Methyl Orange and Phenolphthalein (Total) Acidity

Method 8201 and 8202

10 to 4000 mg/L as CaCO<sub>3</sub>

Digital Titrator

Scope and application: For water, wastewater and seawater.



### 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 Phenolphthalein Indicator Powder Pillow, use 4 drops of Phenolphthalein Indicator Solution.

Color or turbidity in the sample can make it difficult to see the color change at the endpoint. For these samples, use a pH meter to determine the titration endpoint. The end point for methyl orange acidity is pH 3.7. The end point for phenolphthalein acidity is pH 8.3.

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

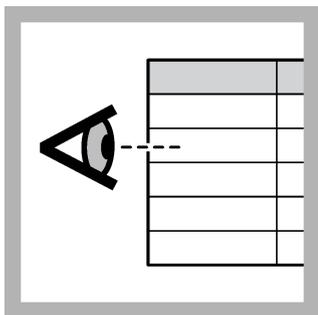
Description	Quantity
Bromphenol Blue Indicator Powder Pillow	1
Phenolphthalein Indicator Powder Pillow	1
Sodium Hydroxide Titration Cartridge	1
pH meter and probe (for samples that have a lot of color or turbidity)	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (use a size 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 5 for order information.

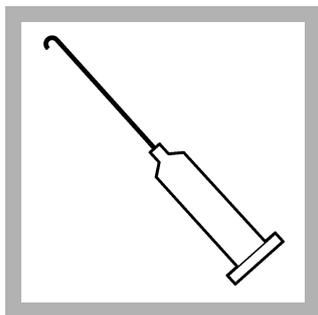
#### Sample collection

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

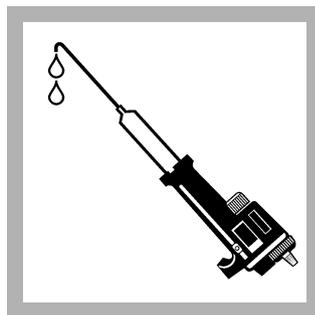
## Test procedure—Methyl orange acidity (Method 8201)



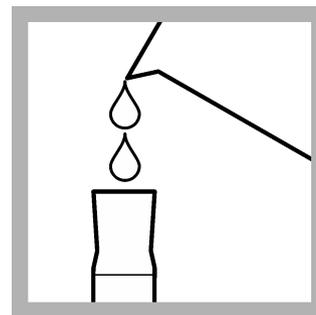
1. Select a sample volume and titration cartridge from [Table 1](#) on page 4.



2. Insert a clean delivery tube into the digital titration cartridge. Attach the cartridge to the Digital Titrator.



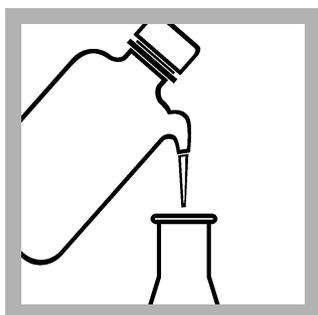
3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



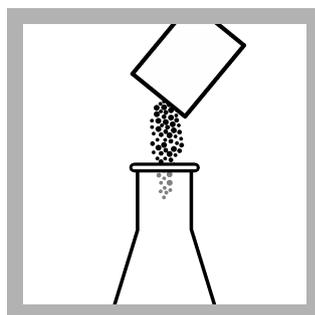
4. Use a graduated cylinder or pipet to measure the sample volume from [Table 1](#) on page 4.



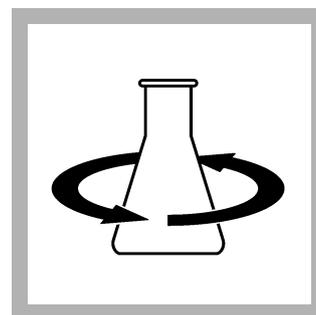
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



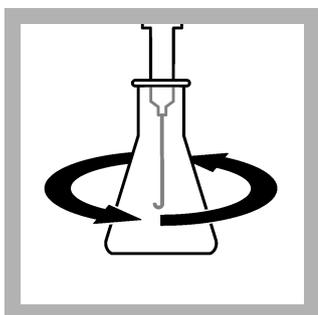
6. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



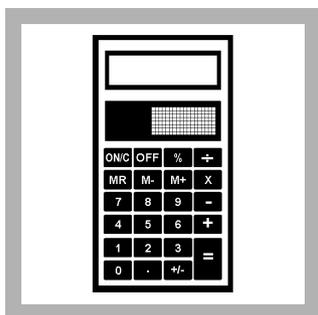
7. Add the contents of one Bromphenol Blue Indicator Powder Pillow. The indicator is not necessary if a pH meter is used.



