ALKALINITY

PURPOSE

Using Standard Methods to determine the total and phenolphthalein alkalinity and to calculate the hydroxide, carbonate and bicarbonate alkalinity.

THEORY

Alkalinity and pH exist in a complex relationship. Total alkalinity, temperature, and the presence of other ions all have an influence on the relationship between pH and the different forms of alkalinity. The chemical species, which are responsible for alkalinity, are greatly affected by, and in turn affect pH. In natural waters, the 2 species, which commonly contribute to alkalinity are a) hydroxide (OH⁻) and b) the salts of weak acids such as bicarbonate (HCO₃⁻), carbonate (CO₃²⁻) and, less frequently, borate, silicate and phosphate. Other compounds, such as humic acid and tannic acid, may also contribute to total alkalinity in some water systems but are generally not considered significant. The most important ionic species in the majority of water samples are OH⁻, CO₃²⁻ and HCO₃⁻, therefore, the conventions for measuring alkalinity have been based on their equilibrium characteristics.

A water sample can be titrated with strong acid to determine alkalinity. As the acid is added, the alkalinity resists pH change until points of equivalence are reached at which time the pH drops dramatically with the continued addition of only small amounts of the acid.

When the pH is greater than 9.5, OH⁻ (hydroxide alkalinity) may be present, and CO₃²⁻ will be at its maximum concentration.

Phenolphthalein Alkalinity

The first end point of the titration occurs at a pH 8.3. If a sample contains both carbonate and hydroxide alkalinity, then as the titration reaches pH 8.3, all of the OH⁻ converts to H₂O and the CO₃²⁻ will be neutralized to HCO₃⁻. At this equivalence point, the indicator phenolphthalein changes from pink to colorless and
therefore it is called the phenolphthalein end point ($V_p$).

Note that OH$^-$ will have been completely neutralized below pH 8.3 and above pH 8.3, HCO$_3^-$ is not present because hydroxide and bicarbonate alkalinity are mutually exclusive.

The second end point occurs at pH 4.5 and is known as the methyl orange end point ($V_{mo}$). At pH 4.5, all of the HCO$_3^-$ is converted to carbonic acid (H$_2$CO$_3$), and the indicator methyl orange/bromocresol green changes from blue to green ($V_{mo}$).

Alkalinity does not exist at pH below 4.5 due to the equilibrium established between dissolved CO$_2$ and carbonate acid H$_2$CO$_3$ in water.

**Total Alkalinity**

The total amount (moles) of acid required to neutralize OH$^-$, CO$_3^{2-}$ and HCO$_3^-$ and reach pH 4.5 is defined as the total alkalinity, TA.

**APPLICATIONS OF ALKALINITY DATA IN ENVIRONMENTAL ENGINEERING PRACTICE (Ref 2)**

**Buffer Capacity**

Alkalinity describes the buffering capacity of water against pH change from the addition of acids. This buffering capacity is essential to biological systems, which could otherwise be adversely affected by large pH fluctuations. Algae blooms affect alkalinity in a significant way because they tend to decrease carbon dioxide levels, resulting in a dangerously high pH. The pH in such cases may surpass 9.5.

Industrial process, such as coagulation, can decrease or eliminate alkalinity. This problem is readily overcome by adding sodium carbonate or sodium hydroxide to the effluent prior to discharge. In terms of public health, alkalinity is of little significance.

**Corrosion Control**

Alkalinity is an important parameter involved in corrosion control. It must be known in order to calculate the Langelier saturation Index.

**Coagulation**

Alkalinity is a major item that must be considered in Coagulation. It
must be present in excess of that destroyed by the acid released by the coagulant for effective and complete coagulation to occur.

**Water Softening**

Alkalinity is a major item that must be considered in calculating the lime and soda ash requirements in softening of water by precipitation methods. The alkalinity of softened water is a consideration in terms of whether such waters meeting drinking standards.

