2320 ALKALINITY*#(1)

2320 A. Introduction

1. Discussion
Alkalinity of a water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the end-point pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents. The measured values also may include contributions from borates, phosphates, silicates, or other bases if these are present. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of a water for irrigation. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes. Raw domestic wastewater has an alkalinity less than, or only slightly greater than, that of the water supply. Properly operating anaerobic digesters typically have supernatant alkalinitities in the range of 2000 to 4000 mg calcium carbonate (CaCO₃)/L.¹

2. Reference

2320 B. Titration Method

1. General Discussion
   a. Principle: Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the end-point pH used. For methods of determining inflection points from titration curves and the rationale for titrating to fixed pH end points, see Section 2310B.1a.

   For samples of low alkalinity (less than 20 mg CaCO₃/L) use an extrapolation technique based on the near proportionality of concentration of hydrogen ions to excess of titrant beyond the equivalence point. The amount of standard acid required to reduce pH exactly 0.30 pH unit is measured carefully. Because this change in pH corresponds to an exact doubling of the hydrogen
ion concentration, a simple extrapolation can be made to the equivalence point.\(^1,\!^2\)

*b. End points:* When alkalinity is due entirely to carbonate or bicarbonate content, the pH at the equivalence point of the titration is determined by the concentration of carbon dioxide (CO\(_2\)) at that stage. CO\(_2\) concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration. The pH values in Table 2320:I are suggested as the equivalence points for the corresponding alkalinity concentrations as milligrams CaCO\(_3\) per liter. ‘‘Phenolphthalein alkalinity’’ is the term traditionally used for the quantity measured by titration to pH 8.3 irrespective of the colored indicator, if any, used in the determination. Phenolphthalein or metacresol purple may be used for alkalinity titration to pH 8.3. Brom cresol green or a mixed brom cresol green-methyl red indicator may be used for pH 4.5.

c. *Interferences:* Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally. Do not filter, dilute, concentrate, or alter sample.

d. *Selection of procedure:* Determine sample alkalinity from volume of standard acid required to titrate a portion to a designated pH taken from ¶ 1b. Titrate at room temperature with a properly calibrated pH meter or electrically operated titrator, or use color indicators. If using color indicators, prepare and titrate an indicator blank.

Report alkalinity less than 20 mg CaCO\(_3\)/L only if it has been determined by the low-alkalinity method of ¶ 4d.

Construct a titration curve for standardization of reagents.

Color indicators may be used for routine and control titrations in the absence of interfering color and turbidity and for preliminary titrations to select sample size and strength of titrant (see below).

e. *Sample size:* See Section 2310B.1e for selection of size sample to be titrated and normality of titrant, substituting 0.02N or 0.1N sulfuric (H\(_2\)SO\(_4\)) or hydrochloric (HCl) acid for the standard alkali of that method. For the low-alkalinity method, titrate a 200-mL sample with 0.02N H\(_2\)SO\(_4\) from a 10-mL buret.

*f. Sampling and storage:* See Section 2310B.1f.

2. **Apparatus**

See Section 2310B.2.

3. **Reagents**

*a. Sodium carbonate solution,* approximately 0.05N: Dry 3 to 5 g primary standard Na\(_2\)CO\(_3\) at 250°C for 4 h and cool in a desiccator. Weigh 2.5 ± 0.2 g (to the nearest mg), transfer to a 1-L volumetric flask, fill flask to the mark with distilled water, and dissolve and mix reagent. Do not keep longer than 1 week.
b. **Standard sulfuric acid or hydrochloric acid, 0.1N:** Prepare acid solution of approximate normality as indicated under Preparation of Desk Reagents. Standardize against 40.00 mL 0.05N Na₂CO₃ solution, with about 60 mL water, in a beaker by titrating potentiometrically to pH of about 5. Lift out electrodes, rinse into the same beaker, and boil gently for 3 to 5 min under a watch glass cover. Cool to room temperature, rinse cover glass into beaker, and finish titrating to the pH inflection point. Calculate normality:

\[
N = \frac{A \times B}{53.00 \times C}
\]

where:

- \(A\) = g Na₂CO₃ weighed into 1-L flask,
- \(B\) = mL Na₂CO₃ solution taken for titration, and
- \(C\) = mL acid used.

Use measured normality in calculations or adjust to 0.1000N; 1 mL 0.1000N solution = 5.00 mg CaCO₃.

c. **Standard sulfuric acid or hydrochloric acid, 0.02N:** Dilute 200.00 mL 0.1000N standard acid to 1000 mL with distilled or deionized water. Standardize by potentiometric titration of 15.00 mL 0.05N Na₂CO₃ according to the procedure of ¶ 3b; 1 mL = 1.00 mg CaCO₃.

d. **Bromcresol green indicator solution, pH 4.5 indicator:** Dissolve 100 mg bromcresol green, sodium salt, in 100 mL distilled water.

e. **Mixed bromcresol green-methyl red indicator solution:** Use either the aqueous or the alcoholic solution:

1) Dissolve 100 mg bromcresol green sodium salt and 20 mg methyl red sodium salt in 100 mL distilled water.

2) Dissolve 100 mg bromcresol green and 20 mg methyl red in 100 mL 95% ethyl alcohol or isopropyl alcohol.

f. **Metacresol purple indicator solution, pH 8.3 indicator:** Dissolve 100 mg metacresol purple in 100 mL water.

g. **Phenolphthalein solution, alcoholic, pH 8.3 indicator.**

h. **Sodium thiosulfate, 0.1N:** See Section 2310B.3i.

