Alkalinity

DOC316.53.01151

USEPA[1] Buret Titration Method[2]

Method 8221

(0 to 5,000 mg/L as $CaCO_3$)

Buret Titration

Scope and Application: For water, wastewater and seawater

[1] USEPA Accepted

[2] Adapted from *Standard Methods for the Examination of Water and Wastewater, 2320 B*

Test preparation

Before starting the test:

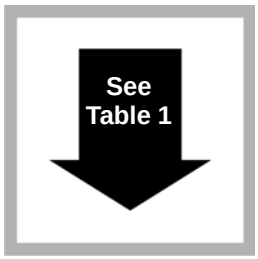
Read the entire procedure before starting the test.
A pH meter is required for NPDES reporting and is recommended for best results.
Substitute six drops of Phenolphthalein Indicator Solution for the Phenolphthalein Indicator Powder Pillow if necessary
Substitute six drops of Bromcresol Green-Methyl Red Indicator Solution for the Bromcresol Green-Methyl Red Powder Pillow if necessary.
Results in mg/L as $CaCO_3$ ÷ 17.12 = grains per gallon

Collect the following items:

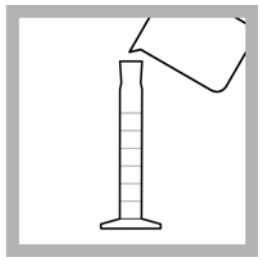
Description	Quantity
Bromcresol Green-Methyl Red indicator powder pillow	1
Phenolphthalein indicator powder pillow	1
Sulfuric acid standard solution, 0.020 N	varies[1]
Buret clamp, double	1
Buret, Class A, 25-mL	1
Graduated cylinder	varies[1]
Erlenmeyer flask, 250-mL	1
Funnel, Micro	1
Support Stand	1

[1] See *Consumables and replacement items* on page 6.

Buret titration (Method 8221)



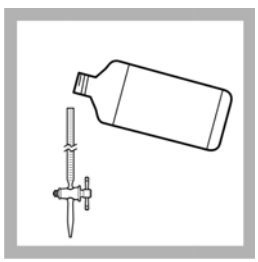
1. Select a sample volume from the *Sample volume selection for expected concentration* table that corresponds to the expected alkalinity concentration in mg/L as calcium carbonate ($CaCO_3$).



2. Use a graduated cylinder or pipet to measure the sample volume.

3. Transfer the sample into a 250-mL Erlenmeyer flask. Dilute to about 50-mL with deionized water if necessary.

4. Add the contents of one Phenolphthalein Indicator Powder Pillow. Swirl to mix. (Omit this step when using a pH meter.)



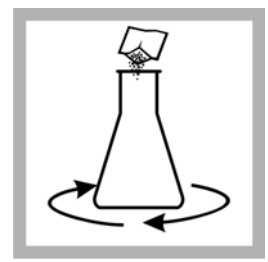
5. Fill a 25-mL buret to the zero mark with 0.020 N Sulfuric Acid standard solution.

6. While swirling the flask, titrate the sample until the solution color changes from pink to colorless (pH 8.3).

If the solution is colorless before titrating with sulfuric acid, the phenolphthalein alkalinity is zero.

7. Calculate:

mL Titrant × multiplier used = mg/L phenolphthalein alkalinity as $CaCO_3$.

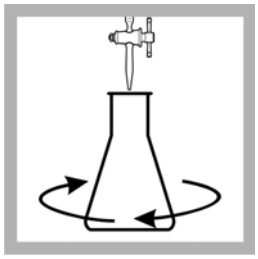


8. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow to the titrated sample. Swirl to mix.

Do not add indicator if a pH meter is used.

Specific sample composition may require titration to a specific pH (see the *Alkalinity relationship* table).

Buret titration (Method 8221)



9. Continue the titration until a light pink end point is reached.

10. Calculate:

mL Titrant × multiplier used = mg/L total alkalinity as $CaCO_3$.

