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# Luminescence based measurement of dissolved oxygen in natural waters

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Real-Time Water Quality Monitoring Workshop 2007



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# Measurement of Dissolved Oxygen

- Why measure DO?
  - The measurement of DO is essential in assessing its effects on natural waters, process streams, and control of sewage treatment
  - There are many situations where it is required to report DO in discharges and water bodies as a regulatory tool
  - Therefore, precision and accuracy in the measurement of DO are critical issues of interest in estimating the degree of water quality or purification, and calculating important economic issues such as industrial discharge loading costs



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# Dissolved Oxygen Determinants

- Current Approved DO Methodologies
  - Winkler Titration Procedure (Wet chemistry)
    - EPA Method 360.2
    - ASTM Standard D888-92 (Method A)
  - Membrane Probe (Clark-type Electrodes)
    - EPA Method 360.1
    - ASTM Standard D888-92 (Method B)
  - Luminescence (Optode)
    - EPA interim approval in region 4
    - ASTM Standard D888-05 (Method C)



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# Oxygen Sensors: Principle of Operation

- Winkler Titration
  - Destructive chemical oxidation-reduction reaction
  - Limitations
    - Subject to numerous interferences
      - Oxidizing and reducing agents
      - Nitrate and nitrite ion
      - Ferris and ferric ion
      - Suspended solids and organic matter
    - Practical issues
      - Field use impractical for real-time studies
      - Labor Intensive
      - Variations are minimized only through use of automated titration



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# Oxygen Sensors: Principle of Operation

- Membrane Electrode – “Clark cell electrodes”
  - Oxygen consumptive reduction is measured in a system with an electrolyte and two metallic electrodes
  - Oxygen must diffuse through a membrane to be reduced at a cathode
  - Limitations
    - Requires high flow across membrane
    - Narrow linearity range
    - Electrolyte and electrode degradation
    - Membrane fouling



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# Oxygen Sensors: Principle of Operation

- Luminescence-Based Oxygen Sensors – “Optodes”
  - Measures the light emission characteristics of a luminescent reaction
  - In the presence of oxygen the luminescence is quantitatively reduced or quenched
  - Dissolved oxygen concentration is inversely proportional to the luminescence lifetime of the light emitted by the photo-luminescence process
    - The lower the DO concentration, the greater the signal to noise ratio
  - Limitations
    - Only one known interferent (chlorine dioxide at percent levels)



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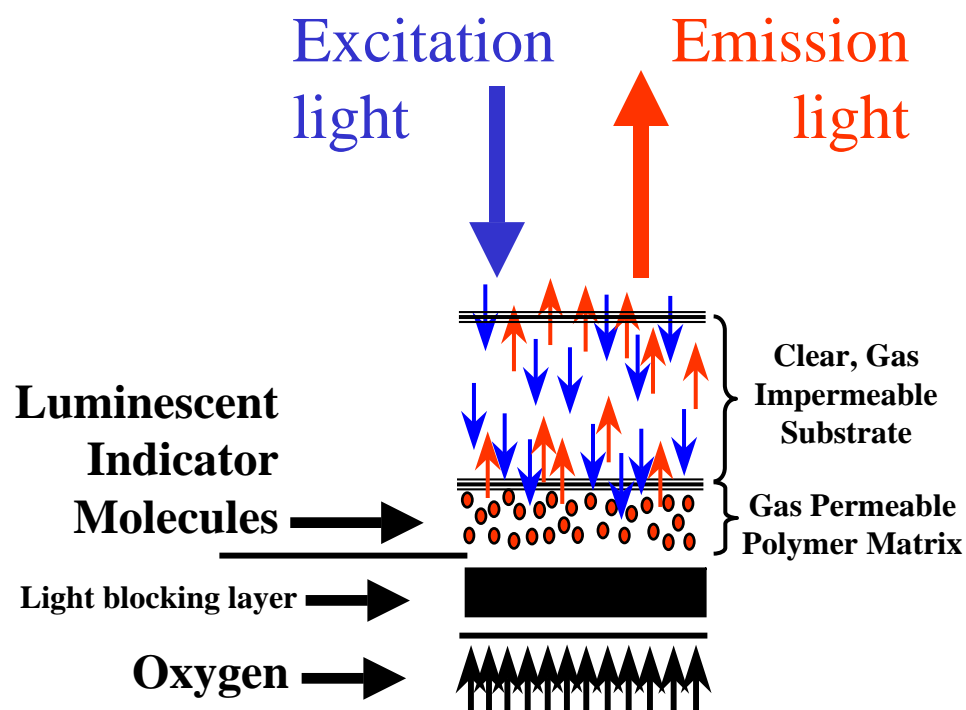
# Optodes: Principle of Operation

