Dissolved Oxygen Measurement

Hach LDO® Technology

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

Chad Bertram
Applications Development Manager

Hach LDO® Regulatory Approval

ASTM Method D888-05 Published
August 15, 2005

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

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

JAN – 3 2006

OFFICE OF WATER

MEMORANDUM

SUBJECT: Recommendation for Interim Approval of ASTM International Standard Test Method D 888-05 (ATP Case No. N05-0046)

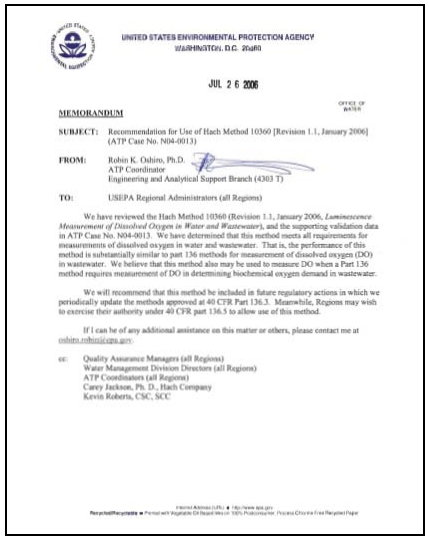
FROM: William A. Telliard
Director of Analytical Methods

TO: USEPA Regional Administrators (all Regions)

In accordance with the authority specified at 40 CFR part 136.5, I recommend that each EPA Region grant interim approval of ASTM International D 888-05 *Standard Test Methods for Dissolved Oxygen in Water* (ATP Case No. N05-0046) for measurement of dissolved oxygen (DO) in wastewater and in for use in measuring DO in methods approved at Title 40 of the *Code of Federal Regulations*, Part 136.3 (40 CFR Part 136.3) for measuring biochemical oxygen demand (BOD). EPA has reviewed the methods and supporting validation data and determined that the methods, including a new procedure, Test Method C (Luminescence-Based Sensor Procedure), meet all requirements for approval as compliance monitoring methods. We recommend that the interim approval be effective from the date of this memorandum to the effective date of a final rule(s) promulgating the methods in the *Federal Register*.

If I can be of any additional assistance on this matter or others, please contact me at telliard.william@epa.gov or at 202/566-1061 at your convenience.

cc: Quality Assurance Managers (all Regions)
Water Management Division Directors (all Regions)
ATP Coordinators (all Regions)
Len Morrissey, ASTM International
Kevin Roberts, CSC, SCC



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

JUL 26 2006

OFFICE OF WATER

MEMORANDUM

SUBJECT: Recommendation for Use of Hach Method 10360 [Revision 1.1, January 2006] (ATP Case No. N04-0013)

FROM: Robin K. Oshiro, Ph.D.
ATP Coordinator
Engineering and Analytical Support Branch (4303 T)

TO: USEPA Regional Administrators (all Regions)

We have reviewed the Hach Method 10360 (Revision 1.1, January 2006, *Luminescence Measurement of Dissolved Oxygen in Water and Wastewater*), and the supporting validation data in ATP Case No. N04-0013. We have determined that this method meets all requirements for measurements of dissolved oxygen in water and wastewater. That is, the performance of this method is substantially similar to part 136 methods for measurement of dissolved oxygen (DO) in wastewater. We believe that this method also may be used to measure DO when a Part 136 method requires measurement of DO in determining biochemical oxygen demand in wastewater.

We will recommend that this method be included in future regulatory actions in which we periodically update the methods approved at 40 CFR Part 136.3. Meanwhile, Regions may wish to exercise their authority under 40 CFR part 136.5 to allow use of this method.

If I can be of any additional assistance on this matter or others, please contact me at oshiro.robin@epa.gov

cc: Quality Assurance Managers (all Regions)
Water Management Division Directors (all Regions)
ATP Coordinators (all Regions)
Carey Jackson, Ph. D., Hach Company
Kevin Roberts, CSC, SCC