Table 33 Sample volume selection for expected concentration

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Sulfuric Acid	Multiplier
0–500	50	20353	20
400–1000	25	20353	40
1000–2500	10	20353	100
2000–5000	5	20353	200

The end points in the *Alkalinity endpoints* table are recommended for determining total alkalinity in water samples of various compositions and alkalinity concentrations.

Table 34 Alkalinity endpoints

Sample composition	End point pH	
	Total Alkalinity	Phenolphthalein Alkalinity
Alkalinity about 30 mg/L	pH 4.9	pH 8.3
Alkalinity about 150 mg/L	pH 4.6	pH 8.3
Alkalinity about 500 mg/L	pH 4.3	pH 8.3
Silicates or phosphates present	pH 4.5	pH 8.3
Industrial wastes or complex system	pH 4.5	pH 8.3
Routine or Automated Analyses	pH 4.5	pH 8.3

Total alkalinity primarily includes hydroxide, carbonate, and bicarbonate alkalinities. The concentration of these types in a sample may be determined when the phenolphthalein and total alkalinities are known (*Alkalinity relationship* table).

Table 35 Alkalinity relationship

Row	Result of Titration	Hydroxide Alkalinity Equals:	Carbonate Alkalinity Equals:	Bicarbonate Alkalinity Equals:
1	Phenolphthalein Alkalinity equal to 0	0	0	Total Alkalinity
2	Phenolphthalein Alkalinity equal to Total Alkalinity	Total Alkalinity	0	0
3	Phenolphthalein Alkalinity less than one-half of Total Alkalinity	0	Phenolphthalein Alkalinity times 2	Total Alkalinity minus two times Phenolphthalein Alkalinity
4	Phenolphthalein Alkalinity equal to one-half of Total Alkalinity	0	Total Alkalinity	0
5	Phenolphthalein Alkalinity greater than one-half of Total Alkalinity	2 times Phenolphthalein Alkalinity minus Total Alkalinity	2 times the difference between Total and Phenolphthalein Alkalinity	0

Use the *Alkalinity relationship* table with the following procedure:

1. Does the phenolphthalein alkalinity equal zero? If yes, use Row 1.
2. Does the phenolphthalein alkalinity equal total alkalinity? If yes, use Row 2.
3. Divide the total alkalinity by 2 to calculate one-half the total alkalinity.
4. Select Row 3, 4 or 5 based on comparing the result of step c (one-half total alkalinity) with the phenolphthalein alkalinity.
5. Perform the required calculations if any.
6. Check your results. The sum of the three alkalinity types will equal the total alkalinity.

Example:
A sample has 170 mg/L as $CaCO_3$ phenolphthalein alkalinity and 250 mg/L as CaCO3 total alkalinity. What is the concentration of hydroxide, carbonate, and bicarbonate alkalinities?

- **a.** The phenolphthalein alkalinity does not equal zero but 170 mg/L.
- **b.** The phenolphthalein alkalinity does not equal total alkalinity (170 mg/L vs. 250 mg/L).
- **c.** One-half of the total alkalinity equals 125 mg/L.
- **d.** Because the phenolphthalein alkalinity of 170 mg/L is greater than one-half the total alkalinity of 125 mg/L, select Row 5.

The hydroxide alkalinity is equal to:

$$2 \times 170 = 340$$

$$340 - 250 = 90 \text{ mg/L hydroxide alkalinity}$$

The carbonate alkalinity is equal to:

$$250 - 170 = 80$$

$$80 \times 2 = 160 \text{ mg/L carbonate alkalinity}$$

The bicarbonate alkalinity is equal to zero mg/L.

Check:

90 mg/L hydroxide alkalinity + 160 mg/L carbonate alkalinity + 0 mg/L bicarbonate alkalinity = 250 mg/L

The answer is correct.

The sum of each type equals the total alkalinity (250 mg/L).

