

## Method 8203

## Phenolphthalein and Total using Sulfuric Acid Method

### Digital Titrator

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

**Scope and Application:** For water, wastewater, and seawater



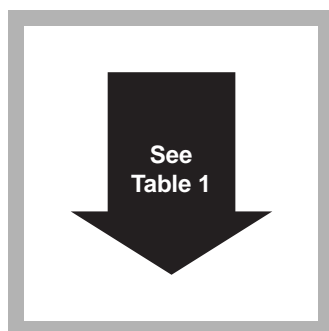
### Tips and Techniques

- For added convenience when stirring, use the TitraStir® apparatus (Cat. No. 19400-00, -10).
- Four drops of Phenolphthalein Indicator Solution (Cat. No. 162-32) may be substituted for the Phenolphthalein Indicator Powder Pillow.
- Four drops of Bromcresol Green-Methyl Red Indicator Solution (Cat. No. 23292-32) may be substituted for the Bromcresol Green-Methyl Red Indicator Powder Pillow.
- meq/L Alkalinity = mg/L as CaCO<sub>3</sub> ÷ 50

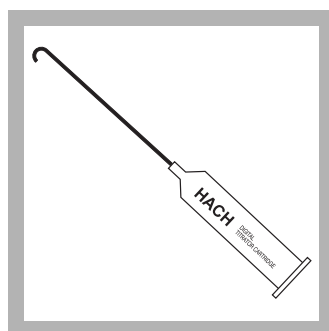


### Digital Titrator

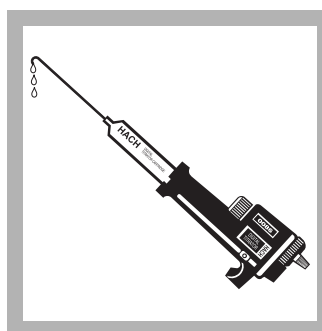
### Method 8203



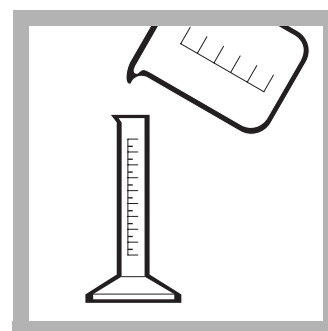
**1.** Select the sample volume and Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>) Titration Cartridge that correspond to the expected alkalinity concentration as mg/L calcium carbonate (CaCO<sub>3</sub>) from *Table 1*.



**2.** Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body.

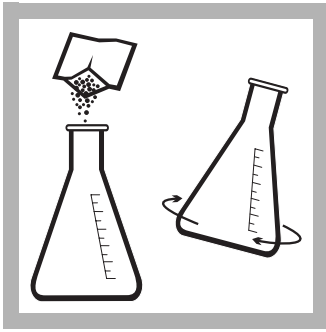


**3.** Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

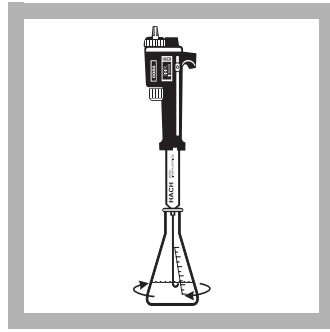


**4.** Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean, 250-mL Erlenmeyer flask. Dilute to the 100-mL mark with deionized water, if necessary.

# Alkalinity

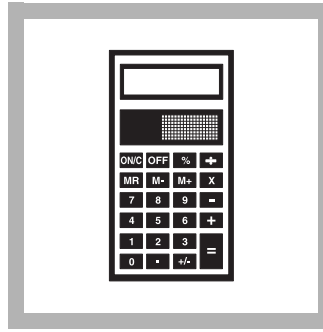


5. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix.

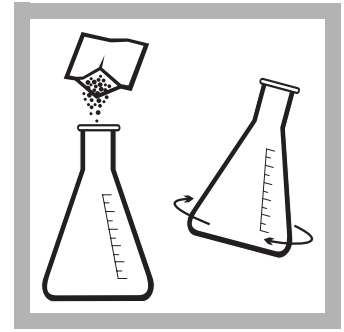


6. If the solution turns pink, titrate to a colorless end point. Place the delivery tube tip into the solution and swirl the flask while titrating with sulfuric acid. Record the number of digits required.

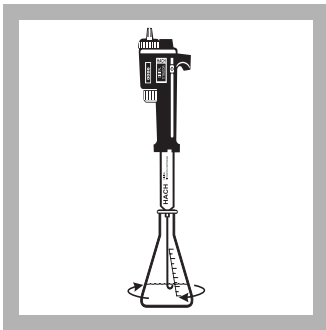
If the solution is colorless before titrating with Sulfuric acid, the Phenolphthalein (P) alkalinity is zero. Proceed to step 8.



7. Calculate:  
 Digits Required X  
 Digit Multiplier =  
 mg/L as CaCO<sub>3</sub> P Alkalinity



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



9. Continue the titration with sulfuric acid to a light pink (pH 4.5) color, as required by sample composition. Record the number of digits required.

**Note:** A pH meter may be used to titrate to a specific pH as required by sample composition. See Table 2.



10. Calculate:  
 Digits Required X  
 Digit Multiplier =  
 mg/L as CaCO<sub>3</sub> Total (T or M)  
 Alkalinity

Carbonate, bicarbonate, and hydroxide concentrations may be expressed individually using the relationships shown in Table 3.

