Objectives: Measure mineral and phenolphthalein acidity

Background:
Acids contribute to corrosiveness and influence chemical reaction rates, chemical speciation and biological processes. Acidity of water is its quantitative capacity to react with a strong base to a designated pH. The measured value may vary significantly with the end point pH used in the determination. When the chemical composition of the sample is known study mineral acids, weak acids such as carbonic and acetic and hydrolyzing salts such as iron or aluminum sulfate may contribute to the measured acidity according to the method of determination.

Mineral acidity: It is measured by titration to a pH of about 3.5, the methyl orange end point (also known as methyl orange acidity). Total acidity: Titration of a sample to the phenolphthalein end point of pH 8.3 measures mineral acidity plus acidity due to weak acids, thus this is called as total acidity (or phenolphthalein acidity). In water analysis, this test does not bear significant importance because methyl orange acidity invariably remains absent in the raw water and even phenolphthalein acidity (that too principally due to the excessive-prevalence of dissolved carbon dioxide and carbonic acids) normally does not exist to a significant extent in the raw water.

Importance: As far as water analysis is concerned, acidity test does not bear significant importance because methyl orange acidity invariably remains absent in the raw water and even phenolphthalein acidity (that too principally due to the excessive-prevalence of dissolved carbon dioxide and carbonic acids) normally does not exist to a significant extent in the raw water.

Procedure:

pH meter; Reagents: Sodium hydroxide titrant (0.02 N); Phenolphthalein Indicator; Methyl Orange Indicator

Steps:
1. Take 50 ml sample in a conical flask and add 2-3 drops of methyl orange indicator solution.
2. Fill the burette with 0.02 N NaOH solution and titrate till the colour of solution just changes to faint orange colour, indicating the end point. Record the volume of titrant consumed as V₁ in ml. Calculate the methyl orange acidity using Eq (1a):

Methyl orange acidity (or Mineral Acidity) = (V₁×1000)/(Sample volume)                      (1a)

When the 0.02 N NaOH solution, used in titration is not standardized, mineral acidity is calculated using following Eq (1b):

Methyl orange acidity= (V₁×N×50×1000)/(Sample vol.)                      (1b)
3. For phenolphthalein acidity test, add 2-3 drops of phenolphthalein indicator solution to water sample from step 2 and continue the titration till the faint pink colour develops in the solution (i.e., the end point of titration). Record the volume of titration consumed as $V_2$ (mL) and calculate total acidity or phenolphthalein acidity using Eq.(2):

$$\text{Total acidity (or Phenolphthalein Acidity)} = \frac{V_2 \times N \times 50 \times 1000}{\text{Sample vol.}}$$

(2)

Questions to Answer:
A water sample has a methyl orange acidity of 60 mg/L. Calculate the quantity of lime in mg/L of Ca(OH)$_2$ required to raise the pH to 3.7?

Reference Materials:

Experiment 2B: Alkalinity

(Methods: 4500 B. Electrometric Method; 2320 B. Titration Method)

Objective:
Using dye indicators measure phenolphthalein alkalinity and total alkalinity. Calculate hydroxide, carbonate and bicarbonate alkalinity.

Background:
The alkalinity of the water is a measure of its capacity to neutralize acids. The alkalinity of natural waters is due primarily to the salts of week acids. Bicarbonates represent the major form of alkalinity. Alkalinity can be expressed as follows:

\[
\text{Alkalinity (mol/L)} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]
\]  

Figure 1 presents the carbonate speciation diagram at different pH values. Waters rich in bicarbonates (HCO$_3^-$) have high acid neutralizing capacity (high alkalinity).

![Figure 1. Carbonate Species](image)

Alkalinity is measured by titrating a sample with acid. A titration curve of a bicarbonate containing water is presented in Figure 2.
Figure 2. Alkalinity Titration Curve

Alkalinity is significant in many uses and treatments of natural waters and wastewaters. As alkalinity of many surface waters constitute of carbonates, bicarbonate and hydroxide contents, it is assumed to be an indicator of these constituents as well. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of 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.

Procedure:

1. Collect 50 mL water sample, add 3 drops of phenolphthalein indicator, titrate the 50 mL sample with 0.02N sulfuric acid to pH 8.3 and estimate phenolphthalein alkalinity (Eq. 2a) (phenolphthalein indicator will change color, from pink to clear, at pH 8.3).

\[
\text{Phenolphthalein Alkalinity (in mg/L as CaCO}_3\text{)} = \left( A1 \times N \times 50,000 \right) / V \tag{2a}
\]

Where: \( A1 \) = volume of sulfuric acid used in mL; \( N \) = normality of acid used to titrate; \( V \) = volume of sample used in mL.

2. Use the same sample. Add 3 drops of bromcresol green indicator. Titrate the 50 mL sample with 0.02N 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 (Eq. 2b):\[
\text{Total Alkalinity (in mg/L as CaCO}_3\text{)} = \left( A2 \times N \times 50,000 \right) / V \tag{2b}
\]

Where: \( A2 \) = volume of acid used in mL starting from step 1 (i.e., A2>A1); All other parameters are defined in Eq. 2a.

(Note: If after adding phenolphthalein indicator no colour 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 CaCO$_3$) = 50,000 × 10$^{[\text{pH}-\text{pKw}]}$; pK$_{w}$ = 15 at 24°C  \hspace{1cm} (3a)
Carbonate alk. (mg/L as CaCO$_3$) = 2 × [Phenolphthalein alk.-hydroxide alk.]  \hspace{1cm} (3b)
Bicarbonate alk. (mg/L as CaCO$_3$) = Total alk.-[Carbonate alk.+ hydroxide alk.]  \hspace{1cm} (3c)

Questions to Answer:
1. Calculate the phenolphthalein and total alkalinitie s of following sample: A 50-ml sample required 5.3 ml N/50 sulfuric acid to reach the phenolphthalein end point, and total of 15.2 ml to reach the bromcresol green end point.
2. How does pH play a role in affecting alkalinitie and acidity of a given water sample?

Reference Materials:


Practice Problems (Not for submission)
1. A sample of water collected in the field had a pH of 6.8, which changed to 7.5 by the time the sample was brought to the laboratory. Give a possible explanation for this change.
2. How does carbon dioxide dissolution in lake water affect algal bloom?
3. For the following samples, calculate hydroxide, carbonate, and bicarbonate alkalinity by the procedure (Alkalinity and pH measurements). The sample size is 100 mL, N/50 sulfuric acid is used as the titrant and the water temperature is 25°C.

<table>
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<tr>
<th>Sample</th>
<th>pH</th>
<th>Total mL titrant to reach end point</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Phenolphthalein</td>
</tr>
<tr>
<td>A</td>
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</tr>
<tr>
<td>D</td>
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<tr>
<td>C</td>
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