Hach Method 10360
Luminescence Measurement of Dissolved Oxygen in Water and Wastewater
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1.0 Scope and Application

1.1 This method is for the determination of dissolved oxygen (DO) in surface and ground water, and municipal and industrial wastewater.
1.2 The method may be used as a replacement for the modified Winkler and membrane electrode procedures for the measurement of DO in wastewater treatment processes such as aeration and biological nutrient basins, effluent outfalls, receiving water, and in Biochemical Oxygen Demand (BOD) determinations where it is desired to perform nondestructive DO measurements.
1.3 The method is for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act.
1.4 This method is capable of measuring DO in the range of 0.20 to 20 mg/L.
1.5 For this method, the Method Detection Limit (MDL; 40 CFR 136, Appendix B) has been determined as 0.05 mg/L and the Minimum Level (ML; Reference 15.4) has been set at 0.20 mg/L.

2.0 Summary of Method

2.1 This luminescence-based sensor procedure measures the light emission characteristics from a luminescence-based reaction that takes place at the sensor-water interface. A light emitting diode (LED) provides incident light required to excite the luminophore substrate. In the presence of dissolved oxygen the reaction is suppressed. The resulting dynamic lifetime of the excited luminophore is evaluated and equated to DO concentration.

3.0 Interferences

3.1 There are no known interferences at normal wastewater concentrations that interfere with DO detection and quantification using this method.

4.0 Safety

4.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of any chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in References 15.5-15.6.

5.0 Equipment

Note: *Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

5.1 Luminescent dissolved oxygen meter and sensor (Hach Company LDO®, Hydrolab LDO®, or equivalent).
5.1 BOD bottle 300-mL

5.2 Magnetic Stirring plate (optional)
5.3 Magnetic stirring device (optional)

6.0 Standards

6.1 Initial Calibration – add approximately j inch of reagent water to a clean BOD bottle and stopper.
6.1.1 Shake vigorously for ~ 30 seconds.
6.1.2 Allow 30 minutes for the BOD bottle and its contents to equilibrate to room temperature.
6.1.3 The stopper may now be removed from the BOD bottle and the probe inserted for calibration purposes.
6.2 Calibration Verification, Initial Precision and Recovery, and On-going Precision and Recovery, -Add approximately 1500 mL of organic-free water to a 2-L beaker.
6.2.1 Allow the water to equilibrate to room temperature (± 2° C).
6.2.2 Using a steady stream of air (≈ 10 – 40 mL per minute) aerate the water for a minimum of 30 minutes.
6.2.3 At the completion of aeration, let water re-equilibrate to room temperature (± 2° C) for 30 minutes and note the barometric pressure of the laboratory during preparation.
6.2.4 Transfer the aerated water to a BOD bottle until overflowing and stopper.
6.2.5 Calculate the theoretical dissolved oxygen concentration using a dissolved oxygen table such as Hitchman (1978).
6.3 Method Detection Limit – Preparing dissolved oxygen reference water at concentrations other than air-saturated water requires specialized equipment and expertise not generally available to routine analysis laboratories. It is recommended that these samples be obtained through a commercial source.
6.3.1 Using a NIST traceable source of oxygen and nitrogen, saturate reagent water to a desirable DO concentration.
6.3.2 Collect the prepared water in 300-mL BOD bottles and stopper.

7.0 Sample Collection Preservation and Storage

7.1 See Title 40 of the Code of Federal Regulations Part 136.3, Table II (Section 15.3) for information regarding required sample collection containers, preservation techniques and holding times,

8.0 Quality Control

8.1 It is recommended that each laboratory that uses this method be required to operate a formal quality assurance program (Reference 15.1). The minimum requirements of this program consist of an initial demonstration of laboratory capability and ongoing analyses of laboratory prepared water standards as a test of continued performance to assess accuracy and precision. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.
8.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.
8.1.2 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision and recovery sample that the analysis system is in control. These procedures are described in Sections 8.3 and 8.4, respectively.
8.1.3 Accompanying QC for the determination of DO is required per analytical batch. An analytical batch is a set of samples processed during a contiguous 8-hour period. Each analytical batch must be accompanied by a calibration verification and ongoing precision and recovery sample, resulting in a minimum of three analyses (1 CV, 1 sample, and 1 OPR).
8.2 Initial demonstration of laboratory capability.