- Intensity based measurements
  - Measure the intensity of luminescence and correlate it to DO concentration
  - Susceptible to fouling and mechanical degradation
- Lifetime based measurements
  - Measures the change in lifetime of the luminescence signal and correlates it to DO concentration
  - Require somewhat more sophisticated electronics
  - High level of immunity to fouling and mechanical degradation

# How do lifetime based optodes work?

- The influence of Oxygen on the optode
  - When oxygen contacts the polymer matrix containing the luminescent chemical, it impacts both the intensity and the phase angle of the emitted red light
  - The intensity of the red light decreases
  - The amount of time it takes for the material to relax is reduced (phase angle changes)

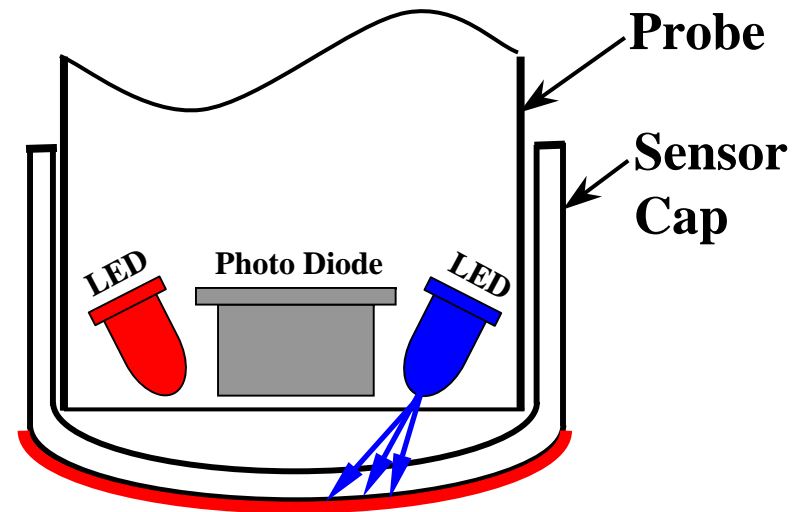
## SENSOR CROSS SECTION





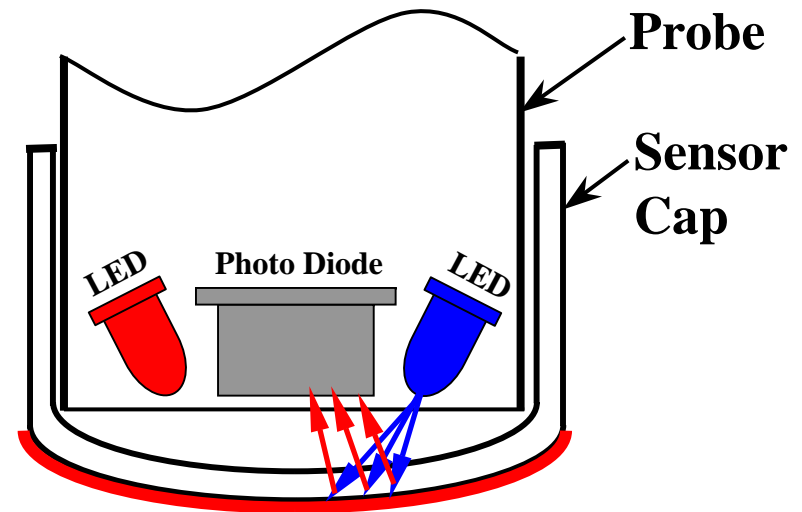
## How do lifetime based optodes work?

