DETERMINATION OF DISSOLVED OXYGEN

The classical method for the determination of dissolved oxygen in aqueous solutions is known as the Winkler Method. In an alkaline solution, dissolved oxygen will oxidize manganese(II) to the trivalent state

$$8 \text{OH}^-(aq) + 4 \text{Mn}^{2+}(aq) + \text{O}_2(aq) + 2 \text{H}_2\text{O}(l) \Rightarrow 4 \text{Mn(OH)}_3(s)$$

Potassium iodide is also added to the solution which is oxidized by the manganic hydroxide when the solution is acidified.

$$2 \text{Mn(OH)}_3(s) + 3 \text{I}^- (aq) + 6 \text{H}^+(aq) \Rightarrow \text{I}_3^-(aq) + 3 \text{H}_2\text{O}(l) + 2 \text{Mn}^{2+}(aq)$$

The triiodide produced is then titrated with sodium thiosulfate, $\text{S}_2\text{O}_3^{2-}$.

$$2 \text{S}_2\text{O}_3^{2-}(aq) + \text{I}_3^-(aq) \Rightarrow \text{S}_4\text{O}_6^{2-}(aq) + 3 \text{I}^- (aq)$$

Therefore, for each mole of dissolved oxygen, four moles of thiosulfate are used in the titration. The convoluted set of steps is necessary to produce a fast, stoichiometric titration. Success of the method is critically dependent upon the manner in which the sample is manipulated; at all stages, every effort must be made to assure that oxygen is neither introduced to nor lost from the sample. Biological Oxygen Demand (BOD) bottles are designed to minimize the entrapment of air.

The sample should be free of any solutes that will oxidize iodide or reduce iodine. Numerous modifications have been developed to permit use of the Winkler method in the presence of such species.

In this experiment the thiosulfate solution will be standardized against triiodide generated from primary standard potassium iodate.

$$\text{KIO}_3(aq) + 8 \text{I}^-(aq) + 6\text{H}^+(aq) \Rightarrow 3\text{I}_3^-(aq) + 3\text{H}_2\text{O}(l) + \text{K}^+(aq)$$

**PROCEDURE**

**Preparation of Approximately .050 M Sodium Thiosulfate Solution.**

Boil about 1 liter of deionized water for at least 5 minutes. Cool and add about 12 g of Na$_2$S$_2$O$_3$.5H$_2$O and 0.2 g of Na$_2$CO$_3$. Stir until the solution is complete, then transfer to a clean stoppered bottle (glass or plastic). Store in the dark. (How long will this last? Find out!)

**Standardization of Thiosulfate Solution.**

Weigh by difference (to the nearest 0.1 mg) about 0.6 g samples of dried, primary standard KIO$_3$ into a small beaker. Dissolve in 75 ml of water, and add about 6 g of iodate-free KI. Transfer with several rinses to a 250 ml volumetric flask. Bring to the mark with deionized water and mix well. Use a 2.00 ml pipet to transfer an aliquot of this standard solution to conical flask. Add about 40 ml of deionized water and 10 ml of 1.0 M HCl, and titrate immediately with the thiosulfate solution until the color of the solution becomes pale yellow. Run triplicate determinations. Calculate the mean and standard deviation of your standard thiosulfate. Follow the titration using a redox electrode. (How does this electrode work? Find out!)
Dissolved Oxygen Samples.

Transfer the sample to a 300 ml BOD bottle, taking care to minimize exposure to air. (Some filling methods will be demonstrated.) Fill the bottle to overflowing. Add 1 ml of MnSO₄ solution; discharge the reagent well below the surface (some overflow will occur). Similarly, introduce 1 ml of the KI-NaOH solution. Place the stopper in the bottle; be sure that no air becomes entrapped. Invert the bottle several times to distribute the precipitate uniformly.

When the precipitate has settled leaving the supernat clear, shake again. When the precipitate has settled at least 3 cm below the stopper, introduce 1 ml of concentrated (18 M) H₂SO₄ well below the surface. (Care should be taken to avoid exposure to the overflow, as the solution is quite alkaline.) Replace the stopper and mix until the precipitate dissolves. Pipet 50 ml of the acidified sample into a 500 ml conical flask. Titrate with 0.050 M Na₂S₂O₃ until the iodine color becomes faint.

Analyze triplicate samples.

Special Solutions That You Will Need

a. KI-NaOH solution. 15 g of KI is dissolved in 25 ml of water plus 66 ml of saturated NaOH, then diluted to 100 ml.

b. Manganese(II) Sulfate. 48 g of MnSO₄.4H₂O in sufficient deionized water to make 100 ml.

Report

A full report is not necessary. Each boat group should generate a spreadsheet showing results, and calculations, and answer the questions below.

Report the concentration of dissolved oxygen in M and mg/L for sample. Compare your results to the YSI probe results. How confident are you that the two techniques produce the same result?

Comment on the various uncertainties and biases involved in this analysis. What do you think the limit of accuracy is in this experiment (that is, estimate the cumulative value of the random and determinant errors)?