Determination of dissolved oxygen

B.Sc. Part-I, Practical, Lecture-2

Dissolved oxygen can be measured by several common techniques, each with advantages and disadvantages. The method described here is the Winkler titration method.

The Winkler Method is a technique used to measure dissolved oxygen in freshwater systems. Dissolved oxygen is used as an indicator of the health of a water body, where higher dissolved oxygen concentrations are correlated with high productivity and little pollution. This test is performed on-site, as delays between sample collection and testing may result in an alteration in oxygen content.

The description of this method was taken from *Standard Methods for Examination of Water and Wastewater* (APHA et al, 1995). The iodometric method can be one of the most precise and reliable procedures for DO analysis. This is a titration-based method based on the reaction of DO with divalent manganese (Mn^{++}) ions. Briefly, after adding a known amount of dissolved divalent manganese ions and iodide to a known volume of sample, the pH is increased by adding base and the bottle is then stoppered. An insoluble precipitate of manganous hydroxide forms. Dissolved oxygen present in the sample oxidizes an equivalent amount of the manganous hydroxide precipitate, forming chemically different hydroxides. The sample is next acidified, which causes the precipitate to dissolve, releasing the iodide originally consumed in the solution. The amount of iodine released is then measured by titration with a standard solution of thiosulfate ($Na_2S_2O_3$) and a starch indicator. The solution is blue as long as I_2 is present. When all of the I_2 has been removed from solution by thiosulfate, the solution clears. The volume of thiosulfate used to clear the solution is then used to calculate the concentration of DO in the sample (1 mL of 0.025M $Na_2S_2O_3$ = 1 mg-DO/L for a 200 mL sample). The DO concentration can also be determined directly using an absorption spectrophotometer.

Methodology

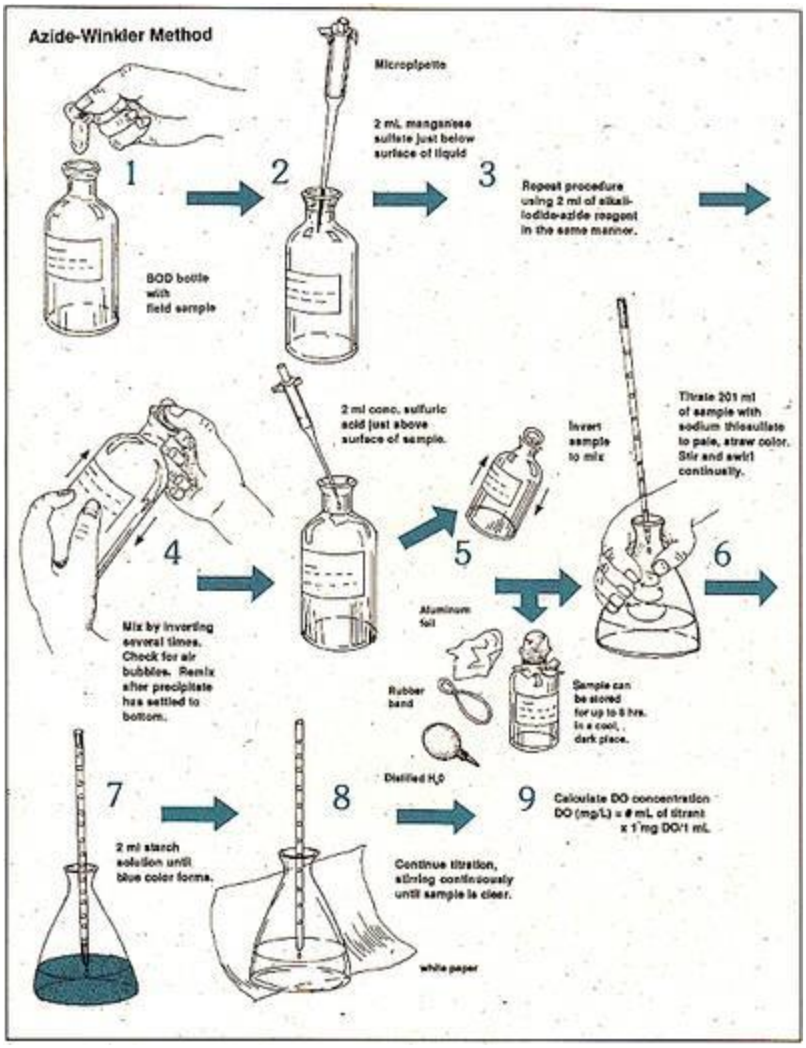
The Winkler Method uses titration to determine dissolved oxygen in the water sample. A sample bottle is filled completely with water (no air is left to skew the results). The dissolved oxygen in the sample is then "fixed" by adding a series of reagents that form an acid compound that is then titrated with a neutralizing compound that results in a colour change. The point of colour change is called the "endpoint," which coincides with the dissolved oxygen concentration in the sample. Dissolved oxygen analysis is best done in the field, as the sample will be less altered by atmospheric equilibration.

