The Winkler Titration

Measurement of Dissolved Oxygen in Water

Introduction

The Winkler method is the standard technique for the determination of dissolved oxygen in fresh and salt water. This scaled-down procedure requires reduced sample volume, reduced reagent volumes, less expense, and less time.

Concepts

- Dissolved oxygen
- Biological oxygen demand
- Water quality
- Winkler titration

Materials

Sodium thiosulfate solution, $Na_2S_2O_3 \cdot 5H_2O$, 0.0025 M
Sulfuric acid, H_2SO_4, 18 M (concentrated)
Winkler solution #1 (manganous sulfate)
Winkler solution #2 (alkaline-iodide)
Erlenmeyer flask, 125-mL
Pipets, Beral-type, thin-stem
Rubber stoppers, No. 2
Starch powder, soluble
Syringe, 10-mL
Test tube rack
Test tubes, 20 × 150 mm

*Quantities will depend on the number of samples to betested. Review the procedure to determine your requirements.

Safety Precautions

This activity requires the use of hazardous components and/or has the potential for hazardous reactions. Sulfuric acid is extremely corrosive to eyes, skin and other tissue. Winkler solution #2 contains sodium hydroxide and sodium iodide, and is also severely corrosive and strongly alkaline. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Please review current Safety Data Sheets for additional safety, handling, and disposal information.

Preparation

Prepare the starch and sodium thiosulfate solutions within a day of use. Refrigerate until use. To make the starch solution, combine 5 g of starch (soluble, potato) with a few milliliters of distilled or deionized water and mix to a uniform paste. Add boiling water up to 100 mL. Stir and continue to heat until starch is completely dissolved. Prepare the sodium thiosulfate solution by dissolving 0.62 g of $Na_2S_2O_3 \cdot 5H_2O$ (grind the large crystals in a mortar to facilitate weighing) in approximately 500 mL of boiled and cooled distilled or deionized water in a 1000-mL volumetric flask. Dilute up to the 1000 mL mark with additional preboiled water. This solution is perishable, and light and temperature sensitive.

Procedure

1. Collect water samples to be tested in the 20 × 150 mm test tubes. Fill the tubes completely, holding the tube horizontally and gently lowering it through the water surface. Stopper the tubes—some water will be displaced—taking care to minimize entrapment of air bubbles. Proceed immediately to step 2.
2. With a Beral-type pipet, add 6 drops of Winkler solution #1 (manganous sulfate solution) directly to the sample tube, holding the pipet tip as close to the sample surface as possible. With a second pipet, add 6 drops of Winkler solution #2 (alkaline-iodide solution) in the same fashion. Stopper the tube and invert several times to mix. This step fixes, or sequesters, the dissolved oxygen in the sample. Fixed samples can be held up to 48 hours before proceeding.
3. Allow the precipitate formed in step 2 to settle to at least one half the volume of the tube (approximately 10–15 minutes).

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4. Add 6–7 drops of concentrated sulfuric acid to each sample tube, stopper and invert several times to mix (the instructor may wish to perform this step). The acid solubilizes the precipitate, giving a clear, yellow-gold solution.
5. With the 25-mL graduated cylinder, transfer 20 mL from the sample tube into a 125-mL Erlenmeyer flask. (Use top solution only—not the bottom with precipitate.)
6. Fill the 10-mL syringe with the sodium thiosulfate solution and *note the starting volume*. Titrate the sample in the flask with the sodium thiosulfate solution in the syringe until the sample fades to a pale straw color.
7. Add 6 drops of starch solution to the flask and swirl to mix. The sample will turn dark purple-blue. Continue titrating with the sodium thiosulfate solution to the colorless endpoint.
8. Record the total number of milliliters of sodium thiosulfate dispensed from the syringe. This value is directly proportional to the amount of oxygen dissolved in the original sample. Milliliters (mL) of sodium thiosulfate used equals dissolved oxygen concentration in milligrams per liter (mg/L); also equivalent to parts per million (ppm).

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures, and review all federal, state and local regulations that may apply, before proceeding. Tested samples, and any unused starch and sodium thiosulfate solutions, can be disposed of by rinsing down the drain with excess water according to Flinn Suggested Disposal Method #26b.

Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):

Unifying Concepts and Processes: Grades K–12
Evidence, models, and explanation
Constancy, change, and measurement
Content Standards: Grades 5–8
Content Standard A: Science as Inquiry
Content Standard B: Physical Science, properties and changes of properties in matter
Content Standard C: Life Science, structure and function in living systems, populations and ecosystems
Content Standards: Grades 9–12
Content Standard A: Science as Inquiry
Content Standard B: Physical Science, chemical reactions
Content Standard C: Life Science, interdependence of organisms; matter, energy, and organization in living systems
Content Standard F: Science in Personal and Social Perspectives, natural resources, environmental quality, natural and human-induced hazards

Discussion

The relevant chemical reactions occurring throughout the procedure are outlined below:

$$Mn^{2+} + 2OH^- + 1/2\ O_2 \rightarrow \text{oxygen-manganese complex} + H_2O \quad (1)$$

$$\text{oxygen-manganese complex} + 4H^+ + 2I^- \rightarrow I_2 + Mn^{2+} + 2H_2O \quad (2)$$

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI \quad (3)$$

Addition of the manganous sulfate and the alkaline-iodide results in the formation of an insoluble oxygen-manganese complex (1), the precipitate in step 2. The oxygen is stable in this form for several days. Both the manganous sulfate and the alkaline-iodide are added in excess to ensure reaction with all of the oxygen. Treatment with the sulfuric acid dissolves the complex and liberates free iodine (2), imparting the distinctive yellow-gold color. The amount of free iodine is proportional to the amount of oxygen dissolved in the original sample. By titrating a measured portion of the sample against a standardized sodium thiosulfate solution (3), the amount of free iodine—and the corresponding amount of oxygen—is determined. The starch "indicator" (which forms a distinctly colored complex with the free iodine) is used to provide an unmistakable visual endpoint for the titration.

The concentration of dissolved oxygen (DO) is one of the most important indicators of the overall health of a body of water. Waters with consistently high levels of DO (> 6 mg/L) typically support the most diverse biological communities. Waters with consistently low DO levels (< 3 mg/L) may be virtually devoid of aquatic life or may harbor only a few species adapted to such conditions.

References

Bunce, N. J. *Environmental Chemistry*; Wuerz: Winnipeg, Canada, 1991; pp 118–120.

Mitchell, M. K.; Stapp, W. B. *Field Manual for Water Quality Monitoring;* 9th ed.; Thomson-Shore: Dexter, Michigan, 1995; pp 27–33.

Materials for *The Winkler Titration* are available from Flinn Scientific, Inc.

Catalog No.	Description
W0010 (W0005)	Winkler Solution #1, 100 mL, 500 mL
W0011 (W0006)	Winkler Solution #2, 100 mL, 500 mL
S0122	Starch, Potato, Soluble, 100 g
S0114	Sodium Thiosulfate, Crystal, 500 g
S0143	Sulfuric Acid, 18 M, 473 mL

Consult the Flinn Scientific website for current prices.