Oxygen, Dissolved

DOC316.53.01161

Azide Modification of Winkler Method[1, 2]

Method 8229

1 to more than 10 mg/L

Buret Titration

Scope and application: For water, wastewater and seawater.

[1] USEPA approved.
[2] Adapted from *Standard Methods for the Examination of Water and Wastewater*, Standard Method 4500 O C.

Test preparation

Before starting

As an alternative to the powder pillows, use standard APHA solutions for dissolved oxygen. Use 1 mL of Manganous Sulfate Solution, 1 mL of Alkaline Iodide-Azide Reagent and 1 mL of Sulfuric Acid (concentrated) as an alternative to the powder pillows. Add the solutions below the surface of the liquid.
The optional TitraStir Titration Stand can hold the buret and stir the sample.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Description	Quantity
BOD bottle, 300 mL	1
Alkaline Iodide-Azide Reagent Powder Pillow	1
Manganous Sulfate Powder Pillow	1
Sulfamic Acid Powder Pillow	1
Sodium Thiosulfate Standard Solution (titrant), 0.025 N	varies
Starch Indicator Solution	varies
Buret, Class A, 25 mL	1
Graduated cylinder, 250 mL	1
Funnel, micro	1
Support stand with buret clamp	1
Water, deionized	varies

Refer to Consumables and replacement items on page 4 for order information.

Sample collection

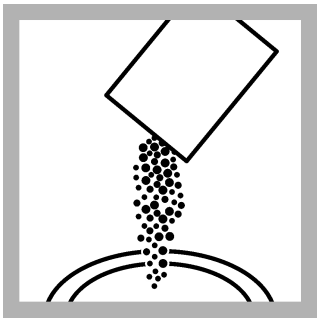
Good sample collection and handling techniques are important to get correct results. The dissolved oxygen content of the sample can change with depth, turbulence, temperature, sludge deposits, light, microbial action, mixing, travel time and other factors. A single dissolved oxygen test frequently is not an accurate reflection of the overall condition of a body of water. Several samples taken at different times, locations and depths are recommended for most reliable results.

- Collect samples in clean BOD Bottles.

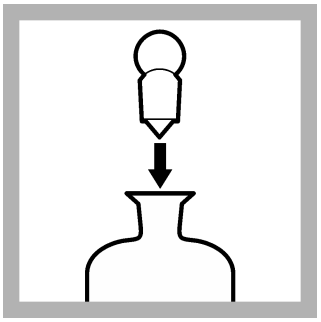
- If prompt analysis is not possible, do steps 1 through 4 of the procedure and keep the samples protected from light at 10 to 20 °C (50 to 68 °F).
- Pour a small quantity of water into the flared lip area of the stopper to seal the bottle.
- Push a BOD bottle cap on the flared lip.
- Keep samples for a maximum of 8 hours. For analysis start with step 5.

Test procedure

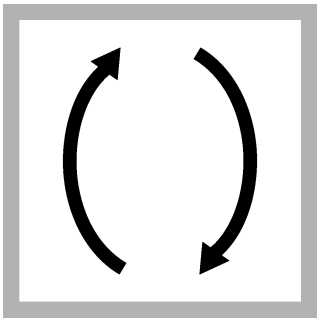
1. Collect a water sample in a clean 300-mL BOD bottle. Let the sample overflow the bottle for 2 or 3 minutes to remove trapped air bubbles and to make sure that a representative sample is collected.



2. Add the contents of one Manganous Sulfate Powder Pillow and one Alkaline Iodide-Azide Reagent Powder Pillow to the sample.

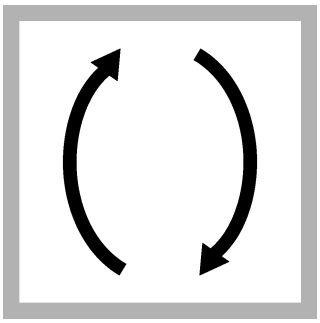


3. Immediately put the stopper in the bottle. Make sure that no air is inside the bottle.

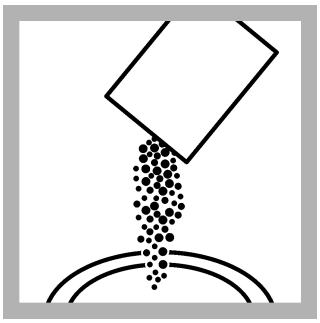


4. Invert the bottle at least 5 times to mix.
A flocculent precipitate forms. The floc is orange/brown if oxygen is in the sample or white if there is no oxygen.