Table 1

Range (mg/L as CaCO <sub>3</sub> )	Sample Volume (mL)	Titration Cartridge (N H <sub>2</sub> SO <sub>4</sub> )	Catalog Number	Digit Multiplier
10–40	100	0.1600	14388-01	0.1
40–160	25	0.1600	14388-01	0.4
100–400	100	1.600	14389-01	1.0
200–800	50	1.600	14389-01	2.0
500–2000	20	1.600	14389-01	5.0
1000–4000	10	1.600	14389-01	10.0

**Table 2 End Point pH**

Sample Composition	End Point	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

## Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or 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.

## Alkalinity Relationship Table

Total alkalinity primarily includes hydroxide, carbonate and bicarbonate alkalinities. The concentration of these alkalinities in a sample may be determined when the phenolphthalein and total alkalinities are known (see *Table 3*).

**Table 3 Alkalinity Relationship**

Row	Result of Titration	Hydroxide Alkalinity Equals:	Carbonate Alkalinity Equals:	Bicarbonate Alkalinity Equals:
1	Phenolphthalein Alkalinity = 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

To use the table follow these steps:

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

**For example:**

A sample has 170 mg/L as CaCO<sub>3</sub> phenolphthalein alkalinity and 250 mg/L as CaCO<sub>3</sub> total alkalinity. What is the concentration of hydroxide, carbonate and bicarbonate alkalinities?

The phenolphthalein alkalinity does not equal 0 (it is 170 mg/L), see step a.

The phenolphthalein alkalinity does not equal total alkalinity (170 mg/L vs. 250 mg/L), see step b.

One-half of the total alkalinity (250 g/L) equals 125 mg/L. Because the phenolphthalein alkalinity (170 mg/L) is greater than one-half the total alkalinity (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 equals 0 mg/L.**

Check: (See step f)

$$90 \text{ mg/L hydroxide alkalinity} + 160 \text{ mg/L carbonate alkalinity} + 0 \text{ mg/L bicarbonate alkalinity} = 250 \text{ mg/L}$$

The above answer is correct; the sum of each type equals the total alkalinity.

## Accuracy Check

**End Point Confirmation**

A solution of one pH 8.3 Buffer Powder Pillow (Cat. No. 898-68) and one Phenolphthalein Powder Pillow in 50 mL of deionized water is recommended as a comparison for determining the proper end point color.

A solution of one Bromcresol Green-Methyl Red Powder Pillow and one pH 4.5 Buffer Powder Pillow (895-68) in 50 mL of deionized water is recommended as a comparison for judging the pH 4.5 end point color.

## Standard Additions Method (Sample Spike)

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off an Alkalinity Voluette<sup>®</sup> Ampule Standard, 0.500 N.
2. Use a TenSette Pipet (Cat. No. 19700-01) to add 0.1 mL of standard to the sample titrated in steps 6 or 9. Resume titration back to the same end point. Record the number of digits needed.
3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.
4. Each 0.1 mL addition of standard should require 25 additional digits of 1.600 N titrant or 250 digits of 0.1600 N titrant. If these uniform increases do not occur, refer to *Section 3.4 Method Performance* to determine the cause.

## Interferences

Highly colored or turbid samples may mask the color change at the end point. Use a pH meter (Cat. No. 51700-10) for these samples, titrating to a pH 8.3 for phenolphthalein alkalinity and the appropriate pH (see *Table 2*) for total alkalinity.

Chlorine at levels above 3.5 mg/L may cause a yellow-brown color upon the addition of the Bromocresol Green-Methyl Red Powder Pillow. Add one drop of 0.1 N Sodium Thiosulfate (Cat. No. 323-32) to eliminate this interference.

## Summary of Method

The sample is titrated with sulfuric acid to a colorimetric end point corresponding to a specific pH. Phenolphthalein alkalinity is determined by titration to a pH of 8.3, as evidenced by the color change of phenolphthalein indicator, and indicates the total hydroxide and one half the carbonate present. M (methyl orange) or T (total) alkalinity is determined by titration to a pH between 3.7 and 5.1, and includes all carbonate, bicarbonate and hydroxide. Alternatively, total alkalinity end points may be determined by using a pH meter and titrating to the specific pH required for the sample composition.

# Alkalinity

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## Required Reagents

Description	Unit	Cat. No
Alkalinity Reagent Set (about 100 tests) (varies with sample characteristics).....		22719-00
Includes:		
Bromcresol Green-Methyl Red Powder Pillows.....	100/pkg.....	943-99
Phenolphthalein Powder Pillows.....	100/pkg.....	942-99
Sulfuric Acid Titration Cartridge, 1.600 N.....	each.....	14389-01
Sulfuric Acid Titration Cartridge, 0.1600 N.....	each.....	14388-01
Water, demineralized.....	4 L.....	272-56

## Required Apparatus

Select one or more based on sample concentration

Cylinder, graduated, 10-mL.....	each.....	508-38
Cylinder, graduated, 25-mL.....	each.....	508-40
Cylinder, graduated, 50-mL.....	each.....	508-41
Cylinder, graduated, 100-mL.....	each.....	508-42
Digital Titrator.....	each.....	16900-01
Flask, Erlenmeyer, 250-mL.....	each.....	505-46

## Required Standards

Alkalinity Standard Solution, Voluette® Ampule 0.500 N Na <sub>2</sub> CO <sub>3</sub> , 10-mL.....	16/pkg.....	14278-10
Buffer Powder Pillows, pH 4.5.....	25/pkg.....	895-68
Buffer Powder Pillows, pH 8.3.....	25/pkg.....	898-68



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