

Phenolphthalein and Total Alkalinity¹

Method 8221

0 to 5000 mg/L as CaCO₃

Buret Titration

Scope and application: For water, wastewater and seawater.

¹ This procedure can be used for *Standard Methods for the Examination of Water and Wastewater* 2320 B for USEPA NPDES reporting.



Test preparation

Before starting

A pH meter must be used for NPDES reporting and is recommended for best results.

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.

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 Standard Solution, 0.020 N	varies
pH meter and probe (for samples that have a lot of color or turbidity)	1
Buret, Class A, 25 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

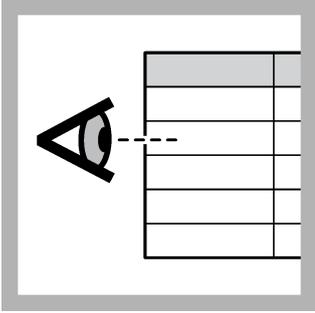
Refer to [Consumables and replacement items](#) on page 5 for order information.

Sample collection

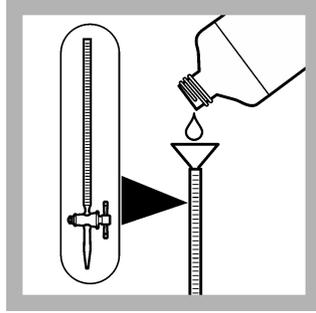
- Collect samples in clean glass or plastic bottles with tight-fitting caps. Completely fill the bottle and immediately tighten the cap.
- Prevent agitation of the sample and exposure to air.
- Analyze the samples as soon as possible for best results.
- If immediate analysis is not possible, keep the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

- Let the sample temperature increase to room temperature before analysis.

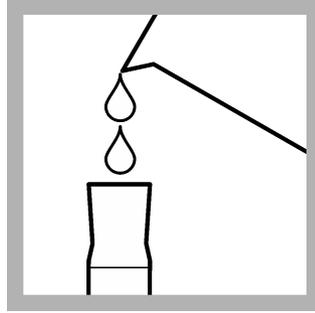
Test procedure



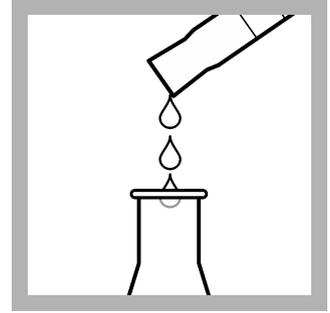
1. Select a sample volume and titrant from [Table 1](#) on page 3.



2. Fill a 25-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.



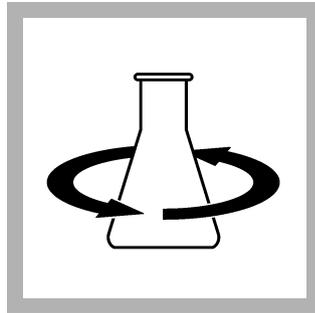
4. Pour the sample into a clean, 250-mL Erlenmeyer flask.



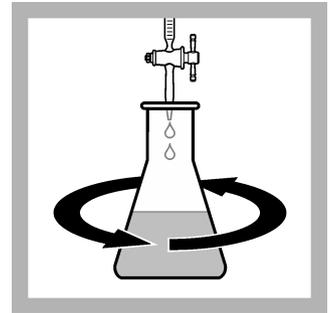
5. If the sample volume is less than 50 mL, dilute to approximately 50 mL with deionized water.



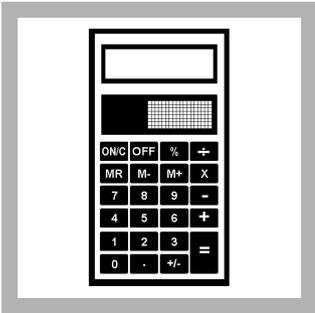
6. Add the contents of one Phenolphthalein Indicator Powder Pillow. The indicator is not necessary if a pH meter is used.