8.2.1 Method Detection Limit (MDL) – The MDL and ML for DO is not a requirement in Method 10360. However, its demonstration is recommended as a part of the laboratory's overall QC program.
8.2.2 An achieved MDL and ML less than or equal to the MDL and ML in Table 2 is recommended prior to the practice of this method. The ML is established by multiplying the MDL by 3.18 and rounding to the number nearest to (1, 2, or 5) x 10^n, where n is a positive or negative integer.
8.2.3 Initial precision and recovery (IPR) - To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:
8.2.3.1 Prepare and measure four samples of the IPR standard (Section 6.2) according to the procedure beginning in Section 10.
8.2.3.2 Using the results of the set of four analyses, compute the average percent recovery (X) and the standard deviation of the percent recovery (s) for DO. Use the following equation for calculation of the standard deviation of the percent recovery:

$$s = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}}$$

,

where:
n = Number of samples
x = Concentration in each sample

8.2.3.3 Compare s and X with the corresponding limits for initial precision and recovery in Table 1. If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the range for recovery, system performance is unacceptable. In this event correct the problem, and repeat the test.
8.3 Calibration verification –DO calibration is performed immediately prior to sample analysis.
8.3.1 Prepare a calibration verification standard (Section 6.2) with each analytical batch. Analyze according to the procedure beginning in Section 10 and compare the recovery results to those in Table 3. Actual average recovery and standard deviation should be within the specifications in Table 1.
8.4 Ongoing calibration and precision and recovery - To demonstrate that the analysis system is in control, and acceptable precision and accuracy is being maintained with each analytical batch, the analyst shall perform the following operations:
8.4.1 Prepare a precision and recovery standard (Section 6.2) with each analytical batch according to the procedure beginning in Section 10.
8.4.2 At the end of each analytical batch of samples, analyze a precision and recovery standard and compare the concentration recovery with the limits for ongoing precision and recovery in Table 1. If the recovery is in the range specified, measurement process is in control and analysis of samples may proceed. If, however, the recovery is not in the specified range, the analytical process is not in control. In this event, correct the problem, recalibrate and verify the calibration and reanalyze analytical batch, repeating the ongoing precision and recovery test.
8.4.3 The laboratory should add results that pass the specification in Table 1 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of

laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of the percent recovery (sr). Express the accuracy as a recovery interval from R 2sr to R + 2sr. For example, if R = 95% and sr = 5%, the accuracy is 85% to 105%.

8.5 Depending upon specific program requirements, field replicates may be required to assess the precision and accuracy of the sampling and sample transporting techniques.

9.0 Calibration and Standardization

9.1 Because of the possible diversity of future LDO instrument hardware, no detailed operating conditions are provided. The analyst is advised to follow the recommended operating conditions provided by the manufacturer. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions satisfy the analytical requirements of this method and to maintain quality control data verifying instrument performance and analytical results.

9.2 Water-saturated air (Section 6.1) is used for instrument calibration.

9.3 Calibration verification (Section 8.3) is performed with air-saturated water prior to any DO sample measurements to the method specifications.

10.0 Procedure

10.1 Instrument Setup and Sample Analysis – follow the instrument manufacturer's instructions for instrument setup and sample analysis.

11.0 Data Analysis and Calculations

11.1 Follow instrument manufacturer's instructions.

12.0 Method Performance Acceptance Criterion	**Section**	**Limit**
Method Detection Limit	8.2.2	0.05 mg/L
Minimum Level	8.2.2	0.20 mg/L
Initial Accuracy Initial Precision	8.2.3 8.2.3	95% to 105% 2.1%
Ongoing Accuracy Ongoing Precision	8.2.3 8.2.3	95% to 105% 2.1%

13.0 Pollution Prevention

13.1 There are no standards or reagents used in this method that pose any threat to the environment.

14.0 Waste Management

14.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect air, water, and land by minimizing and control all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

14.2 For further information on waste management, consult "The Waste Management manual for Laboratory Personnel", and Less is Better: Laboratory Chemical Management for Waste Reduction", both available from the American Society's Department of Government relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.0 References

15.1 Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA, EMSL-CI, Cincinnati, OH 45268, EPA-600-4-79-019, March 1979.

15.2 Hitchmen, M.L. (1978) *Chemical analysis*. Vol. 49. *Measurement of Dissolved Oxygen*. Wiley and sons, New York.

15.3 Title 40, Code of Federal Regulations (40 CFR), Part 136.

15.4 Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water@ (EPA-821-B-98-003, March 1999).

15.5 "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976)

15.6 "Safety in Academic Chemistry Laboratories," American Chemical Society, Committee on Chemical Safety, 3rd Edition, 1979.