Alkalinity

DOC316.53.01166

Phenolphthalein and Total Alkalinity

Method 8203

10 to 4000 mg/L as $CaCO_3$

Digital Titrator

Scope and application: For water, wastewater and seawater.

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 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

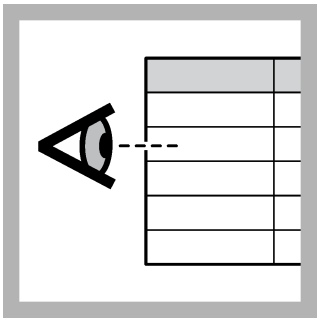
Description	Quantity
Bromcresol Green-Methyl Red Indicator Powder Pillow	1
Phenolphthalein Indicator Powder Pillow	1
Sulfuric Acid Titration Cartridge	1
pH Meter and probe (for samples that have a lot of color or turbidity)	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder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

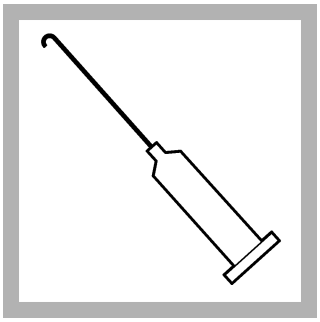
Sample collection

- 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.

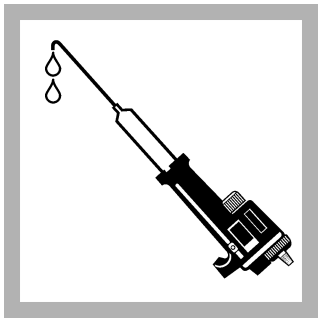
Test procedure



1. Select a sample volume and titration cartridge from Table 1 on page 3.

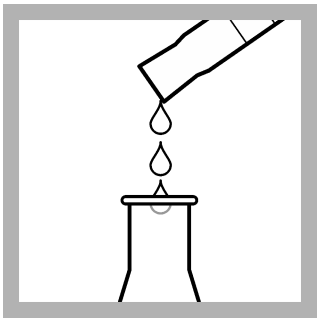


2. Insert a clean delivery tube into the digital titration cartridge. Attach the cartridge to the Digital Titrator.

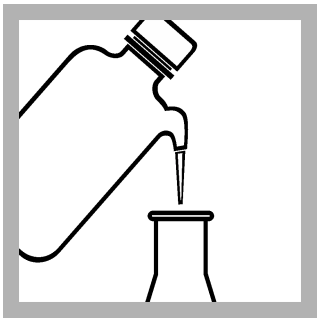


3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.

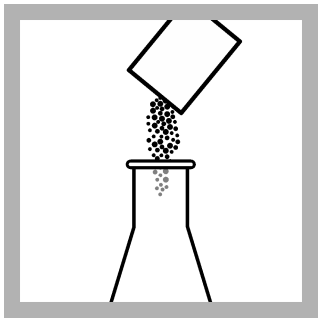
4. Use a graduated cylinder to measure the sample volume from Table 1 on page 3.



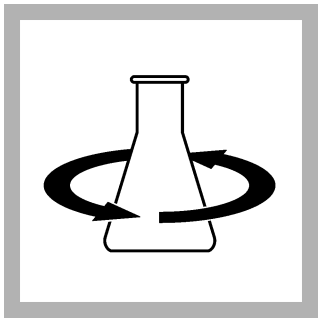
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



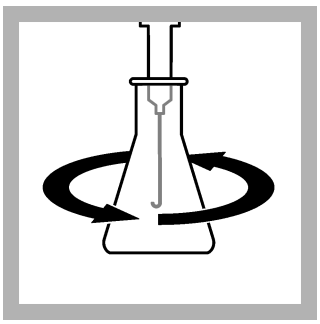
6. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



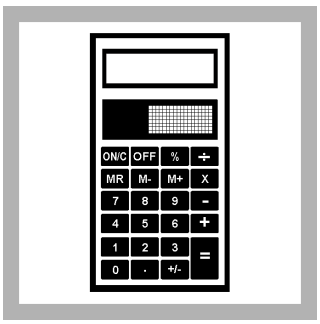
7. Add the contents of one Phenolphthalein Indicator Powder Pillow.
The indicator is not necessary if a pH meter is used.



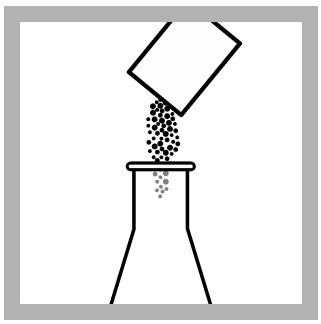
8. Swirl to mix.
If the solution is colorless or the pH is less than 8.3, the Phenolphthalein alkalinity is zero. Go to step 11.



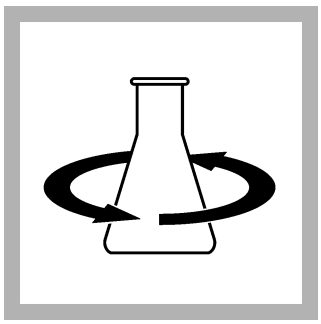
9. Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes from pink to colorless, or until the pH is 8.3. Record the number of digits on the counter.



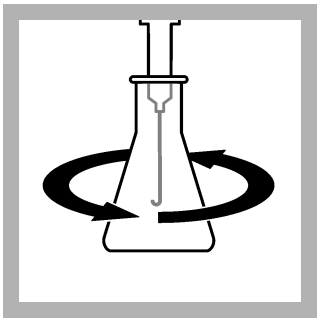
10. Use the multiplier in Table 1 on page 3 to calculate the concentration. Digits used × digit multiplier = mg/L as $CaCO_3$ Phenolphthalein alkalinity.



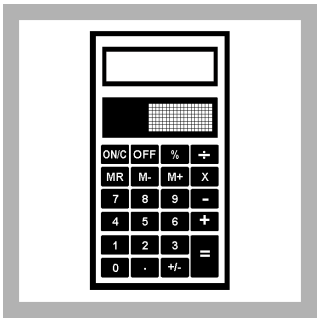
11. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow.
The indicator is not necessary if a pH meter is used.



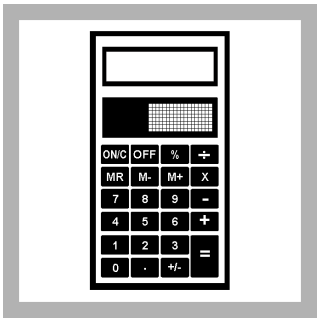
12. Swirl to mix.



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 3 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
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

Table 2 Alkalinity pH endpoints (continued)

Sample composition	Phenolphthalein alkalinity	Total alkalinity
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
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 3 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 Standard Solution, 0.500 N (25-g/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 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® Ampule 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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