- A sensor cap is coated with a luminescent material
- Blue light from an LED strikes the luminescent chemical on the sensor cap
- The luminescent chemical instantly becomes excited



## How do lifetime based optodes work?

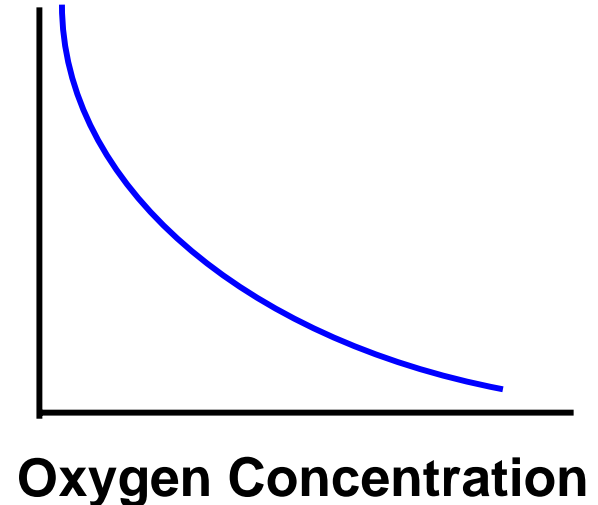
- As the excited chemical relaxes, it releases red light
- The red light is detected by a photo diode
- The time it takes for the luminescent chemical to return to a relaxed state is measured



# How do lifetime based optodes work?

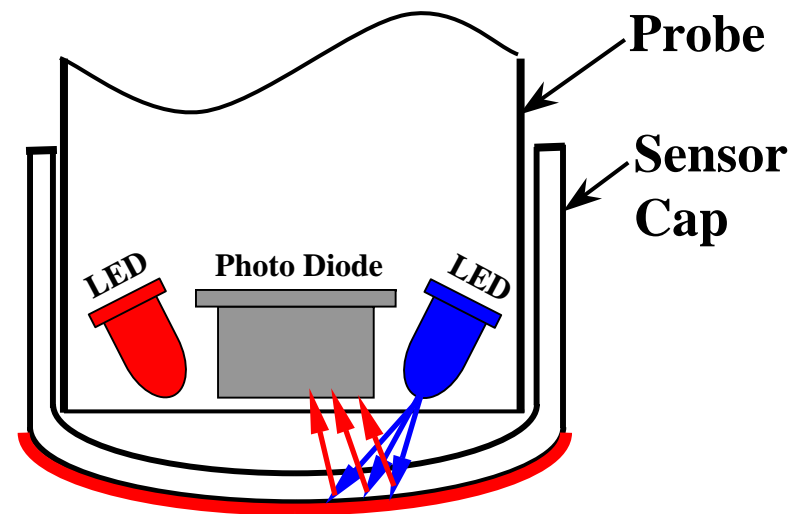
- The higher the oxygen concentration, the less red light that is given off by the sensor

**Red Light  
Emission  
Intensity**



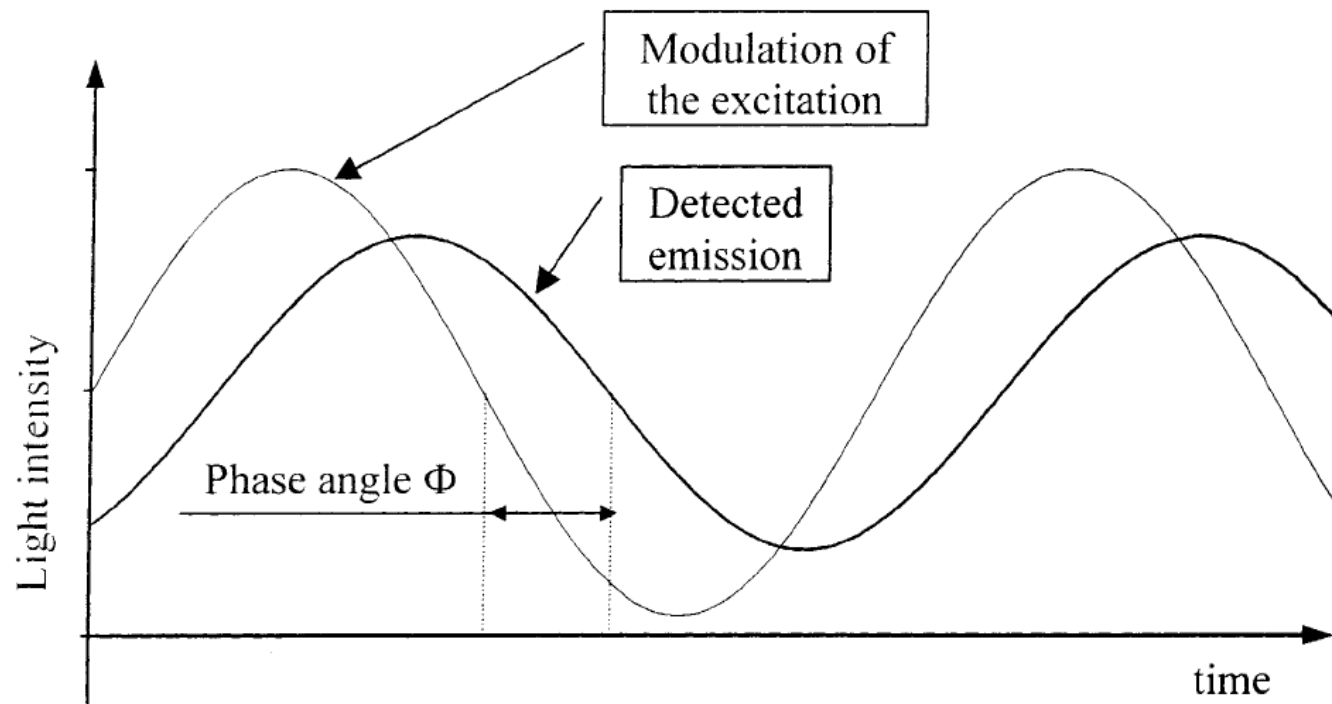
## How do lifetime based optodes work?

