2 Determination of Dissolved Oxygen by Winkler's Method

Aim: To estimate dissolved oxygen (DO) content in the given water sample by Winkler's method.

Principle

Dissolved oxygen (DO) determination measures the amount of dissolved (or free) oxygen present in water or wastewater. Aerobic bacteria and aquatic life such as fish need dissolved oxygen to survive. If the amount of free or DO present in the wastewater process is too low, the aerobic bacteria that normally treat the sewage will die. DO is determined by the titrimetric method developed by Winkler.

1. Dissolved molecular oxygen in water is not capable of reacting with KI, therefore an oxygen carrier such as manganese hydroxide is used. $Mn(OH)_2$ is produced by the action of KOH on $MnSO_4$.
2. $Mn(OH)_2$ so obtained reacts with dissolved molecular oxygen to form a brown precipitate of basic manganic oxide, $MnO(OH)_2$.
3. $MnO(OH)_2$ then reacts with concentrated sulphuric acid to liberate nascent oxygen.
4. Nascent oxygen results in oxidation of KI to I_2.
5. This liberated iodine is then titrated against standard sodium thiosulphate solution using starch as an indicator.
6. Thiosulphate reduces iodine to iodide ions and itself gets oxidized to tetrathionate ion. (Refer the reactions below.)

Reactions

$$2NaOH + MnSO_4 \longrightarrow Mn(OH)_2 + K_2SO_4 \quad ...(1)$$

$$2Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2 \quad ...(2)$$

$$MnO(OH)_2 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + [O] \quad ...(3)$$

$$2KI + H_2SO_4 + [O] \longrightarrow K_2SO_4 + H_2O + I_2 \quad ...(4)$$

$$I_2 + I^- \longrightarrow I_3^- \quad ...(5)$$

$$2S_2O_3^{2-} + I_3^- \longrightarrow 3I^- + S_4O_6^{2-} \quad ...(6)$$

Calculations

1000 mL of 1N $Na_2S_2O_3$ = 8 g oxygen

$\therefore$ V mL of 0.025 N EDTA = $\frac{V \times 0.025 \times 8}{1000}$ g oxygen per 100 mL water sample

= $V \times 0.025 \times 8$ mg oxygen per 100 mL water sample

= V × 0.025 × 8 × 10 mg oxygen per 1000 mL water sample

Result

The given water sample has _____ ppm of dissolved oxygen.

Precautions

1. Do not allow air to trap while sampling water during BOD analysis.
2. Dip the tip of the pipette just at the bottom of the BOD bottle and gently release the reagents.
3. Take care that the chemicals do not flow out from the bottle while shaking/swirling.
4. Observe the colour changes during the BOD reaction, if any.