**Industry wastes**

Many regulatory agencies prohibit the discharge of wastes containing caustic (hydroxide) alkalinity to receiving waters. Similarly the discharge of such waters to sewers is also prohibited.

Alkalinity is an important consideration determining the amenability of wastewaters to biological treatment.

**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 (Ref 1).

**APPARATUS**

1. magnetic stirrer and stir bars
2. Buret, 25ml
3. Volumetric pipets
4. Miscellaneous glassware

**REAGENT**

**NTR**

0.02 N sulfuric acid titrant
Phenolphthalein indicator
Methyl red-Bromcresol green Indicator
**PROCEDURE**

The most accurate way to determine alkalinity is to conduct a potentiometric titration (Standard Method 2320 B. 4b) using a pH meter to establish $V_p$ and $V_{mo}$. In this method a pH meter is used to record pH as acid is added incrementally, and the results can be depicted graphically. A pH meter is not only more accurate than colorimetric indicators (Standard Methods 2320 B.4a), but it is less affected by interference from naturally occurring chemicals in a water sample. However the potentiometric method has its own interferences (See Interferences above).

The end points of pH 8.3 and 4.5 hold true for solutions that are essentially pure (such as the ones used in this lab), natural waters however may contain other compounds that contribute slightly to the total alkalinity in ways that may alter the point of inflection. It is possible to detect such shifts in the potentiometric titration

In this laboratory Standard Method 2320 B. 4a will be followed.

**Colorimetric Titration**

1. Pipet a 50.00 mL aliquot of the sample into a 150ml beaker.
2. Add a stir bar, place the beaker on magnetic stirrer and stir gently.
3. Add phenolphthalein indicator (5 drops) and note the color.
4. Titrate the sample with 0.02 N $H_2SO_4$. Add the acid in increments of 0.5 to 1.0 ml.
5. Record the Volume ($V_p$) at which the color changes from pink to colorless.
6. Add the methyl red – bromocresol green indicator (5 drops).
7. Continue titration. Record the Volume $V_{mo}$ at which the solution changes color again.

**CALCULATION**

(1) **Total Alkalinity and Ophenolphthalein Alkalinity**

Although the ionic species responsible for alkalinity change as the pH is lowered during the titration, all alkalinity is expressed in equivalent mg/L $CaCO_3$. To do this, the moles of $H^+$ added during the titration is converted to moles of $CaCO_3$ (atomic weight = 50g/mole)
Phenolphthalain Alkalinity as mg CaCO₃ per 50 mL of sample:

\[ A \cdot N \cdot \frac{50}{mL_{sample}} \cdot \frac{1000}{g} \]

Total Alkalinity as mg CaCO₃ per 50 mL of sample:

\[ B \cdot N \cdot \frac{50}{mL_{sample}} \cdot \frac{1000}{g} \]

Where,

- \( A \): mL of standard acid used to reach Phenolphthalein end point
- \( B \): mL of standard acid used to reach the second end point
- \( N \): normality of the standard acid.

**(2) Hydroxide, Carbonate and Bicarbonate Alkalinity**

Carbonate alkalinity is present when the phenolphthalein is not zero but is less than the total alkalinity.

Hydroxide alkalinity is present if the phenolphthalein alkalinity is more than half the total alkalinity.

Bicarbonate alkalinity is present if the phenolphthalein alkalinity is less than half the total alkalinity.

The table below (Ref 1) may be used to calculate the Hydroxide, Carbonate and Bicarbonate alkalinity from the total alkalinity and phenolphthalein alkalinity results:

<table>
<thead>
<tr>
<th>Result of titration</th>
<th>Hydroxide alk. as CaCO₃</th>
<th>Carbonate alk. as CaCO₃</th>
<th>Bicarbonate alk. as CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>P=0</td>
<td>0</td>
<td>0</td>
<td>T</td>
</tr>
<tr>
<td>P&lt;T/2</td>
<td>0</td>
<td>2P</td>
<td>T-2P</td>
</tr>
<tr>
<td>P=T/2</td>
<td>0</td>
<td>2P</td>
<td>0</td>
</tr>
<tr>
<td>P&gt;T/2</td>
<td>2P-T</td>
<td>2(T-P)</td>
<td>0</td>
</tr>
<tr>
<td>P=T</td>
<td>T</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
P = Phenopthalein Alkalinity, T = Total Alkalinity

