Experiment-3

Determination of Alkalinity From the Effluent water Sample

Introduction
Alkalinity is primarily a way of measuring the acid neutralizing capacity of water. In other words, its ability to maintain a relatively constant pH. Alkalinity mainly due to $\text{CO}_3^{2-}$, $\text{HCO}_3^-$, and $\text{OH}^-$ in terms of concentration of this constitutes which maintained constant pH. It is also due to borate, phosphate, silicate and other bases if they are prevent the $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ ions act as buffer systems & prevent in drastic change in pH. The ability of natural water to act as a buffer is controlled in part by the amount of calcium and carbonate ions in solution. Carbonate ion and calcium ion both come from calcium carbonate or limestone. So water that comes in contact with limestone will contain high levels of both $\text{Ca}^{+2}$ and $\text{CO}_3^{2-}$ ions and have elevated hardness and alkalinity.

Environmental significance
- Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes.
- Large amount of alkalinity imparts bitter taste in water.
- The principal objection of alkaline water is the reactions that can occur between alkalinity and certain cations in waters. The resultant precipitate can corrode pipes and other accessories of water distribution systems.
- Alkalinity is used to determine the suitability of water for irrigation, industrial use, raw water characterization and water and wastewater monitoring.
- Alkalinity is also important as an indicator of a water body's ability to resist pH change with the addition of acid from an accidental spill or acid precipitation and prevent pH changes that are harmful to aquatic life.
- Wastewaters containing excess caustic (hydroxide) alkalinity are not to be discharged into natural water bodies or sewers.
- Alkalinity as carbonate and bicarbonate of saline water is very important in tertiary recovery processes for recovering petroleum.
- Alkaline water offers better wetting to the formation rock and improve oil release.
- As an additional benefit, ions that provide alkalinity absorb on rock surfaces occupying adsorption sites and decrease the loss of recovery chemical by adsorption.
- The alkalinity value is necessary in the calculation of carbonate scaling tendencies of saline waters.
- The alkalinity acts as a pH buffer in coagulation and lime-soda softening of water.
- In wastewater treatment, alkalinity is an important parameter in determining the amenability of wastes to the treatment process and control of processes such as anaerobic digestion, where bicarbonate alkalinity, total alkalinity, and any fraction contributed by volatile acid salts become considerations.
Principle:
Alkalinity measures the acid-neutralizing capacity of a water sample. The alkalinity in a water sample measured by the amount of standard acid needed to lower the pH. Based on stoichiometry of the reaction and number of moles of Sulphuric acid needed to reach the end point, the concentration of alkalinity in water is calculated.

Total Alkalinity
Total alkalinity is the total concentration of bases in water expressed as parts per million (ppm) or milligrams per liter (mg/L) of calcium carbonate (CaCO$_3$). These bases are usually bicarbonates (HCO$_3$) and carbonates (CO$_3$), and they act as a buffer system that prevents drastic changes in pH. For example, in waters with low alkalinity, pH might fluctuate from 6 or lower to as high as 10 or above; while in high alkalinity waters, pH might fluctuate from about 7.5 to 8.5.

Total alkalinity is not the same as hardness. Calcium (Ca$^{++}$) and magnesium (Mg$^{++}$) are primarily responsible for hardness. However, in most waters, alkalinity and hardness have similar values because the carbonates and bicarbonates responsible for total alkalinity are usually brought into the water in the form of calcium carbonate or magnesium carbonate. Waters with high total alkalinity are not always hard, since the carbonates can be brought into the water in the form of sodium or potassium carbonate.

Phenolphthalein Alkalinity
Phenolphthalein alkalinity is present only when free carbon dioxide (CO$_2$) is absent and therefore exists only when the pH exceeds 8.3. Phenolphthalein alkalinity should never be over half the total alkalinity; otherwise, a caustic alkalinity is produced.

Difference between total and phenolphthalein alkalinity
There exist three species of alkalinity; bicarbonate, carbonate and hydroxide. The concentration of each species will vary with pH. Total alkalinity is the measurement of all species of alkalinity in the water. The concentration of each of the three species can be determined by titrating a water sample with acid of a known concentration and using chemical indicators, phenolphthalein (P indicator), methyl orange (M indicator), or a pH meter to determine "endpoints". The chemical indicators change color at a certain pH points (the endpoint). The mix of alkaline species change as pH decreases.