8. Swirl to mix.

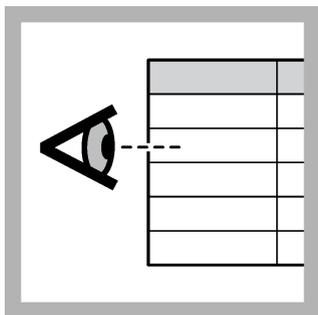


9. Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes from yellow to blue-violet (pH 3.7). Record the number of digits on the counter.

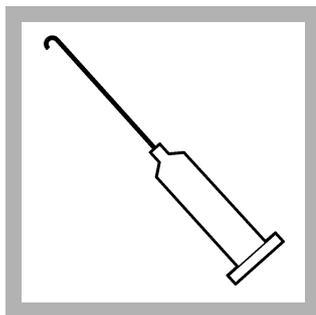


10. Use the multiplier in [Table 1](#) on page 4 to calculate the concentration. Digits used  $\times$  digit multiplier = mg/L as CaCO<sub>3</sub> methyl orange acidity.

## Test procedure—Phenolphthalein (total) acidity (Method 8202)



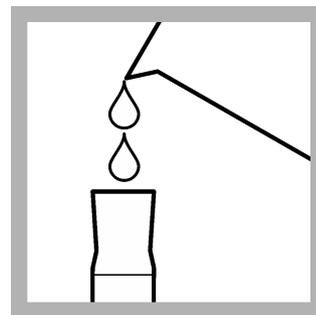
1. Select a sample volume and titration cartridge from [Table 1](#) on page 4.



2. Insert a clean delivery tube into the digital titration cartridge. Attach the cartridge to the Digital Titrator.



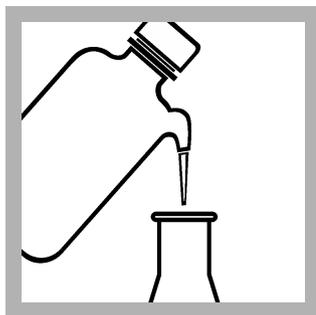
3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



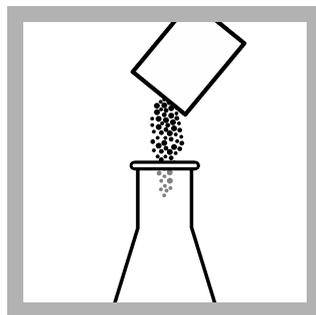
4. Use a graduated cylinder or pipet to measure the sample volume from [Table 1](#) on page 4.



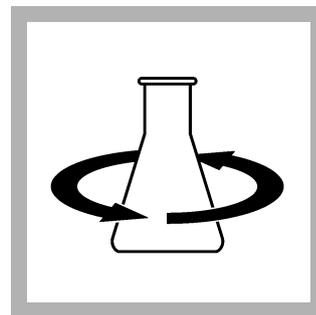
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



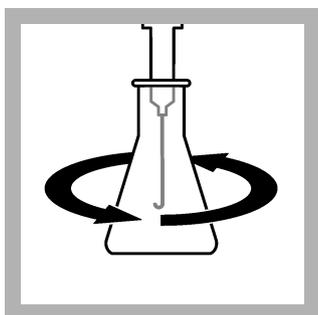
6. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



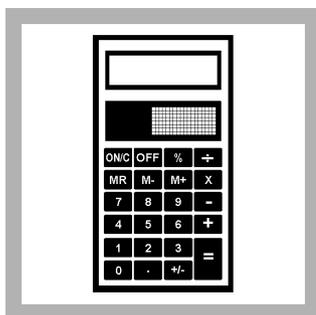
7. Add the contents of one Phenolphthalein Indicator Powder Pillow. The indicator is not necessary if a pH meter is used.



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 colorless to a light pink color that stays pink for 30 seconds (pH 8.3). Record the number of digits on the counter.



