ALKALINITY MEASUREMENTS

1. OBJECTIVE AND IMPORTANCE OF EXPERIMENT

- The alkalinity of a water is a measure of its capacity to neutralize acids.
- Alkalinity acts as buffers to resist a drop in pH resulting from acid addition.
- Although many materials may contribute to the alkalinity of a water, the major portion of the alkalinity in natural waters: (1) hydroxide, (2) carbonate, and (3) bicarbonate.
- Also, other salts of weak acids, such as borate, silicate, and phosphate, may be present in small amounts.
- For most practical purposes, alkalinity due to other materials in natural waters is insignificant and may be ignored.
- 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.

Alkalinity parameter is used in a variety of ways in Environmental Engineering practices. Such as;

- Chemical coagulation
- Water softening
- Corrosion control
- Buffer capacity
- Industrial wastes
- Biological processes

1.1. Measurement Principals

- Alkalinity is measured volumetrically by titration with H_2SO_4 and is reported $CaCO_3$.
- If initial pH is above 8.3, the titration is made in two steps.
- In the first step the titration is conducted until the pH is lowered to 8.3, the point at which phenolphthalein indicator turns from pink to colorless.
- The second phase of titration is conducted until the pH is lowered to about 4.5, corresponding to the bromcresol green end point. This is also called “Total Alkalinity”.

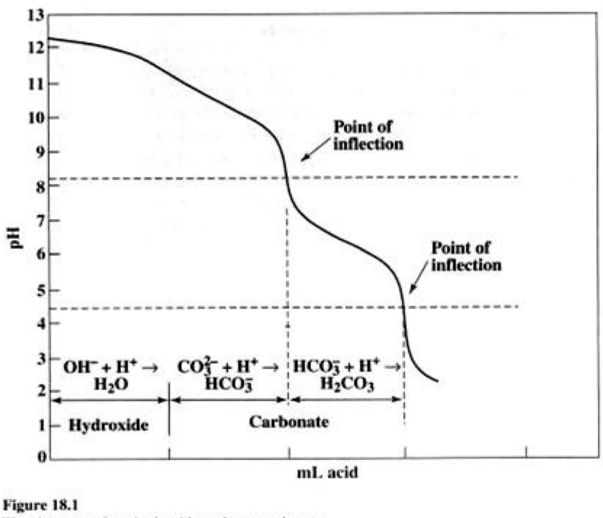

Figure 18.1
Titration curve for a hydroxide-carbonate mixture.

$OH^- + H^+ \longrightarrow H_2O$

$CO_3^{2-} + H^+ \longrightarrow HCO_3^-$ (Bicarbonate)

$HCO_3^- + H^+ \longrightarrow H_2CO_3$ (Carbonic Acid)

1.2. 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.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and Equipment

- pH meter
- Standard sulfuric acid solution (0,02 N and 0,1 N)
- Methyl orange indicator
- Phenolphthalein indicator
- 0,02 N NaOH solution

2.2. Experimental Procedure

- Clean pH electrode by distilled water.
- Collect 50 mL water sample in an erlenmayer flask, add 3 drops of phenolphthalein indicator, titrate the 50 mL sample with 0.02N sulfuric acid to pH 8.3 and estimate phenolphthalein alkalinity (phenolphthalein indicator will change color, from pink to clear, at pH 8.3).
- Phenolphthalein Alkalinity (in mg/L as CaCO3) = $(A1 \times N \times 50{,}000) / V$
  Where: A1 = volume of sulfuric acid used in mL; N = normality of acid used to titrate;
  V= volume of sample used in mL
- Use the same sample. Add 5 drops of methyl orange indicator. Titrate the 50 mL sample with 0.02 N sulfuric acid to pH 4.5 and estimate total alkalinity (bromcresol green indicator will change color, from blue to yellow, at pH 4.5).
- Amount of acid used at this moment starting from step1 (i.e., A2) is used to react with the hydroxide, carbonate, and bicarbonate and it constitutes of total alkalinity:
  Total Alkalinity (in mg/L as CaCO3) = $(A \times N \times 50{,}000) / V$
  Where: A2 = volume of acid used in mL starting from step 1 (i.e., A2>A1) (Note: If after adding phenolphthalein indicator no color develops, it means no phenolphthalein alkalinity and it can be reported as "Phenolphthalein alkalinity absent".)
- Calculation from Alkalinity and pH measurements:
- Hydroxide alk. (mg/L as CaCO3)= $50{,}000 \times 10$
- Carbonate alk. (mg/L as CaCO3)= 2 × [Phenolphthalein alk.-hydroxide alk.] (3b)
- Bicarbonate alk. (mg/L as CaCO3)= Total alk.-[Carbonate alk.+ hydroxide alk.] (3c)

2.3. Calculations

Alkalinity (mg $CaCO_3$/L) = (S x N x 50000) / mL sample

A = Standard H_2SO_4 solution consumption, mL

N = Normality of H_2SO_4

3. REPORTS AND OBSERVATIONS

1- Calculate the alkalinity as $CaCO_3$ of water that contains 85 mg/L of HCO_3^-, 120 mg/L of CO_3^{2-}, and 2 mg/L of OH^-.

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