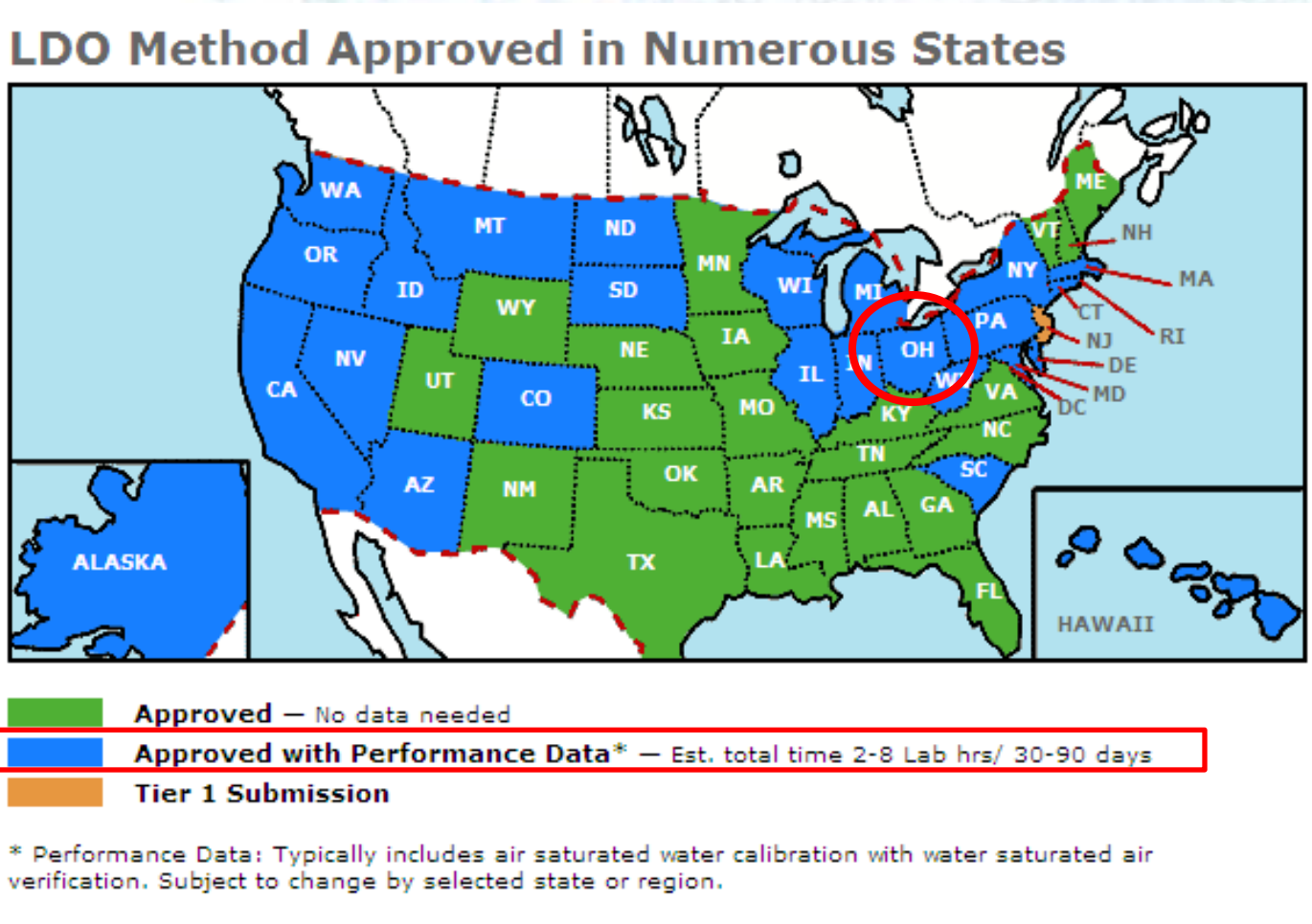
USEPA Proposed Method Update Rule
August 6, 2010