Hydroxide alkalinity disappears below pH 10.3, carbonate below 8.3 and bicarbonate below 4.3 (or thereabout). The phenolphthalein indicator turns from pink to clear at or below pH 8.3. The methyl orange indicator turns from orange to yellow below pH 4.3. The amount of acid required to produce a color change is used to calculate the amount of P and M alkalinity. The P and M results are used to calculate "O" or hydroxide alkalinity. Depending on the ionic constituents of the water, these relationships can change or be interfered with.

Importance of Improving Alkalinity
The most common method of increasing alkalinity in waters is by adding agricultural limestone (calcium carbonate). Applications of lime to fish ponds on soils of low calcium content resulted in greater fish production. The applications of lime to lakes increased pH and total alkalinity and also cleared water of brown stain from humic substances. Clear water results in deeper light penetration and greater photosynthesis, as well as increased zooplankton production.

Fertilization does not produce adequate phytoplankton (algae bloom) in many ponds with soft waters and acid muds because carbon dioxide is in short supply, and added phosphate
adheres tightly to the bottom muds. Addition of lime to these ponds elevates total bicarbonate alkalinity and increases pH in the water. Neutralization of bottom muds with lime prevents phosphate from adhering to it, thereby increasing phosphorus concentrations in the water. As a result of these changes in water quality, phytoplankton blooms develop upon application of inorganic fertilizers. Liming soft water ponds to increase alkalinitities to at least 20 ppm is beneficial to fish production.

**Total Alkalinity**
Alkalinity of water is its capacity to neutralize a strong acid and is characterizing by of the all hydroxyl ions.

**Reagent**
1. **Std. 0.01N H₂SO₄ solution**: Dilute 2.8ml of concentrated H₂SO₄ to 1 litre with distilled water. Dilute 100 ml of this solution to again 1 litre for getting 0.01N H₂SO₄. Standardize with 0.01N Na₂CO₃ using methyl orange as indicator
2. **Std. 0.02N AgNO₃ solution**: 3.40g of AgNO₃ is dissolve in double distilled water and make up to 1 litre. This is to be standardize against the standard NaCl or KCl solution and stored in amber coloured bottle away from light
3. **Phenolphthalein indicator**: 0.25% solution in 60% ethyl alcohol
4. **Methyl orange indicator**: 0.1% solution in distilled water

**Procedure**
1. Rinse the burette with 0.02N Sulphuric acid and discard the solution.
2. Fill the burette with 0.02N sulphuric acid and adjust it to zero.
3. Pipette out 10 ml of sample and pour it into a 250 ml of conical flask.
4. Add few drops of phenolphthalein indicator to the contents of conical flask. The colour of the solution will turn to pink. This colour change is due to alkalinity of hydroxyl ions in the water sample.
5. Titrate it against 0.02N sulphuric acid till the pink color disappears. This indicates that all the hydroxyl ions are removed from the water sample.
6. Note down the titter value (X). This value is used in calculating the phenolphthalein alkalinity.
7. To the same solution in the conical flask add few drops of mixed indicator.
8. The colour of the solution turns to blue. This colour change is due to CO₃²⁻ & HCO₃⁻ ions in water sample.
9. Continue the titration from the point where stopped for the phenolphthalein alkalinity.
10. Titrate till the solution becomes red. The entire volume (Y) of sulphuric acid is noted down and it is accountable in calculating the total alkalinity.
Observation and calculation

(1) Reading table for phenolphthalein alkalinity (PA) and total alkalinity (TA)

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>ml of aliquot taken</th>
<th>0.1 N std. H₂SO₄ solution in burette (ml)</th>
<th>Reading with phenolphthalein (PA)</th>
<th>Reading with methyl orange (TA)</th>
<th>pink to disappear</th>
<th>yellow colour change to rosy red</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Initial (ml)</td>
<td>Final (ml)</td>
<td>Difference (ml)</td>
<td>Initial (ml)</td>
</tr>
<tr>
<td>Pilot</td>
<td>10</td>
<td></td>
<td>10</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td></td>
<td>10</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td></td>
<td>10</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td></td>
<td>10</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mean (ml)</td>
<td>X=</td>
<td>Mean (ml)</td>
<td>Y=</td>
</tr>
</tbody>
</table>