4. **Procedure**

a. **Color change:** See Section 2310B.4b.
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b. Potentiometric titration curve: Follow the procedure for determining acidity (Section 2310B.4c), substituting the appropriate normality of standard acid solution for standard NaOH, and continue titration to pH 4.5 or lower. Do not filter, dilute, concentrate, or alter the sample.

c. Potentiometric titration to preselected pH: Determine the appropriate end-point pH according to ¶ 1b. Prepare sample and titration assembly (Section 2310B.4c). Titrate to the end-point pH without recording intermediate pH values and without undue delay. As the end point is approached make smaller additions of acid and be sure that pH equilibrium is reached before adding more titrant.

d. Potentiometric titration of low alkalinity: For alkalinites less than 20 mg/L titrate 100 to 200 mL according to the procedure of ¶ 4c, above, using a 10-mL microburet and 0.02N standard acid solution. Stop the titration at a pH in the range 4.3 to 4.7 and record volume and exact pH. Carefully add additional titrant to reduce the pH exactly 0.30 pH unit and again record volume.

5. Calculations
   a. Potentiometric titration to end-point pH:

\[
\text{Alkalinity, mg CaCO}_3/\text{L} = \frac{A \times N \times 50000}{\text{mL sample}}
\]

where:

- \( A \) = mL standard acid used and
- \( N \) = normality of standard acid

or

\[
\text{Alkalinity, mg CaCO}_3/\text{L} = \frac{A \times t \times 1000}{\text{mL sample}}
\]

where:

- \( t \) = titer of standard acid, mg CaCO\(_3\)/mL.

Report pH of end point used as follows: ‘‘The alkalinity to pH _______ = _______ mg CaCO\(_3\)/L’’ and indicate clearly if this pH corresponds to an inflection point of the titration curve.

b. Potentiometric titration of low alkalinity:

Total alkalinity, mg CaCO\(_3\)/L
c. Calculation of alkalinity relationships: The results obtained from the phenolphthalein and total alkalinity determinations offer a means for stoichiometric classification of the three principal forms of alkalinity present in many waters. The classification ascribes the entire alkalinity to bicarbonate, carbonate, and hydroxide, and assumes the absence of other (weak) inorganic or organic acids, such as silicic, phosphoric, and boric acids. It further presupposes the incompatibility of hydroxide and bicarbonate alkalinitites. Because the calculations are made on a stoichiometric basis, ion concentrations in the strictest sense are not represented in the results, which may differ significantly from actual concentrations especially at pH > 10. According to this scheme:

1) Carbonate ($\text{CO}_3^{2-}$) alkalinity is present when phenolphthalein alkalinity is not zero but is less than total alkalinity.

2) Hydroxide ($\text{OH}^-$) alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity.

3) Bicarbonate ($\text{HCO}_3^-$) alkalinity is present if phenolphthalein alkalinity is less than half the total alkalinity. These relationships may be calculated by the following scheme, where $P$ is phenolphthalein alkalinity and $T$ is total alkalinity ($\parallel 1b$):

Select the smaller value of $P$ or $(T−P)$. Then, carbonate alkalinity equals twice the smaller value. When the smaller value is $P$, the balance $(T−2P)$ is bicarbonate. When the smaller value is $(T−P)$, the balance $(2P−T)$ is hydroxide. All results are expressed as CaCO₃. The mathematical conversion of the results is shown in Table 2320:II. (A modification of Table 2320:II that is more accurate when $P = \frac{1}{2}T$ has been proposed.⁴)

Alkalinity relationships also may be computed nomographically (see Carbon Dioxide, Section 4500-CO₂). Accurately measure pH, calculate OH⁻ concentration as milligrams CaCO₃ per liter, and calculate concentrations of $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ as milligrams CaCO₃ per liter from the OH⁻ concentration, and the phenolphthalein and total alkalinitities by the following equations:

\[
\text{CO}_3^{2-} = 2P - 2[\text{OH}^-]
\]
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\[ \text{HCO}_3^- = T - 2P + [\text{OH}^-] \]

Similarly, if difficulty is experienced with the phenolphthalein end point, or if a check on the phenolphthalein titration is desired, calculate phenolphthalein alkalinity as CaCO$_3$ from the results of the nomographic determinations of carbonate and hydroxide ion concentrations:

\[ P = \frac{1}{2} [\text{CO}_3^{2-}] + [\text{OH}^-] \]

6. Precision and Bias

No general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and sample handling before the analysis.

In the range of 10 to 500 mg/L, when the alkalinity is due entirely to carbonates or bicarbonates, a standard deviation of 1 mg CaCO$_3$/L can be achieved. Forty analysts in 17 laboratories analyzed synthetic samples containing increments of bicarbonate equivalent to 120 mg CaCO$_3$/L. The titration procedure of ¶ 4b was used, with an end point pH of 4.5. The standard deviation was 5 mg/L and the average bias (lower than the true value) was 9 mg/L.

Sodium carbonate solutions equivalent to 80 and 65 mg CaCO$_3$/L were analyzed by 12 laboratories according to the procedure of ¶ 4c. The standard deviations were 8 and 5 mg/L, respectively, with negligible bias. Four laboratories analyzed six samples having total alkalinitities of about 1000 mg CaCO$_3$/L and containing various ratios of carbonate/bicarbonate by the procedures of both ¶ 4a and ¶ 4c. The pooled standard deviation was 40 mg/L, with negligible difference between the procedures.

7. References


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8. Bibliography


Endnotes

1 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.