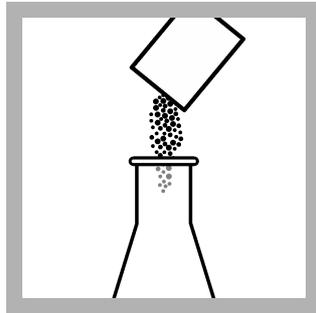
7. Swirl to mix. If the solution is colorless or the pH is less than 8.3, the Phenolphthalein alkalinity is zero. Go to step [10](#).



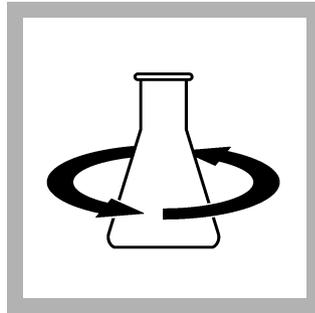
8. Put the flask under the buret. Swirl the flask. Add titrant until the color changes from pink to colorless, or until the pH is 8.3. Do not fill the buret again..



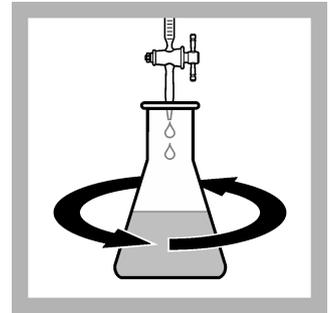
9. Use the multiplier in [Table 1](#) on page 3 to calculate the concentration. mL of titrant \times multiplier = mg/L as CaCO₃ Phenolphthalein alkalinity.



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

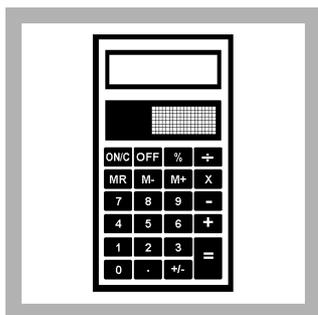
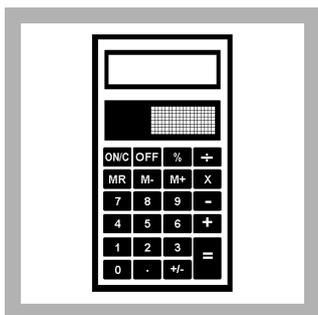


11. Swirl to mix.



12. Put the flask under the buret. 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).

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.



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

14. Calculate the bicarbonate, carbonate and hydroxide alkalinities as shown in [Determine the alkalinity relationships](#) on page 3.

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 $12 \text{ mL} \times 20 = 240 \text{ mg/L as CaCO}_3 \text{ alkalinity.}$

Table 1 Sample volumes and multipliers

Range (mg/L)	Sample volume (mL)	Titrant—sulfuric acid	Multiplier
1–500	50	0.020 N	20
400–1000	25	0.020 N	40
1000–2000	10	0.020 N	100
2000–5000	5	0.020 N	200

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 CaCO₃ phenolphthalein alkalinity and 250 mg/L as CaCO₃ total alkalinity.

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

- Hydroxide alkalinity: $2 \times 170 = 340$; $340 - 250 = 90$ mg/L hydroxide alkalinity
- Carbonate alkalinity: $250 - 170 = 80$; $80 \times 2 = 160$ 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 × 0.02 = 20 meq/L alkalinity as CaCO ₃
Grains per gallon (gpg)	0.0584	500 mg/L alkalinity as CaCO ₃ × 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

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 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.

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.
Bromcresol Green-Methyl Red Indicator Powder Pillows	1 pillow	100/pkg	94399
Phenolphthalein Indicator Powder Pillows	1 pillow	100/pkg	94299
Sulfuric Acid Standard Solution, 0.020 N	varies	1 L	20353
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity/test	Unit	Item no.
Buret clamp, double	1	each	32800
Buret, Class A, 25 mL	1	each	2636540
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.
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 8.3	25/pkg	89868
Clippers	each	96800
Phenolphthalein Indicator Solution, 5-g/L	100 mL MDB	16232
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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