http://www.epa.gov/waterscience/methods/update/methodsprepub.pdf

6. EPA 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



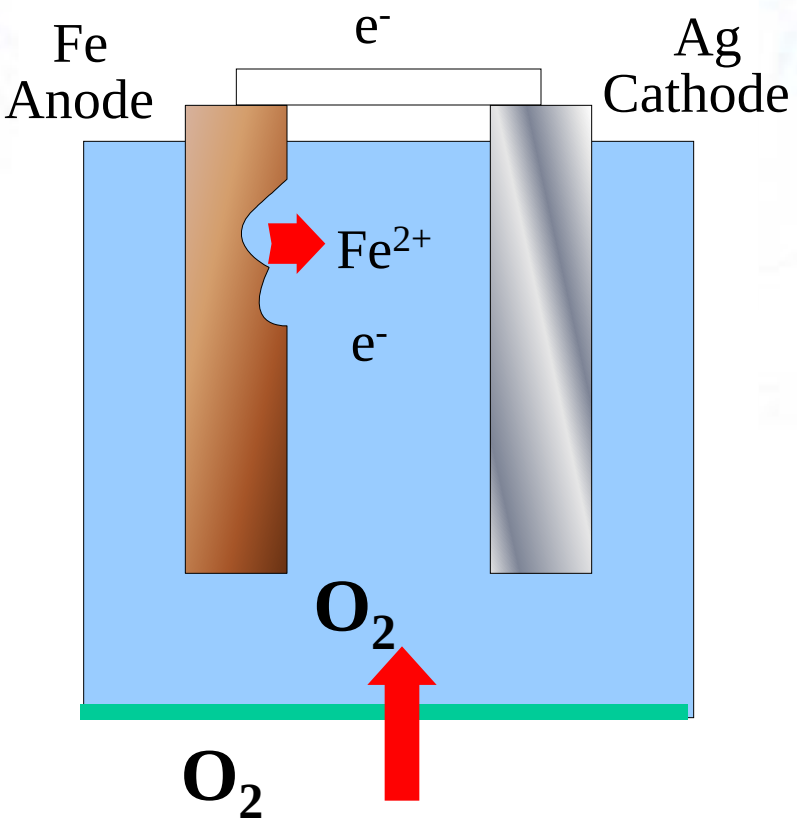
Hach has request forms available for your region at **www.Hach.com** and we can walk you through the process

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 poloragraphic 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

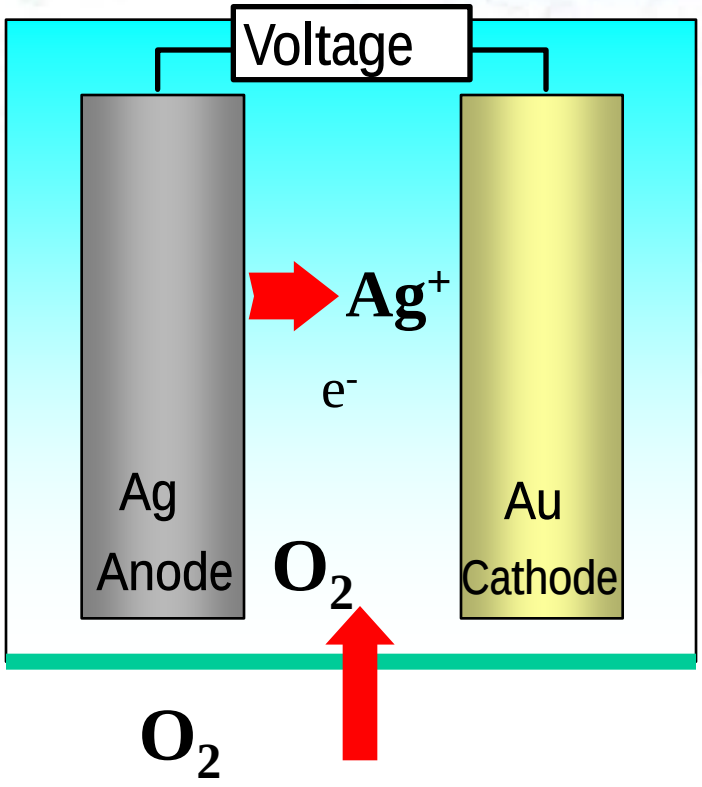
Galvanic DO Measurement

- 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



Poloragraphic 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.

