In this investigation you will be following a planned procedure to test the concentration of dissolved oxygen using the modified Winkler titration method.


Equipment
- gloves
- safety goggles
- DO sample bottle
- liquid waste container
- DO reagent No. 1 (manganous sulfate solution, MnO₄⁻)
- DO reagent No. 2 (alkaline potassium iodide azide: contains potassium hydroxide, KOH; potassium iodide, KI; and sodium azide, NaN₃)
- paper towel
- DO reagent No. 3 (sulfuric acid)
- 20 mL vial with hole in lid and titrator syringe
- sodium thiosulfate (Na₂S₂O₃) and syringe
- starch indicator
- distilled water

Risk assessment

<table>
<thead>
<tr>
<th>Identify</th>
<th>Sulfuric acid is a strong corrosive acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assess</td>
<td>Sulfuric acid will burn eyes and skin if splashes occur</td>
</tr>
<tr>
<td>Control</td>
<td>Always wear gloves to prevent skin contact with chemicals</td>
</tr>
<tr>
<td></td>
<td>Always wear safety goggles to protect eyes from splashes</td>
</tr>
<tr>
<td></td>
<td>Hold all tubes and bottles over the liquid waste container while adding reagents</td>
</tr>
<tr>
<td></td>
<td>Recap and return reagents to the kit after use</td>
</tr>
<tr>
<td></td>
<td>If any chemicals spill onto your clothes or yourself, wash them off immediately with water and inform your teacher</td>
</tr>
</tbody>
</table>
The Winkler method involves Mn$^{2+}$ ions reacting with the dissolved oxygen in the water to form MnO$_2$ as a brown precipitate.

$$O_2^{\text{aq}} + 2\text{Mn}^{2+}^{\text{aq}} + 4\text{OH}^-^{\text{aq}} \rightarrow 2\text{MnO}_2 + 2\text{H}_2\text{O}_l$$

This brown precipitate is dissolved by acid and then reacts with I$^-$ to form iodine.

$$\text{MnO}_2 + 4\text{H}^+^{\text{aq}} \rightarrow \text{Mn}^{4+}^{\text{aq}} + 2\text{H}_2\text{O}_l \quad (1)$$

$$\text{Mn}^{4+}^{\text{aq}} + 2\text{I}^-^{\text{aq}} \rightarrow \text{Mn}^{2+}^{\text{aq}} + \text{I}_2^{\text{aq}} \quad (2)$$

Iodine is titrated with thiosulfate ions ($\text{S}_2\text{O}_3^{2-}$) because the concentration of iodine is directly proportional to the DO concentration.

$$\text{I}_2^{\text{aq}} + 2\text{S}_2\text{O}_3^{2-}^{\text{aq}} \rightarrow 2\text{I}^-^{\text{aq}} + \text{S}_4\text{O}_6^{2-}^{\text{aq}}$$

The net equation for this chemical test is:

$$O_2^{\text{aq}} + 4\text{S}_2\text{O}_3^{2-}^{\text{aq}} + 4\text{H}^+^{\text{aq}} \rightarrow 2\text{S}_4\text{O}_6^{2-}^{\text{aq}} + 2\text{H}_2\text{O}_l$$

Starch reacts with iodine to produce a blue colour. Once the end point is reached, all of the iodine is reduced by the thiosulfate ions to iodide and the blue colour disappears.

This shows that, for each mole of thiosulfate ($\text{S}_2\text{O}_3^{2-}$) used in the titration, there was 0.25 moles of dissolved oxygen in the original sample.

**Method**

1. Hold the DO sample bottle above the liquid waste container and carefully remove the lid.
2. Add eight drops of DO reagent No. 1 (manganeseous sulfate solution) to the sample water.
   
   *Reagent bottles must be held vertically upside down for standard drops.*
3. Add eight drops of DO reagent No. 2 (alkaline potassium iodide azide) to the sample water.
4. Replace the lid on the DO sample bottle and wipe the bottle dry with paper towel.
5. Invert the DO sample bottle several times to mix the solution – brown precipitate will appear.
Dissolved oxygen

6 Stand the DO sample bottle and wait until the precipitate has settled to at least halfway down the bottle.

   *This will take five or more minutes if the water is saline.*

7 Hold the DO sample bottle over the liquid waste container and carefully remove the lid.

8 Add eight drops of DO reagent No. 3 (sulfuric acid) to the sample water.

9 Recap the DO sample bottle and wipe the bottle dry with paper towel.

10 Invert the DO sample bottle for several minutes until the precipitate has completely dissolved.

   **Important:** All brown flakes must be dissolved. If the water has a high DO level this may take several minutes. If brown flakes remain after five minutes, add four more drops of sulfuric acid and continue mixing. If brown flakes still remain, let the bottle stand to settle the precipitate, then pour off the clear coloured solution.

11 Hold the 20 mL vial over the liquid waste container and fill to the 20 mL mark with treated sample. Replace the lid on the vial.

12 Remove the sodium thiosulphate and titrator syringe from the kit.

13 Draw the plunger back halfway and insert the tip of the titrator syringe into the small hole in the top of the sodium thiosulfate bottle. Push the plunger in to expel the air into the bottle.

   *This avoids creating a vacuum in the bottle as the liquid is withdrawn.*

14 Turn the bottle and titrator syringe upside down and while supporting both, slowly pull back on the plunger until the black stopper is aligned with the zero line. If bubbles form on the black stopper, push the plunger in and redraw sodium thiosulfate.

   *This may have to be done several times to eliminate the bubbles.*

15 Turn the bottle upright and carefully remove the titrator syringe by pulling from its base. Insert the titrator syringe into the hole in the lid of the 20 mL vial.

16 Add one drop of sodium thiosulfate at a time by depressing the plunger and gently swirling.
When the solution changes to a light straw yellow colour, remove the plastic lid with the titrator syringe attached and add eight drops of starch indicator. The solution will turn deep blue.

*The starch indicator is added to make the titration end point easier to see.*

Replace the lid and titrator syringe to the 20 mL vial. Swirl to mix the solution.

Continue adding single drops of sodium thiosulfate, swirling a few times in between each drop, until one drop changes the solution from blue to clear.

Record the number of units of sodium thiosulfate used. This is equivalent to the mg/L of dissolved oxygen in the sample water.

Calculate the percentage saturation of DO using the scale on the next page and record this result.

**Important:** Occasionally, the sample may require more than 10 units of sodium thiosulfate to reach the endpoint. Before refilling the titrator syringe, rinse the tip with distilled water and dry it with paper towel. Five units of sodium thiosulfate will be more you need to finish the titration.

Remember to:
- rinse the vial and its lid twice with distilled water over the liquid waste container
- clean the titrator syringe
- return all equipment after use.

**Cleaning the titrator syringe**

a. Pour a small amount of distilled water into the small beaker.

b. Draw water into the syringe and expel into the beaker twice.

c. Dry the outside of the syringe with paper towel.

d. Rinse the beaker twice with distilled water over the liquid waste container.
Dissolved oxygen

Calculation of percentage saturation of DO

a. Plot temperature on the upper scale (water temperature °C).
b. Plot oxygen concentration on the lower scale (oxygen mg per litre).
c. Hold the ruler between the two points.
d. The point where the ruler crosses the middle scale (%) is the percentage saturation of DO.