Experiment No. 1

Determination of alkalinity of a given water sample

Apparatus Required:

1) Pipette; 2) Conical flask; 3) Burette;

4) Beaker; 5) Funnel, and 6) Stand

Chemicals Required:

1) Methyl orange
2) Phenolphthalein,
3) Standard HCl

Theory:

The alkalinity of water is due to the presence of soluble

a. hydroxides,
b. carbonates, and
c. bicarbonates

of alkali and alkaline earth metals.

With respect to the constituents causing alkalinity in natural waters, the following situation may arise.

1. hydroxides only,
2. carbonates only,
3. bicarbonates only,
4. hydroxide and carbonates,
5. carbonates and bicarbonates.

Note: The possibility of hydroxides and bicarbonates existing together is ruled out owing to the fact that they combine with each other forming the respective carbonates:

$$OH^- \quad + \quad HCO_3^- \quad \rightarrow \quad CO_3^{--} \quad + \quad H_2O$$

The type and extent of alkalinity present in the water sample is conveniently determined by titrating an aliquot of the sample with acid using phenolphthalein to detect end-point, (P), and then continuing the titration with methyl orange to another end-point, (M). The reaction-taking place may be represented by the following equations:

$$OH^- \quad + \quad H^+ \rightarrow H_2O \quad ....(1)$$

$$CO_3^{--} \quad + \quad H^+ \rightarrow HCO_3^- \quad ....(2)$$

$$HCO_3^- \quad + \quad H^+ \rightarrow H_2CO_3 \rightarrow H_2O + CO_2 \quad ..(3)$$

The volume of acid run down upto phenolphthalein* end point, (P) corresponds to the completion of reactions (1) and (2) given above while the volume of acid run down after (P) corresponds to the completion of reaction (3). The total amount of acid used from the beginning of the experiment to the end, i.e. (M) corresponds to the total alkalinity and represents the completion of reactions shown by equation (1), (2) and (3).

The results may be summarized in the following Table (1), from which the amount of hydroxides, carbonates and bicarbonates present in the water sample may be computed.

Results of titration to Phenolphthalein end point, (P) and Methyl orange end point, (M)	Hydroxide OH^-	Carbonate CO_3^{--}	Bicarbonate HCO_3^-
(P) = 0	Nil	Nil	(M)
(P) = (M)	(M)	Nil	Nil
(P) = 1/2 (M)	Nil	2(P)	Nil
(P) > 1/2 (M)	2(P)-(M)	2[(M)-(P)]	Nil
(P) < 1/2 (M)	Nil	2(P)	(M)- 2(P)

Alkalinity is generally expressed as parts per million (ppm) in terms of $CaCO_3$ or on degrees Clark.

Procedure:

Transfer 100 ml of the water sample into a conical flask, add 1 to 2 drops of phenolphthalein indicator, and titrate the sample with the standard HCl until the pink colour just persisted. Note the titre value as the phenolphthalein end-point, (P). Then add 2 to 3 drops of methyl orange indicator to the same solution and continue the titration until a sharp color change from yellow to red takes place. Note the total titer value from the beginning of the experiment as methyl orange end-point, (M).

Sample Observation:

S.No.	Volume of the water sample taken (ml)	Volume of HCl, phenolphthalein end-point, (P), ml	Vol. of HCl, methyl orange end point (M), ml
1	100	20	42
2	100	18	41
3	100	18	41

Calculation:

Now, (P) = 18 ml (M) = 41 ml and $\frac{1}{2}$ M = 21 ml

Since (P) < $\frac{1}{2}$ (M), the sample should contain only CO_3^{--} and HCO_3^- and it does not contain OH^- (vide Table 1).

Further, 2(P) should correspond with the volume of HCl with respect to CO_3^{--} and (M) -2(P) should correspond with volume of HCl with respect to HCO_3^-

Thus, volume of N/50 HCl equivalent to CO_3^{--}

= 2(P) = 2 X 18 ml. = 36 ml

and Volume of N/50 HCl equivalent HCO_3^-

= (M)-2(P) = 41 – (2 X 18) = 5 ml.

Now,

Normality of the water sample with respect to CO_3^{--} (N_2) = ?

since, $V_1N_1 = V_2N_2$

$$N_2 = \frac{V_1N_1}{V_2} = \frac{36 \times \frac{N}{50}}{100}$$

$$= 7.2 \times 10^{-3} N$$

Since, Strength = Normality X Equivalent weight (g/l)

Strength of CO_3^{--} $= 7.2 \times 10^{-3} N \times 30 = 0.216$ g/l

Strength of CO_3^{--} in terms of $CaCO_3$

$$= \text{strength of } CO_3^{--} \text{ X } \frac{\text{Equivalent weight of } CaCO_3}{\text{Equivalent weight of } CO_3}$$

$$= 0.216 \times \frac{50}{30} \text{ g/l}$$

= 0.36 g/l [∵ 1 g = 1000 mg]

= 360 mg/l [1 mg/l = 1 ppm]

= 360 ppm [14.3 ppm = 1 Clark]

= 25.17 Clark

Similarly,

Normality of water sample with respect to HCO_3^-, (N_2) = ?

since, $V_1 N_1 = V_2N_2$

$$N_2 = \frac{V_1N_1}{V_2} = \frac{5 \times \frac{N}{50}}{100}$$

$$= 10^{-3}\ N$$

Strength of HCO_3^- = $10^{-3} \times 61 = 0.061$ g/l

(Strength = Normality X Eq. Wt. of HCO_3^-)

Strength of HCO_3^- in terms of $CaCO_3$

$$= \text{strength of } HCO_3^- \text{ X } \frac{\text{Equivalent weight of } CaCO_3}{\text{Equivalent weight of } HCO_3^-}$$

$$= 0.061 \times \frac{50}{61}$$

= 0.05 g/l

= 50 mg/l

= 50 ppm

Results:

Alkalinity with respect to CO_3^{--} in terms of $CaCO_3$ = 360ppm = 25.17 Clark

Alkalinity with respect to HCO_3^- in terms of $CaCO_3$ = 50ppm = 3.5 Clark

Total alkalinity in terms of $CaCO_3$ = 410ppm = 28.67 Clark