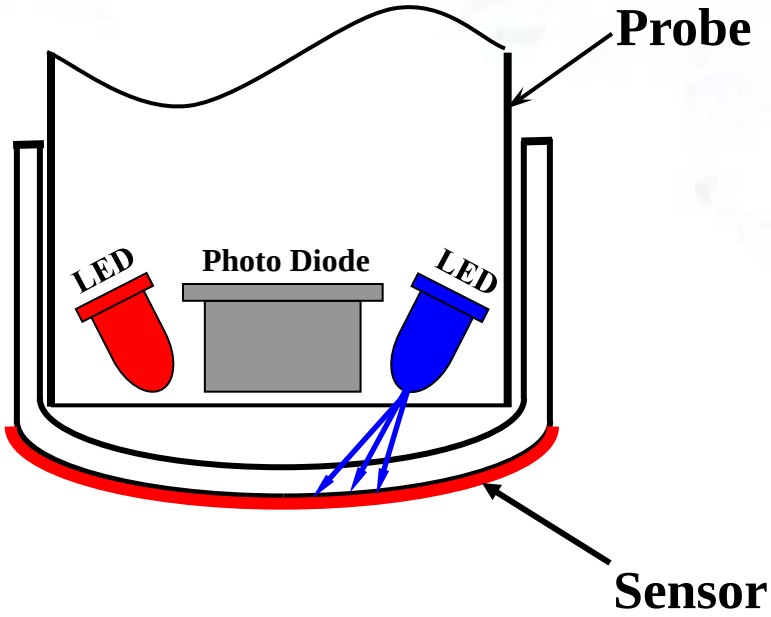


Issues with Electrochemistry

- **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

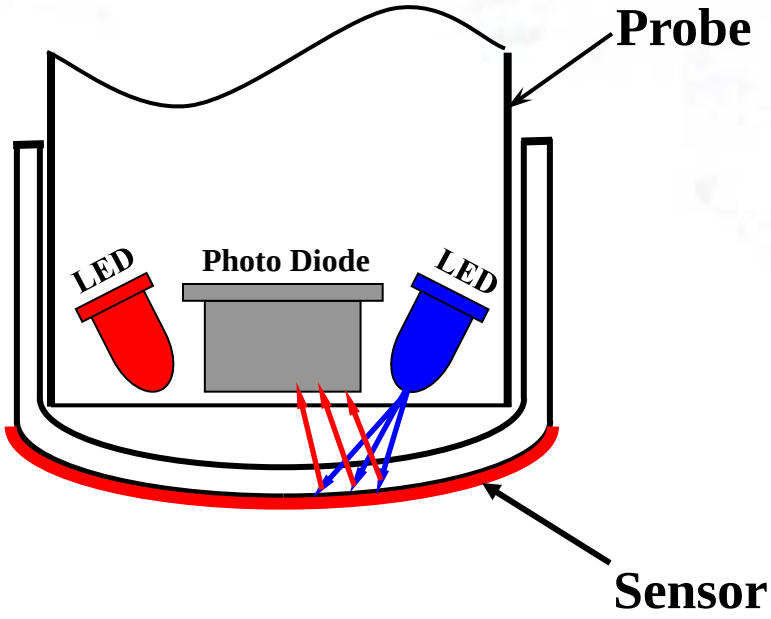
How Does HachLDO® Work?

- 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.



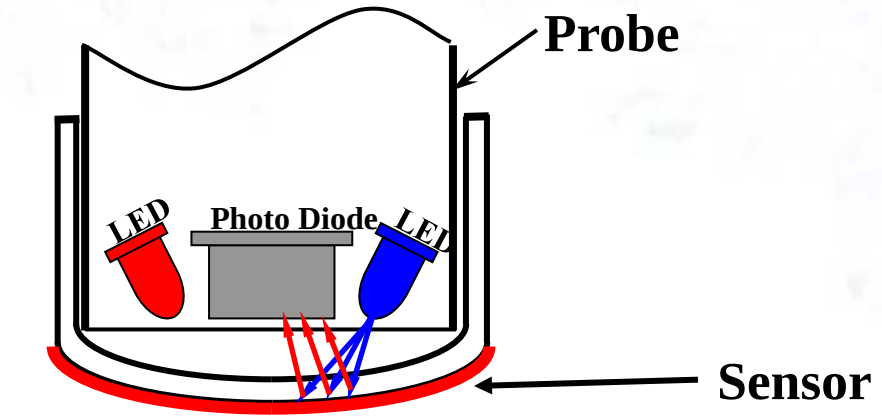
How Does HachLDO® Work?