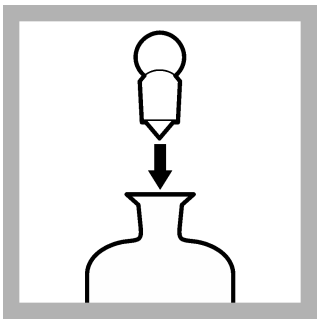
The floc forms slowly in salt water (approximately 5 minutes more are necessary). When the floc formation is complete, proceed to next step.



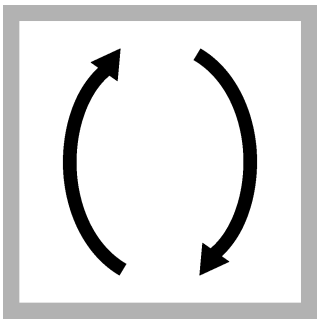
5. Again, invert the bottle at least 5 times to mix.
Wait until the top half of the solution is clear and the floc collects at the bottom to make sure that the reaction of the sample and reagents is complete. Some suspended floc will have no effect on accuracy.



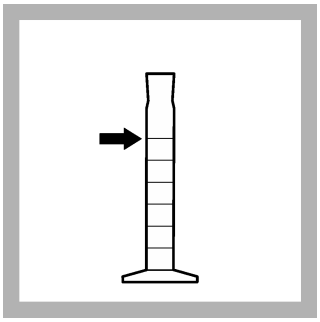
6. Remove the stopper and add the contents of one Sulfamic Acid Powder Pillow to the sample.



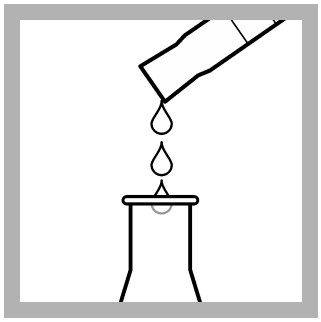
7. Immediately put the stopper in the bottle. Make sure that no air is inside the bottle.



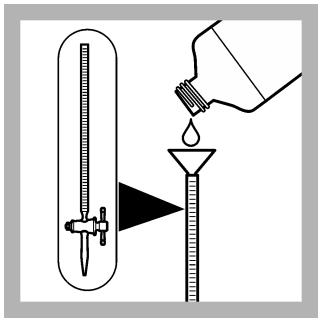
8. Invert the bottle at least 5 times to mix.
The floc dissolves and a yellow color develops if oxygen is in the sample.



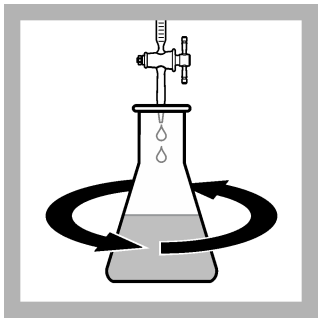
9. Pour the prepared sample into a 250-mL graduated cylinder to the 200-mL mark.



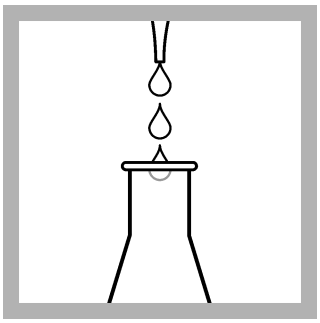
10. Pour the contents of the graduated cylinder into a clean, 250-mL Erlenmeyer flask.



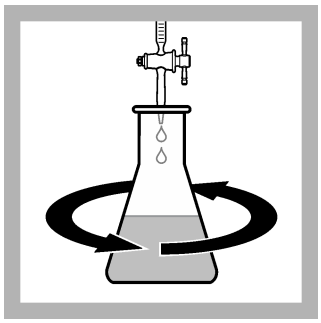
11. Fill a 25-mL buret to the zero mark with 0.025 N Sodium Thiosulfate Standard Solution.



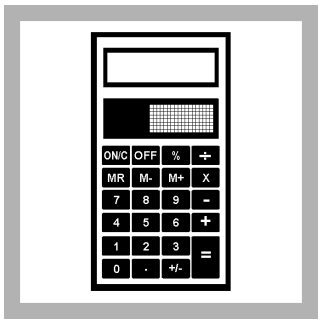
12. Put the flask under the buret. Swirl the flask. Add titrant until the color changes yellow to a pale yellow.



