Estimation of dissolved oxygen (D.O.) by redox titration

Theory

Organic matter discharged into a watercourse serves as a food source for the bacteria present there. The bacteria will break down this matter to produce less complex organic substances, and, eventually, carbon dioxide and water. The bacteria will multiply, using up the available dissolved oxygen as they do so. If the bacterial uptake of oxygen is faster than the rate at which dissolved oxygen is replaced from the atmosphere and from the action of photosynthesis, the water will become depleted in oxygen. In these anaerobic conditions, bacteria will produce offensive products such as hydrogen sulphide and ammonia. The depletion of dissolved oxygen may result in other undesirable effects such as fish kills. The level of dissolved oxygen in a water sample is therefore an indicator of the quality of the sample.

An iodine/thiosulfate titration can be used to measure the dissolved oxygen present in a water sample. Because the dissolved oxygen does not directly react with the redox reagent, an indirect procedure was developed by Winkler.

Under alkaline conditions manganese(II) sulfate produces a white precipitate of manganese(II) hydroxide:

$$1.\ \mathbf{Mn^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Mn(OH)_{2(s)}}$$

This reacts with the dissolved oxygen to produce a brown precipitate.

$$2.\ \mathbf{2Mn(OH)_{2(s)} + O_{2\,(aq)} \rightarrow 2MnO(OH)_{2(s)}}$$

Addition of concentrated H_2SO_4 enables the Mn(IV) compound to release free iodine from KI.

$$3.\ \mathbf{MnO(OH)_{2(s)} + 4H^+_{(aq)} + 2I^-_{(aq)} \rightarrow Mn^{2+}_{(aq)} + I_{2(aq)} + 3H_2O_{(l)}}$$

The free iodine is then titrated with standard sodium thiosulfate in the usual way.

$$4.\ \mathbf{I_{2(aq)} + 2S_2O_3{}^{2-}_{(aq)} \rightarrow 2I^-_{(aq)} + S_4O_6{}^{2-}_{(aq)}}$$

Overall:

$$\mathbf{1\ mole\ O_2 \rightarrow 2\ moles\ MnO(OH)_2 \rightarrow 4\ moles\ S_2O_3{}^{2-}}$$

Procedure

<u>NB</u>: Wear your safety glasses.

Rinse a 250 cm^3 reagent bottle with deionised water, shaking vigorously to wet the inside and so avoid trapped air bubbles. Completely fill the bottle under water with the sample, making sure that there are no trapped air bubbles.

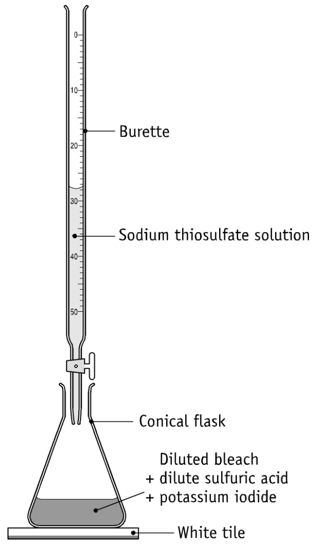
Using a dropper placed well below the surface of the water, add 1 cm^3 (approximately) each of manganese(II) sulfate solution and of alkaline potassium iodide solution to the bottle.

Stopper the bottle so that no air is trapped - a few cm^3 of solution will overflow at this point. Invert the bottle repeatedly for about a minute, and then allow the brown precipitate to settle out.

In order to dissolve the precipitate, carefully add 1 cm^3 of concentrated sulfuric acid to the bottle, by running the acid down the side of the bottle.

Restopper the bottle - avoiding trapping any air. Invert repeatedly to redissolve the precipitate. If all the precipitate has not dissolved at this point add 0.5 cm^3 of acid, invert repeatedly, and allow to stand for one minute. Continue repeating the process of inverting repeatedly followed by addition of acid until all of the precipitate has dissolved. Iodine should now be released resulting in a golden brown solution.

Wash the pipette, burette and conical flask with deionised water. Rinse the pipette with the iodine solution and the burette with the sodium thiosulfate solution.



The free iodine can now be estimated by means of the thiosulfate titration. Measure out 50 cm^3 samples into clean conical flasks and titrate each of these with 0.005 M thiosulfate solution in the usual way.

Add about 1 cm^3 starch indicator as the end point approaches (when the solution becomes pale yellow in colour). Titrate until the blue colour has just disappeared.

Record the results in the usual way taking the average of two accurate titration results, i.e. two titres within 0.1 cm^3 of each other.

Calculate the results in (i) moles of oxygen per litre (ii) grams of oxygen per litre (iii) dissolved oxygen in p.p.m.

Table of results

Copy this table into your practical report book.

Rough titre	=
Second titre	=
Third titre	=
Average of accurate titres	=
Volume of water sample	=
Molarity of thiosulfate solution	=

Specimen Results

Rough titre	= 13.3 cm^3
Second titre	= 13.0 cm^3
Third titre	= 13.0 cm^3
Average of accurate titres	= 13.0 cm^3
Volume of water sample	= 50.0 cm^3
Molarity of thiosulfate solution	= 0.005 M

Specimen Calculations

$$\mathbf{V_A \times M_A \times n_B = V_B \times M_B \times n_A}$$

$50.0 \times M_A \times 4 = 13.0 \times 0.005 \times 1$

$M_A = 13.0 \times 0.005 \times 1 / (50.0 \times 4)$ = 0.000325 M

Concentration of dissolved oxygen = 0.000325 M

= 0.00325 x 32 g/l

= 0.0104 g/l

= 10.4 p.p.m.

Student Questions

Why is the reagent $MnSO_4$ used?

Dissolved oxygen will not react completely in its absence. Iodide is susceptible to air oxidation in an acidic medium:

$$\mathbf{4I^- + 4H^+ + O_2 \rightarrow 2I_2 + 2H_2O}$$

but this is a relatively slow reaction. The use of $MnSO_4$ results in the formation of $Mn(OH)_2$, which reacts completely with dissolved oxygen.

Why is concentrated H_2SO_4 used?

To enable the Mn(IV) species to release the free iodine needed for the redox reaction.

Why must the bottles be shaken vigorously in step 5 of the procedure?

To help the dissolved oxygen to react.

Why are the bottles completely filled? To prevent additional oxygen from the air dissolving in the water. ***If the white precipitate remains on addition of manganese(II) sulfate solution and alkaline potassium iodide solution, what does this indicate about the water sample?*** There is no dissolved oxygen present. The sample appears to be heavily polluted. ***State and explain what the letters B.O.D. mean.*** Biochemical Oxygen Demand. The five day Biochemical Oxygen Demand of a water sample is the amount of dissolved oxygen taken up by bacteria in degrading oxidisable matter, measured after 5 days incubation in the dark at 20 ^{0}C.	