Applications

Dissolved oxygen analysis can be used to determine:

- the health or cleanliness of a lake or stream,
- the amount and type of biomass a freshwater system can support,
- the amount of decomposition occurring in the lake or stream.

Sample Collection, Preparation, Analytical Protocols, and Concerns



Dissolved oxygen should be measured as quickly and carefully as possible. Ideally, samples should be measured in the field immediately after collection.

Reagent List:

- 2ml Manganese sulphate
- 2ml alkali-iodide-azide
- 2ml concentrated sulfuric acid

- 2ml starch solution
- Sodium thiosulfate

Procedure:

1. Carefully fill a 300-mL glass Biological Oxygen Demand (BOD) stoppered bottle brim-full with sample water.
2. Immediately add 2mL of manganese sulphate to the collection bottle by inserting the calibrated pipette just below the surface of the liquid. (If the reagent is added above the sample surface, you will introduce oxygen into the sample.) Squeeze the pipette slowly so no bubbles are introduced via the pipette.
3. Add 2 mL of alkali-iodide-azide reagent in the same manner.
4. Stopper the bottle with care to be sure no air is introduced. Mix the sample by inverting several times. Check for air bubbles; discard the sample and start over if any are seen. If oxygen is present, a brownish-orange cloud of precipitate or floc will appear. When this floc has settled to the bottom, mix the sample by turning it upside down several times and let it settle again.
5. Add 2 mL of concentrated sulfuric acid via a pipette held just above the surface of the sample. Carefully stopper and invert several times to dissolve the floc. At this point, the sample is "fixed" and can be stored for up to 8 hours if kept in a cool, dark place. As an added precaution, squirt distilled water along the stopper, and cap the bottle with aluminium foil and a rubber band during the storage period.
6. In a glass flask, titrate 201 mL of the sample with sodium thiosulfate to a pale straw colour. Titrate by slowly dropping titrant solution from a calibrated pipette into the flask and continually stirring or swirling the sample water.
7. Add 2 mL of starch solution so a blue colour form.
8. Continue slowly titrating until the sample turns clear. As this experiment reaches the endpoint, it will take only one drop of the titrant to eliminate the blue colour. Be especially careful that each drop is fully mixed into the sample before adding the next. It is sometimes helpful to hold the flask up to a white sheet of paper to check for absence of the blue colour.
9. The concentration of dissolved oxygen in the sample is equivalent to the number of millilitres of titrant used. Each mL of sodium thiosulfate added in steps 6 and 8 equals 1 mg/L dissolved oxygen.

Results Analysis

The total number of millilitres of titrant used in steps 6-8 equals the total dissolved oxygen in the sample in mg/L. Oxygen saturation is temperature dependent - gas is more soluble in cold waters, hence cold waters generally have higher dissolved oxygen concentrations. Dissolved oxygen also depends on salinity and elevation, or partial pressure.

Advantages

1. Can be very accurate and precise.
2. Relatively inexpensive (only requiring titration burettes, sample bottles, and chemicals)
3. Available in kits from several manufacturers.

Disadvantages

1. Cannot monitor DO instantaneously or continuously.
2. More time consuming than membrane electrode methods.
3. Nitrite, iron (ferrous and ferric), suspended solids, and colour in the sample can interfere with accurate measurement. Modifications to the method can be made to remove these interferences.