1. Water sample taken
2. Normality of HCl used = N
3. ml of HCl used only with phenolphthalein = A
4. ml of HCl used only with methyl orange = B
5. Total HCl used with both indicator = A+B

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>PA (as CaCO₃) mg/l</th>
<th>TA (as CaCO₃) mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reading (X) X N of H₂SO₄ X Eq. wt.(CaCO₃) X 1000* Aliquot taken (10 ml)</td>
<td>Reading (Y) X N of H₂SO₄ X Eq. wt.(CaCO₃) X 1000* Aliquot taken (10 ml)</td>
</tr>
<tr>
<td></td>
<td>=</td>
<td>=</td>
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<td></td>
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<td>=</td>
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<td></td>
<td>=</td>
<td>=</td>
</tr>
</tbody>
</table>
Remarks:

The phenolphthalein alkalinity is also recorded as calcium carbonate (CaCO$_3$) since the strength of the sulfuric acid (H$_2$SO$_4$) used in the test is such that each milliliter used represents 10 ppm of CaCO$_3$. If the presence of phenolphthalein alkalinity is over half of the total alkalinity in the water, then the water is caustic. Caustic water should be avoided in a domestic supply. Since, it causes burning sensation when tasted.

It is recommended that drinking water shall not have a pH greater than 10.6 nor a normal carbonate alkalinity greater than 120 ppm. Although not stated in the standards, an appreciable alkalinity should always be present.

If the phenolphthalein alkalinity (P) and the total alkalinity (T) is known, the proportion of bicarbonate, carbonate, and caustic alkalinites present as CaCO$_3$ can be computed from the table below.

**Relationship between hydroxide, carbonate and bicarbonate, and phenolphthalein and total alkalinity**

Amount of Alkalinity Present as (Assuming all of the alkalinity is due to carbonate, bicarbonate, or hydroxide):

<table>
<thead>
<tr>
<th>Result of Titration</th>
<th>Hydroxide Alkalinity as CaCO$_3$</th>
<th>Carbonate Alkalinity as CaCO$_3$</th>
<th>Bicarbonate Alkalinity as CaCO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P = 0</td>
<td>0</td>
<td>0</td>
<td>T</td>
</tr>
<tr>
<td>P &lt; ½ T</td>
<td>0</td>
<td>2P</td>
<td>T - 2P</td>
</tr>
<tr>
<td>P = ½ T</td>
<td>0</td>
<td>2P</td>
<td>0</td>
</tr>
<tr>
<td>P &gt; ½ T</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= Phenolphthalein alkalinity  
T = Total alkalinity

**Example 1:**  
Assume that the phenolphthalein, or P alkalinity is 0 and the total, or T, alkalinity is 80. Note from the table that when P equals 0, all alkalinity is bicarbonate; therefore, there are 80 ppm alkalinity as bicarbonate.

**Example 2:**  
Assume that P equals 50 ppm and T equals 80 ppm. In this instance, the situation is found in Line 4 of the table. It is noted that when 2P (2 x 50 = 100) is more than T (80 ppm), 2P minus T equals the hydroxide or caustic alkalinity. Therefore, (2 x 50) - 80 = 100 - 80 = 20 ppm caustic alkalinity; and 2 (80 - 50) = 2 x 30 = 60 ppm carbonate alkalinity.

**Inference**

Alkalinity is a measure of the capacity of water to neutralize acids. The predominant chemical system present in natural waters is one where carbonates, bicarbonates and hydroxides are present. The bicarbonate ion is usually prevalent. However, the ratio of these ions is a function of pH, mineral composition, temperature and ionic strength. Water
may have a low alkalinity rating but a relatively high pH or vice versa, so alkalinity alone is not of major importance as a measure of water quality. Alkalinity is not considered detrimental to humans but is generally associated with high pH values, hardness and excess dissolved solids. High alkalinity waters may also have a distinctly flat, unpleasant taste. Based on the testing, it is found that the alkalinity of the sample is 83 \( \text{mg/L} \). As per the provisional code, alkalinity should not exceed 200 \( \text{mg/L} \) for potable water. For the fresh water alkalinity ranges between 20 - 100 \( \text{mg/L} \). Alkalinity of tested sample is within the limits specified in the standards. Hence the water sample is fit for drinking.