Exercise no. 6

Determination of dissolved oxygen by Winkler titration

Introduction

The chemical determination of oxygen concentration in water samples is based on the method first proposed by Winkler (1888). Oxygen in the water sample oxidizes iodide ion (I^-) to iodine (I_2) quantitatively. The amount of iodine generated is then determined by titration with a standard thiosulfate ($S_2O_3^{2-}$) solution. The endpoint is determined by using starch as a visual indicator. The amount of oxygen can then be calculated from the titer: one mole of O_2 reacts with four moles of thiosulfate.

Experimental procedures

Dilute the analytical sample with distilled water in a measuring flask to the mark (100 mL) and mix completely. **Pipette** 10 mL of the solution into the conical flask, add 70 mL of deionized water, 1 mL of $MnSO_4$ solution and 2 mL of KI solution. The solution in the conical flask should be treated as 100 mL of the water sample.

Dissolved oxygen is fixed by the addition of Mn(II) under basic conditions, resulting in a brown precipitate, manganic hydroxide ($MnO(OH)_2$). When oxygen is not present in the water sample, the precipitate is white:

$$2Mn^{2+} + 4\,OH^- \leftrightarrow 2Mn(OH)_2 \quad \text{white precipitate}$$

$$2Mn(OH)_2 + O_2 \leftrightarrow 2MnO(OH)_2 \quad \text{brown precipitate}$$

Prior to analysis, acidified the sample to pH 1.0-2.5 by adding 1 mL of concentrated H_2SO_4. This causes the precipitated hydroxides to dissolve, liberating Mn(IV) ions. Mn(IV) ions oxidize previously added iodide ions to iodine:

$$2MnO(OH)_2 + 4H^+ \leftrightarrow 2\,Mn^{4+} + 4H_2O$$

$$Mn^{4+} + 2I^- \leftrightarrow Mn^{2+} + I_2$$

Then, titrate the iodine with 0.025 M thiosulfate to obtain **light yellow colour** of solution. At the end of titration, add 1-2 drops of **starch** indicator and titrate till **blue colour disappear**. During the titration, iodine is reduced to iodide and the thiosulfate is oxidized to tetrathionate:

$$I_2 + 2S_2O_3^{2-} \leftrightarrow S_4O_6^{2-} + 2I^-$$

Repeat the titration to obtain three concordant results (not differing more than 0.2 mL). Calculate the amount of dissolved oxygen presents in the sample using formula:

$$\mathbf{X = 0.2 \cdot V \cdot 10}$$

0.2 – amount of O_2 per 1 mL of 0.025 M $Na_2S_2O_3$
V – volume of thiosulfate solution [mL]