REFERENCES


increments of 0.02N sulfuric acid (H₂SO₄) (Section 2320B.3c) to reduce pH to 4 or less. Remove electrodes. Add 5 drops 30% H₂O₂ and boil for 2 to 5 min. Cool to room temperature and titrate with standard alkali to pH 8.3 according to the procedure of 4d.

b. Color change: Select sample size and normality of titrant according to criteria of ¶1e. Adjust sample to room temperature, if necessary, and with a pipet discharge sample into an erlenmeyer flask, while keeping pipet tip near flask bottom. If free residual chlorine is present add 0.05 mL (1 drop) 0.1M Na₂S₂O₃ solution, or destroy with ultraviolet radiation. Add 0.2 mL (5 drops) indicator solution and titrate over a white surface to a persistent color change characteristic of the equivalence point. Commercial indicator solutions or solids designated for the appropriate pH range (3.7 or 8.3) may be used. Check color at end point by adding the same concentration of indicator used with sample to a buffer solution at the designated pH.

c. Potentiometric titration curve:

1) Rinse electrodes and titration vessel with distilled water and drain. Select sample size and normality of titrant according to the criteria of ¶1e. Adjust sample to room temperature, if necessary, and with a pipet discharge sample while keeping pipet tip near the titration vessel bottom.

2) Measure sample pH. Add standard alkali in increments of 0.5 mL or less, such that a change of less than 0.2 pH units occurs per increment. After each addition, mix thoroughly but gently with a magnetic stirrer. Avoid splashing. Record pH when a constant reading is obtained. Continue adding titrant and measure pH until pH 9 is reached. Construct the titration curve by plotting observed pHe values versus cumulative milliliters titrant added. A smooth curve showing one or more inflections should be obtained. A ragged or erratic curve may indicate that equilibrium was not reached between successive alkali additions. Determine acidity relative to a particular pH from the curve.

d. Potentiometric titration to pH 3.7 or 8.3: Prepare sample and titration assembly as specified in ¶4c1). Titrate to pre-selected end-point pH (¶ 1d) without recording intermediate pH values. As the end point is approached make smaller additions of alkali and be sure that pH equilibrium is reached before making the next addition.

5. Calculation

\[
\text{Acidity, as mg CaCO}_3\text{/L} = \frac{[(A \times B) - (C \times D)] \times 50000}{\text{mL sample}}
\]

where:

- \(A\) = mL NaOH titrant used,
- \(B\) = normality of NaOH,
- \(C\) = mL H₂SO₄ used (¶ 4e), and
- \(D\) = normality of H₂SO₄.

Report pH of the end point used, as follows: "The acidity to pH ___ = ____ mg CaCO₃/L." If a negative value is obtained, determine the alkalinity according to Section 2320.

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 analysis.

Fifty analysts in 17 laboratories analyzed synthetic water samples containing increments of bicarbonate equivalent to 20 mg CaCO₃/L. Titration according to the procedure of ¶ 4d gave a standard deviation of 1.8 mg CaCO₃/L, with negligible bias. Five laboratories analyzed two samples containing sulfuric, acetic, and formic acids and aluminum chloride by the procedures of §§ 4b and 4d. The mean acidity of one sample (to pH 3.7) was 487 mg CaCO₃/L, with a standard deviation of 11 mg/L. The bromophenol blue titration of the same sample was 90 mg/L greater, with a standard deviation of 110 mg/L. The other sample had a potentiometric titration of 547 mg/L, with a standard deviation of 54 mg/L, while the corresponding indicator result was 85 mg/L greater, with a standard deviation of 56 mg/L. The major difference between the samples was the substitution of ferric ammonium citrate, in the second sample, for part of the aluminum chloride.