13. Add 1 mL of Starch Indicator Solution.
A dark blue color develops.



14. Put the flask under the buret. Swirl the flask. Add titrant until the color changes from a dark blue to a colorless end point.



15. Calculate the concentration.
mL of titrant = mg/L DO

Interferences

Nitrite interference is removed by the azide in the reagents. Other reducing or oxidizing substances may interfere. If these are in the sample, use an alternative method, such as the High Range Dissolved Oxygen Method (colorimetric, Method 8166) or a dissolved oxygen electrode.

Prepare activated sludge samples

Prepare activated sludge samples for the test as follows:

1. Add 10 mL of Copper Sulfate-Sulfamic Acid Inhibitor Solution to a clean, 1000-mL graduated cylinder.
2. Use a tube to fill the cylinder with sample. Put the end of the tube near the bottom of the cylinder. Let approximately 200 mL of sample flow over the cylinder.
3. Swirl the cylinder to mix the contents. Let the suspended solids go to the bottom of the cylinder.
4. Use a siphon tube to collect the transparent top layer in a 300-mL BOD bottle. Put the end of the tube near the bottom of the BOD bottle. When the water flows over the BOD bottle, remove the tube. Make sure that no air bubbles are in the bottle.
5. Start at step 2 of the test procedure.

Accuracy check

Standard solution method

Use the standard solution method to validate the test procedure and the concentration of the titrant.

Items to collect:

- Iodate-Iodide Standard Solution, 0.00125 N (equivalent to 10 mg/L as O_2)

1. Add 200 mL of 0.00125 N Iodate-Iodide Standard Solution to a 250-mL Erlenmeyer flask.
2. Add one Sulfamic Acid Powder Pillow to the bottle.
3. Start at step 12 of the test procedure. Titrate the prepared standard solution to the endpoint. Record the mL of titrant added in step 14.
4. Compare the actual result to the correct result. The correct result for this titration is 10.0 mL of titrant. If more than 10.5 mL of titrant was used, discard the titrant. Get new titrant.

Summary of method

The Azide Modification of the Winkler Method is the standard test for dissolved oxygen. In the analysis, manganous ion reacts with the dissolved oxygen in the alkaline solution to form a manganese (IV) oxide hydroxide flocculent. Then, Azide is added to suppress interference from nitrite, which would react with the iodide. Then, the solution is acidified and the manganese (IV) floc is decreased by iodide to make free iodine as I^{3-} in proportion to the oxygen concentration. Then, the liberated iodine is titrated to the starch-iodide end point.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Alkaline Iodide-Azide Powder Pillows	1 pillow	50/pkg	107266
Manganous Sulfate Powder Pillows	1 pillow	50/pkg	107166
Sodium Thiosulfate Standard Solution, 0.025 N	varies	1 L	2409353
Starch Indicator Solution	1 mL	100 mL MDB[1]	34932
Sulfamic Acid Powder Pillows	1 pillow	50/pkg	2076266

Required apparatus

Description	Quantity/test	Unit	Item no.
Bottle, with stopper, BOD, 300-mL	1	each	62100
Buret clamp, double	1	each	32800
Buret, Class A, 25 mL	1	each	2636540
Support stand	1	each	56300
Funnel, micro	1	each	2584335
Cylinder, graduated, 250 mL	1	each	50846
Flask, Erlenmeyer, 250 mL	1	each	50546

Recommended standards

Description	Unit	Item no.
Iodate-Iodide Standard Solution, 0.00125 N	500 mL	40149

[1] MDB is Marked Dropper Bottle

Optional reagents and apparatus

Description	Unit	Item no.
APHA reagents:	—	—
Alkaline Iodide-Azide Reagent Solution	500 mL	27749
Manganous Sulfate Solution	500 mL	27549
Sodium Thiosulfate Standard Solution, 0.025 N	1 L	35253
Sulfuric Acid, ACS	500 mL	97949
Cap, BOD Bottle Snap-over	6/pkg	241906
BOD Bottle, serialized (#1–24), 300 mL	24/pkg	2898700
Copper Sulfate-Sulfamic Acid Inhibitor Solution	100 mL	35732
Copper Sulfate-Sulfamic Acid Inhibitor Solution	500 mL	35749
Stir bar, octagonal	each	2095352
TitraStir® Titration Stand, 115 VAC	each	1940000
TitraStir® Titration Stand, 230 VAC	each	1940010

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