Interferences

Chlorine at levels above 3.5 mg/L cause a yellow-brown color upon the addition of the Bromcresol Green-Methyl Red Indicator Powder Pillow. Residual chlorine interference with the indicator may be removed by adding a drop of 0.1 N Sodium Thiosulfate Standard Solution* before adding the indicator.

Highly colored or turbid samples may mask the color change at the end point. Use a pH meter for these samples, titrating to pH 8.3 for phenolphthalein alkalinity and the appropriate pH (see the *Alkalinity endpoints* table) for total alkalinity.

Sampling and storage

Collect samples in plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation and prolonged exposure to air. Samples should be analyzed as soon as possible after collection but can be stored at least 24 hours by cooling to 4 °C (39 °F) or below. Warm to room temperature before analyzing.

Accuracy check

End point confirmation

- To accurately determine the phenolphthalein alkalinity end point, mix the contents of one Phenolphthalein Indicator Powder Pillow and the contents of one pH 8.3 Buffer Powder Pillow with 50 mL of deionized water in a 250-mL Erlenmeyer flask. The resulting color is the end point.
- To accurately determine the total alkalinity end point, mix the contents of one pH 4.5 Buffer Powder Pillow and the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow with 50 mL of deionized water in a 250-mL Erlenmeyer flask. Titrate to a light pink color change.

Standard additions method (Sample Spike)
Perform the standard additions method check as follows:

1. Break the top off an Alkalinity Voluette® Ampule Standard Solution, 0.500 N.
2. Use the TenSette Pipet* to add 0.1 mL of standard to the sample titrated in step 6 or step 9. Resume titration back to the same end point. Record the volume of titrant needed.
3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.
4. The mL of titrant required should increase by 2.5 mL for each 0.1 mL increment of standard added.

Summary of method

Alkalinity is expressed as P (phenolphthalein) alkalinity or as T (total) alkalinity. Both types are determined by titration with a Sulfuric Acid Standard Solution to an end point evidenced by the color change of an indicator solution or determined with a pH meter. The P alkalinity is determined by titration to a pH of 8.3 and registers the total hydroxide and one half the carbonate present. The T alkalinity is determined by titration to a pH of 4.5. The total alkalinity includes all carbonate, bicarbonate and hydroxide alkalinity. Alternatively, total alkalinity end points may be determined by using a pH meter and titrating to the specific pH required for the sample composition.

* See *Consumables and replacement items* on page 6.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Catalog number
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

Required apparatus

Description	Quantity/test	Unit	Catalog number
Buret Clamp, double	1	each	32800
Buret, Class A, 25-mL	1	each	2636540
Select one or more based on sample volume:			
Cylinder, graduated, 5-mL	—	each	50837
Cylinder, graduated, 10-mL	—	each	50838
Cylinder, graduated, 25-mL	—	each	50840
Cylinder, graduated, 50-mL	—	each	50841
Flask, Erlenmeyer, 250-mL	1	each	50546
Pipet, volumetric, Class A, 5-mL,	—	each	1451537
Pipet, volumetric, Class A, 10-mL	—	each	1451537
Pipet Filler, Safety Bulb	—	each	1465100
Ampule Breaker	—	each	2196800
Funnel, Micro	1	each	2584335
Support Stand	1	each	56300

Required standards

Description	Unit	Catalog number
Alkalinity Standard Solution, Voluette® Ampules, 0.500 N, 10-mL	16/pkg	1427810
Buffer Powder Pillows, pH 4.5	25/pkg	89568
Buffer Powder Pillows, pH 8.3	25/pkg	89868
Water, deionized	4 L	27256

Optional items

Description	Unit	Catalog number
Sodium Thiosulfate Standard Solution, 0.1 N	—	32332
TenSette Pipet, 0.1–1.0 mL	—	1970001
Tips for Tensette Pipet	50/pkg	2185696

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