

7.01

**STANDARD OPERATION PROCEDURES  
FOR MEASURING DISSOLVED OXYGEN  
BY THE "WINKLER-AZIDE" METHOD.**

**Summary**

Measurements made using the "Winkler-Azide" method are considered the most accurate measurement of dissolved oxygen. The "Winkler-Azide" method can be used for making direct measurements of dissolved oxygen in surface waters, field calibrating a dissolved oxygen meter, and performing regularly scheduled dissolved oxygen meter calibrations. The following are the procedures for measuring dissolved oxygen by the "Winkler-Azide method. A detailed description of the method can be found in Standard Methods, (17th Edition, APHA, 1989).

**Interferences**

The most common interferences to the "Winkler-Azide" method are oxidizing and reducing agents, nitrate ion, ferrous iron, and organic matter.

Care should be taken when collecting the sample and when filling the BOD bottle so as to not introduce air bubbles into the sample.

**Equipment and Supplies**

- 300 ml BOD bottles
- 300 ml manganous sulfate solution
- 300 ml alkaline-iodide-azide reagent
- Concentrated sulfuric acid
- Graduated cylinder capable of measuring 203 ml
- Titration equipment capable of measuring to 0.1 ml.
- 0.025 M sodium thiosulfate solution.
- Starch indicator solution.
- Kemmerer or Van Dorn type sampler.

**Procedure**

1. Obtain a sample by completely filling a 300 ml BOD bottle. The bottle is filled slowly taking care to exclude air bubbles. Note: When measuring dissolved oxygen for calibration purposes two samples should be collected at the same time and place. The results of the two should agree within +/- 0.2 mg/l. If not, repeat the procedure.
2. Insert the glass toper to remove excess water trapped in the neck of the bottle.
3. Add 2 ml of manganous sulfate.

4. Add 2 ml of alkaline iodide-azide
5. Stopper the bottle, taking care to exclude air bubbles.
6. Mix well by inverting and righting the bottle rapidly for 1 minute at which time a flocculent will have form.
7. Let the flocculent settle until approximately 1/3 of the bottle has cleared, then mix again.
8. Let the flocculent settle until approximately 2/3 of the bottle has cleared.
9. Add 2 ml sulfuric acid, stopper, and mix. Note: Take care when adding sulfuric acid as any spillage can cause severe burns. If any acid is spilled it should be flushed immediately with water.
10. At this point the oxygen within the sample is fixed and the sample may be stored in the dark for up to 8 hours.
11. Using the graduated cylinder, transfer 203 ml of the sample to the titration vessel.
12. While gently swirling sample, titrate with the sodium thiosulfate solution to a pale straw color.
13. Add 2 ml starch indicator solution. Sample will turn blue.
14. Continue to titrate and swirl the sample until the first disappearance of blue color.
15. Record to nearest 0.1 ml the volume of titrant used as mg/l dissolved oxygen in the sample.