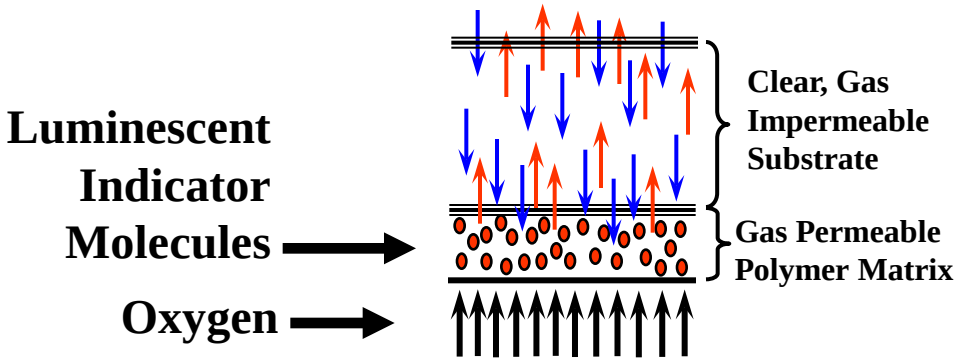
- As the excited chemical relaxes, it releases red light.
- The red light is detected by a photo diode.
- The time it takes (lifetime) for the chemical to return to a relaxed state is measured



How Does HachLDO® Work?

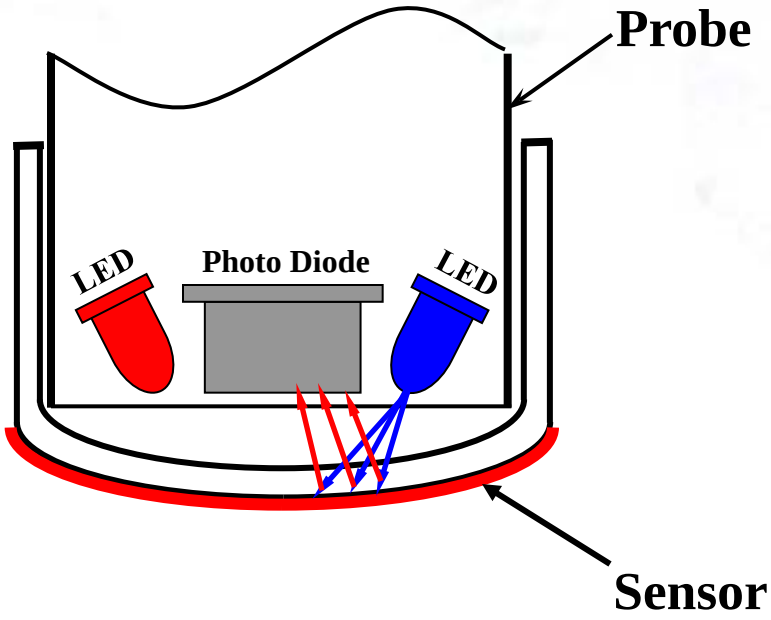
- When oxygen contacts the luminescent chemical, the intensity of the red light decreases
- The amount of time it takes for the material to relax is reduced





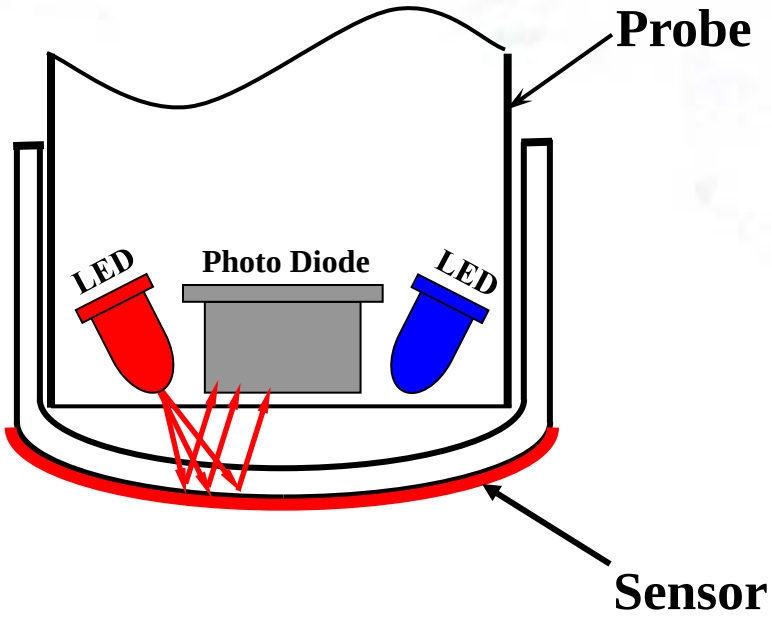
How Does HachLDO® Work?

