Dissolved Oxygen Measurement

Hach LDO® Technology

Comparison to Other Methods, Analytical Performance, and EPA Approval Status

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Hach LDO® Regulatory Approval

ASTM Method D888-05 Published
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USEPA Proposed Method Update Rule
August 6, 2010


Method Interim Approval from USEPA and Specific Approval for Hach Method 10360
January 3, 2006 and July 26, 2006

USEPA is proposing to add ASTM D888-09 Standard Test Method for Dissolved Oxygen in Water. This method determines dissolved oxygen concentrations in water using the titrimetric (Part A), polarographic (Part B) and luminescence-based (Part C) detection methods. This standard test method is applicable to the determination of dissolved oxygen between 0.05-20 ppm in influent, effluent or ambient water testing. ASTM recently updated Part C of this method to include a detailed description of the technology and to update calibration procedures to include a two-point calibration and an air saturated water calibration in addition to a water saturated air calibration. This method may be used for Biological Oxygen Demand (BOD) and Carbonaceous Oxygen Demand (CBOD).

Scheduled to be published in the US CFR by Q2/11
Hach LDO® Approval Status

Hach has request forms available for your region at [www.Hach.com](http://www.Hach.com) and we can walk you through the process.
DO Measurement Technologies

• Winkler Titration (US EPA Method 360.2)
  – Chemical reaction with DO in solution followed by a titration to endpoint

• Electrochemical (US EPA Method 360.1)
  – Electrochemical reaction of DO in an electrochemical cell causing a current or voltage which is measured by a sensitive amp/volt meter
  – Galvanic and polarographic are the common e-chem systems

• Luminescent (Proposed US EPA Method 360.3)
  – A luminescent molecule/substrate is “quenched” by oxygen, depending on the concentration of oxygen more or less “quenching” occurs. The measurement is made by observing the response (lifetime or intensity) of the luminophore at selected wavelengths of light
Galvanic DO Measurement

- Two electrodes of dissimilar metals are immersed in a filling solution; a spontaneous reaction occurs between the two metals.
- Oxygen enters the cell through a membrane and is reduced to hydroxide at the cathode.
- A current is then generated from the anode to the cathode proportional to the amount of oxygen in the sample.

\[ \text{Fe}^{2+} + 2\text{e}^- + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{OH}^- \]
Polarographic DO Measurement

- A constant polarizing voltage is applied across the electrodes.
  - As oxygen permeates the membrane, it is reduced at the cathode.
  - The resulting current flow from the anode to the cathode is directly proportional to the dissolved oxygen content in the electrolyte.
Issues with Electrochemistry

- **Maintenance of measurement system**
  - Membrane
  - Electrolyte

- **Contamination (a.k.a. “poisoning”) of electrodes**

- **Calibration frequency**
  - The electrochemical system itself changes as it is consumed during the measurement
How Does HachLDO® Work?

- A sensor is coated with a luminescent material.
- Blue light from an LED strikes the luminescent chemical on the sensor.
- The luminescent chemical instantly becomes excited.
How Does HachLDO® Work?

- As the excited chemical relaxes, it releases red light.
- The red light is detected by a photo diode.
- The time it takes (lifetime) for the chemical to return to a relaxed state is measured.
How Does HachLDO® Work?

- When oxygen contacts the luminescent chemical, the intensity of the red light decreases.
- The amount of time it takes for the material to relax is reduced.
How Does HachLDO® Work?

- The intensity of the red light is **not** what’s being measured.
- What’s being measured is the time it takes after excitation for red light to be given off.
  - **Lifetime of luminescence**
How Does HachLDO® Work?

- A red LED is also present in the probe.
- Between flashes of the blue LED, a red LED of known intensity, is flashed on the sensor.
- The red LED acts as an internal standard (or reference) for a comparison to the red light given off by the luminescent chemical.
Why is this a Big Deal?

• **Reduced Maintenance**
  - No membrane to replace
    - No more stretching of Teflon and worrying about air bubbles
    - No more punctured membranes
  - No electrolyte to foul or poison
    - No H₂S poisoning of the electrolyte
  - No anode or cathode
    - No cleaning of anodes
    - No more poisoning of electrodes
Why is this a Big Deal?

• Frequent Calibration Not Required
  – No anode to consume and no electrolyte to deplete means extremely stable measurements
  – Internal standard with Red LED
  – No interference from pH swings, wastewater chemicals, H₂S, or heavy metals
Why is this a Big Deal?

• **Accurate and Stable Readings**
  – With nothing to interfere with the readings, HachLDO® produces more stable measurements for a longer time

• **Speed!**
  – Turn it on and it’s running!
  – Response time of less than 30 seconds to 90%!

• **Simple Operation and Maintenance**
  – Only **one** replacement part
  – Inexpensive sensor cap is simple to replace quickly
Comparative Performance
Hach LDO® vs. Membrane Technology

The blue line represents the true theoretical DO value (Hitchman). As you can see, Hach LDO® falls on the line while the conventional membrane technology demonstrates lower accuracy and precision. For more information, refer to Report on the Validation of Proposed EPA Method 350.3 (Luminescence) for the Measurement of Dissolved Oxygen in Water and Wastewater, C. Jackson, 2004 available at www.hach.com.
Questions?

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