

METHOD #: 360.1 Approved for NPDES (Issued 1971)
TITLE: Oxygen, Dissolved (Membrane Electrode)
ANALYTE: CAS # O Oxygen 7782-44-7
INSTRUMENTATION: Probe
STORET No. 00299

1.0 Scope and Application

- 1.1 The probe method for dissolved oxygen is recommended for those samples containing materials which interfere with the modified Winkler procedure such as sulfite, thiosulfate, polythionate, mercaptans, free chlorine or hypochlorite, organic substances readily hydrolyzed in alkaline solutions, free iodine, intense color or turbidity and biological flocs.
- 1.2 The probe method is recommended as a substitute for the modified Winkler procedure in monitoring of streams, lakes, outfalls, etc., where it is desired to obtain a continuous record of the dissolved oxygen content of the water under observation.
- 1.3 The probe method may be used as a substitute for the modified Winkler procedure in BOD determinations.
- 1.4 The probe method may be used under any circumstances as a substitute for the modified Winkler procedure provided that the probe itself is standardized against the Winkler method on samples free of interfering materials.
- 1.5 The electronic readout meter for the output from dissolved oxygen probes is normally calibrated in convenient scale (0 to 10, 0 to 15, 0 to 20 mg/L for example) with a sensitivity of approximately 0.05 mg/L.

2.0 Summary of Method

- 2.1 The most common instrumental probes for determination of dissolved oxygen in water are dependent upon electrochemical reactions. Under steady-state conditions, the current or potential can be correlated with DO concentrations. Interfacial dynamics at the probe-sample interface are a factor in probe response and a significant degree of interfacial turbulence is necessary. For precision performance, turbulence should be constant.

3.0 Sample Handling and Preservation

- 3.1 See 4.1, 4.2, 4.3, 4.4 under Modified Winkler Method (360.2).

4.0 Interferences

- 4.1 Dissolved organic materials are not known to interfere in the output from dissolved oxygen probes.
- 4.2 Dissolved inorganic salts are a factor in the performance of dissolved oxygen probe.
 - 4.2.1 Probes with membranes respond to partial pressure of oxygen which in turn is a function of dissolved inorganic salts. Conversion factors for

seawater and brackish waters may be calculated from dissolved oxygen saturation versus salinity data. Conversion factors for specific inorganic salts may be developed experimentally. Broad variations in the kinds and concentrations of salts in samples can make the use of a membrane probe difficult.

- 4.3 Reactive compounds can interfere with the output or the performance of dissolved oxygen probes.
 - 4.3.1 Reactive gases which pass through the membrane probes may interfere. For example, chlorine will depolarize the cathode and cause a high probe-output. Long-term exposures to chlorine will coat the anode with the chloride of the anode metal and eventually desensitize the probe. Alkaline samples in which free chlorine does not exist will not interfere. Hydrogen sulfide will interfere with membrane probes if the applied potential is greater than the half-wave potential of the sulfide ion. If the applied potential is less than the half-wave potential, an interfering reaction will not occur, but coating of the anode with the sulfide of the anode metal can take place.
 - 4.4 Dissolved oxygen probes are temperature sensitive, and temperature compensation is normally provided by the manufacturer. Membrane probes have a temperature coefficient of 4 to 6 percent/°C dependent upon the membrane employed.
- 5.0 Apparatus
- 5.1 No specific probe or accessory is especially recommended as superior. However, probes which have been evaluated or are in use and found to be reliable are the Weston & Stack DO Analyzer Model 30, the Yellow Springs Instrument (YSI) Model 54, and the Beckman Fieldlab Oxygen Analyzer.
- 6.0 Calibration: Follow manufacturer instructions.
- 7.0 Procedure: Follow manufacturer instructions.
- 8.0 Calculation Follow manufacturer instructions.
- 9.0 Precision and Accuracy: Manufacturer's specification claim 0.1 mg/L repeatability with $\pm 1\%$ accuracy.

Bibliography

- 1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 450, Method 422F (1975).