- The intensity of the red light is <u>not</u> what's being measured.
- What's being measured is the time it takes after excitation for red light to be given off.
  - **<u>Lifetime of luminescence</u>**



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 H_2S poisoning of the electrolyte
  - No anode or cathode
    - No cleaning of anodes
    - No more poisoning of electrodes

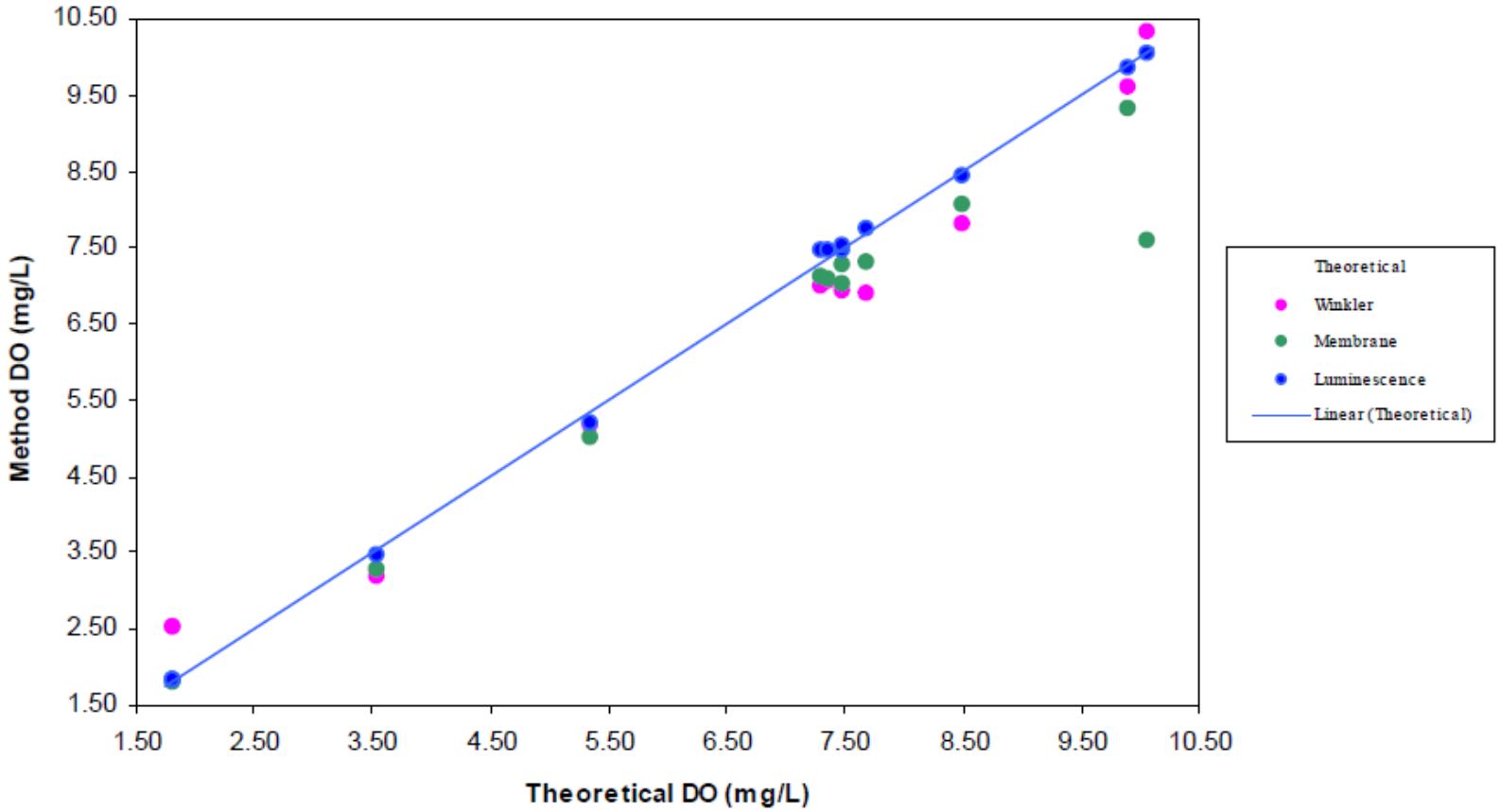
Why is this a Big Deal?

- **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, H_2S, 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 360.3 (Luminescence) for the Measurement of Dissolved Oxygen in Water and Wastewater. C. Jackson, 2004 available at www. hach.com

Hach LDO® Product Line

Questions?

Chad Bertram
Applications Development Manager