7. Bibliography


---

2320 ALKALINITY*

---

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 alkalinites 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.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 (CO₂) at that stage. CO₂ 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 2320:1 are suggested as the equivalence points for the corresponding alkalinity concentrations as milligrams CaCO₃ 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. Bromcresol green or a mixed bromcresol 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 CaCO₃/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 (H₂SO₄) or hydrochloric (HCl) acid for the standard alkali of that method. For the low-alkalinity method, titrate a 200-mL sample with 0.02N H₂SO₄ 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 Na₂CO₃ 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 (see inside front cover). 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 glass into beaker, and finish titrating to the pH inflection point. Calculate normality:

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

where:
- \( A = \text{g Na}_2\text{CO}_3 \text{ weighed into 1-L flask} \)
- \( B = \text{mL Na}_2\text{CO}_3 \text{ solution taken for titration, and} \)
- \( C = \text{mL acid used} \)

Use measured normality in calculations or adjust to 0.1000\(N\); 1 mL 0.1000\(N\) solution = 5.00 mg CaCO\(_3\).

c. \text{Standard sulfuric acid or hydrochloric acid, 0.02}\(N\): Dilute 200.00 mL 0.1000\(N\) standard acid to 1000 mL with distilled or deionized water. Standardize by potentiometric titration of 15.00 mL 0.05\(N\) \text{Na}_2\text{CO}_3 according to the procedure of \(\S\) 3b; 1 mL = 1.00 mg CaCO\(_3\).

d. \text{Brom cresol green indicator solution, pH 4.5 indicator}: Dissolve 100 mg brom cresol green, sodium salt, in 100 mL distilled water.

e. \text{Mixed brom cresol green-methyl red indicator solution}: Use either the aqueous or the alcoholic solution:
1) Dissolve 100 mg brom cresol green sodium salt and 20 mg methyl red sodium salt in 100 mL distilled water.
2) Dissolve 100 mg brom cresol green and 20 mg methyl red in 100 mL 95% ethyl alcohol or isopropyl alcohol.

f. \text{Metacresol purple indicator solution, pH 8.3 indicator}: Dissolve 100 mg metacresol purple in 100 mL water.

g. \text{Phenolphthalein solution, alcoholic, pH 8.3 indicator}.

h. \text{Sodium thiosulfate, 0.1N}: See Section 2310B.3i.

4. Procedure

a. \text{Color change: See Section 2310B.4b}.

b. \text{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. \text{Potentiometric titration to preselected pH}: Determine the appropriate end-point pH according to \(\S\) 1b. Prepare sample and titration assembly (Section 2310B.4e). 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. \text{Potentiometric titration of low alkalinity}: For alkalinities less than 20 mg/L titrate 100 to 200 mL according to the procedure of \(\S\) 4c, above, using a 10-mL micro buret and 0.02\(N\) 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. \text{Potentiometric titration to end-point pH}:

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

where:
- \( A = \text{mL standard acid used} \)
- \( N = \text{normality of standard acid} \)

or

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

where:
- \( t = \text{titer of standard acid, mg CaCO}_3/\text{mL} \)

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. \text{Potentiometric titration of low alkalinity}:

Total alkalinity, mg CaCO\(_3\)/L

\[ = \frac{(2 \times B - C) \times N \times 50000}{\text{mL sample}} \]

where:
- \( B = \text{mL titrant to first recorded pH} \)
- \( C = \text{total mL titrant to reach pH 0.3 unit lower, and} \)
- \( N = \text{normality of acid} \)

c. \text{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 alkalinities. 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 (\(\S\) 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 CaCO\(_3\). The mathematical conversion of the results is shown in Table 2320:II. (A modification of Table 2320:II that is more accurate when \( P = 1/2T \) has been proposed.)*

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


8. Bibliography