10. Use the multiplier in [Table 1](#) on page 4 to calculate the concentration.  $\text{Digits used} \times \text{digit multiplier} = \text{mg/L as CaCO}_3 \text{ phenolphthalein acidity.}$

## 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 100-mL sample was titrated with the 0.1600 N Sodium Hydroxide Titration Cartridge and the counter showed 250 digits at the methyl orange (pH 3.7) endpoint. The concentration is 250 digits x 0.1 = 25 mg/L as CaCO<sub>3</sub> methyl orange acidity.

**Table 1 Sample volumes and digit multipliers**

Range (mg/L as CaCO <sub>3</sub> )	Sample volume (mL)	Titration cartridge	Digit multiplier
10–40	100	0.1600 N NaOH	0.1
40–160	25	0.1600 N NaOH	0.4
100–400	100	1.600 N NaOH	1
200–800	50	1.600 N NaOH	2
500–2000	20	1.600 N NaOH	5
1000–4000	10	1.600 N NaOH	10

## 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 for methyl orange acidity or pH 8.3 for phenolphthalein acidity.
Hydrolyzable metals	<p>Pretreat samples that contain hydrolyzable metals (e.g. iron, manganese or aluminum) before the test for phenolphthalein acidity is started as follows:</p> <ol style="list-style-type: none"><li>1. Measure the sample volume into the flask.</li><li>2. Titrate the sample with a Sulfuric Acid Titration Cartridge until the sample pH is 4 or less. Use a Sulfuric Acid Titration Cartridge of the same normality as the Sodium Hydroxide Titration Cartridge (0.1600 N or 1.600 N) selected for the phenolphthalein test procedure. Record the number of digits on the counter.</li><li>3. Add 5 drops of 30% hydrogen peroxide solution.</li><li>4. Boil the solution for 2–5 minutes.</li><li>5. Let the solution temperature decrease to room temperature.</li><li>6. Use this solution as the sample in the test procedure for phenolphthalein (total) acidity. Record the number of digits on the counter.</li><li>7. Subtract the digits of sulfuric acid that were added in step 2 from the digits of sodium hydroxide that were added in step 6. Multiply the result by the digit multiplier in <a href="#">Table 1</a> on page 4 to find the phenolphthalein acidity in the sample.</li></ol>

## 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 (total) acidity—Add one pH 8.3 buffer powder pillow and one Phenolphthalein 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:

- 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 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 Sodium Hydroxide Titration Cartridge or 250 digits of the 0.1600 N Sodium Hydroxide 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 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.

A phenolphthalein indicator is added to a fresh portion of sample. Then, the sample is titrated with a sodium hydroxide solution until the indicator changes color at the endpoint pH of 8.3. This titration includes both strong and weak acid species and is a measure of the total acidity. The results are expressed in mg/L as calcium carbonate (CaCO<sub>3</sub>) at a specified pH.

### Consumables and replacement items

#### Required reagents

Description	Quantity/Test	Unit	Item no.
Acidity Reagent Set (approximately 100 tests)	—	each	2272800
Bromphenol Blue Indicator Powder Pillows	1	100/pkg	1455099
Phenolphthalein Indicator Powder Pillows	1	100/pkg	94299
Sodium Hydroxide Titration Cartridge, 0.1600 N	varies	each	1437701
Sodium Hydroxide Titration Cartridge, 1.600 N	varies	each	1437901
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

**Required apparatus (continued)**

Description	Quantity/test	Unit	Item no.
Cylinder, graduated, 10-mL	1	each	50838
Cylinder, graduated, 25-mL	1	each	50840
Cylinder, graduated, 50-mL	1	each	50841
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.
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
Buffer Powder Pillows, pH 8.3	25/pkg	89868
Hydrogen Peroxide Solution, 30%, ACS	473 mL	14411
Phenolphthalein Indicator Solution, 5 g/L	100 mL MDB	16232
Pipet, TenSette <sup>®</sup> , 0.1–1.0 mL	each	1970001
Pipet tips for TenSette <sup>®</sup> Pipet, 0.1–1.0 mL	50/pkg	2185696
Stir bar, octagonal	each	2095352
Sulfuric Acid Titration Cartridge, 0.1600 N	each	1438801
Sulfuric Acid Titration Cartridge, 1.600 N	each	1438901
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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