METHOD #: 310.1 Approved for NPDES (Editorial Revision 1978)

TITLE: Alkalinity (Titrimetric, pH 4.5)

ANALYTE: Alkalinity

INSTRUMENTATION: Titration

STORET No. 00410

1.0 Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
1.2 The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 mL.
1.3 Automated titrimetric analysis is equivalent.

2.0 Summary of Method

2.1 An unaltered sample is titrated to an electrometrically determined end point of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.

3.0 Comments

3.1 The sample should be refrigerated at 4°C and run as soon as practical. Do not open sample bottle before analysis.
3.2 Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.
3.3 For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, titrate to an electrometric endpoint of pH 3.9, using the procedure in:Annual Book of ASTM Standards, Part 31, "Water", p 115, D- 067, Method D, (1976).
3.4 Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.

4.0 Apparatus

4.1 pH meter or electrically operated titrator that uses a glass electrode and can be read to 0.05 pH units. Standardize and calibrate according to manufacturer's instructions. If automatic temperature compensation is not provided, make titration at 25 ±2 °C.
4.2 Use an appropriate sized vessel to keep the air space above the solution at a minimum. Use a rubber stopper fitted with holes for the glass electrode, reference electrode (or combination electrode) and buret.
4.3 Magnetic stirrer, pipets, flasks and other standard laboratory equipment.

4.4 Burets, Pyrex 50, 25 and 10 mL.

5.0 Reagents

5.1 Sodium carbonate solution, approximately 0.05 N: Place 2.5 ±0.2 g (to nearest mg) Na_2CO_3 (dried at 250°C for 4 hours and cooled in desiccator) into a 1 liter volumetric flask and dilute to the mark.

5.2 Standard acid (sulfuric or hydrochloric), 0.1 N: Dilute 3.0 mL conc H_2SO_4 or 8.3 mL conc HCl to 1 liter with distilled water. Standardize versus 40.0 mL of 0.05 N Na_2CO_3 solution with about 60 mL distilled water by titrating potentiometrically to pH of about 5. Lift electrode and rinse into beaker. Boil solution gently for 3-5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using:

$$N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1 liter
B = mL Na_2CO_3 solution
C = mL acid used to inflection point

5.3 Standard acid (sulfuric or hydrochloric), 0.02 N: Dilute 200.0 mL of 0.1000 N standardacid to 1 liter with distilled water. Standardize by potentiometric titration of 15.0 mL 0.05N Na_2CO_3 solution as above.

6.0 Procedure

6.1 Sample size
- 6.1.1 Use a sufficiently large volume of titrant (> 20 mL in a 50 mL buret) to obtain good precision while keeping volume low enough to permit sharp end point.
- 6.1.2 For < 1000 mg $CaCO_3$/L use 0.02 N titrant
- 6.1.3 For > 1000 mg $CaCO_3$/L use 0.1 N titrant
- 6.1.4 A preliminary titration is helpful.

6.2 Potentiometric titration
- 6.2.1 Place sample in flask by pipetting with pipet tip near bottom of flask
- 6.2.2 Measure pH of sample
- 6.2.3 Add standard acid (5.2 or 5.3), being careful to stir thoroughly but gently to allow needle to obtain equilibrium.
- 6.2.4 Titrate to pH 4.5. Record volume of titrant.

6.3 Potentiometric titration of low alkalinity
- 6.3.1 For alkalinity of <20 mg/L titrate 100-200 mL as above (6.2) using a 10 mL microburet and 0.02 N acid solution (5.3).
- 6.3.2 Stop titration at pH in range of 4.3-4.7, record volume and exact pH. Very carefully add titrant to lower pH exactly 0.3 pH units and record volume.

7.0 Calculations

7.1 Potentiometric titration to pH 4.5

$$\text{Alkalinity, mg/L } CaCO_3 = \frac{A \times N \times 50{,}000}{\text{mL of sample}}$$

where:
A = mL standard acid
N = normality standard acid

7.2 Potentiometric titration of low alkalinity:

$$\text{Total Alkalinity, mg/L } CaCO_3 = \frac{(2B - C) \times N \times 50{,}000}{\text{mL of sample}}$$

where:

B = mL titrant to first recorded pH
C = total mL titrant to reach pH 0.3 units lower
N = normality of acid

8.0 Precision and Accuracy

8.1 Forty analysts in seventeen laboratories analyzed synthetic water samples containing increments of bicarbonate, with the following results:

Increment as Alkalinity mg/liter, $CaCO_3$	Precision as Standard Deviation mg/liter, $CaCO_3$	Accuracy as Bias, %	Accuracy as Bias, mg/L, $CaCO_3$
8	1.27	+ 10.61	+0.85
9	1.14	+22.29	+2.0
113	5.28	- 8.19	-9.3
119	5.36	- 7.42	-8.8

(FWPCA Method Study 1, Mineral and Physical Analyses)

8.2 In a single laboratory (EMSL) using surface water samples at an average concentration of 122 mg $CaCO_3$/L , the standard deviation was ±3.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 278, Method 403, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", p 113, D-1067, Method B, (1976).