- The intensity of the red light is not what is being measured
- What is being measured is the time it takes after excitation for red light to be given off
  - Lifetime of luminescence



## How do lifetime based optodes work?

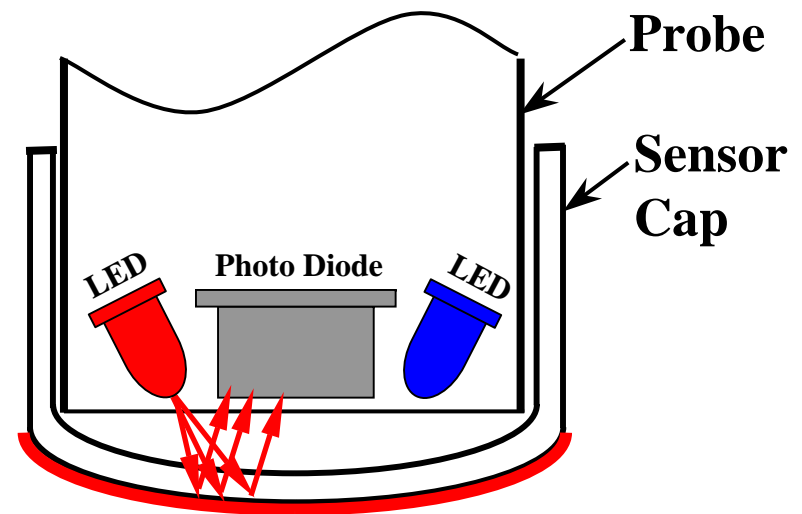
- The phase angle difference between the modulation signal and the emission signal is measured



D. Andrzejewski, I. Klimant, and H. Podbielska, *Sensors and Actuators B (Chemical)* **B84** (2-3), 160 (2002).

## How do lifetime based optodes work?

- A red LED is also present in the probe.
- Between flashes of the blue LED, a red LED is flashed on the sensor
- The red LED acts as an internal standard (or reference) for the optode





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# Field deployment of optodes

- What is the history of the oxygen optode?
  - Study of luminescent quenching in 1919 (Stern, Volmer)
  - Reports of quenching of luminescence by oxygen in 1939 (Kautsky)
  - Oxygen optodes reported in 1975 (Lubbers) (Bergman, 1986)
- Why are oxygen optodes suddenly becoming available for field use?
  - Access to low power light sources – blue LEDs
  - Access to sophisticated low-powered electronics –DSPs
  - Increased knowledge of fluorescent materials and their applications in long-term field deployment
  - Ability to mass-produce sensor caps with repeatable characteristics



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# Comparative Accuracy of DO Determinants

## HachLDO™ laboratory and environmental solutions







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# Technical Specifications

- Range: 0 to 20 mg/L
- Accuracy:  $\pm 0.1$  mg/L @  $< 8$  mg/L  
 $\pm 0.2$  mg/L @  $> 8$  mg/L
- Resolution: 0.01
- Max Depth: 200 meters

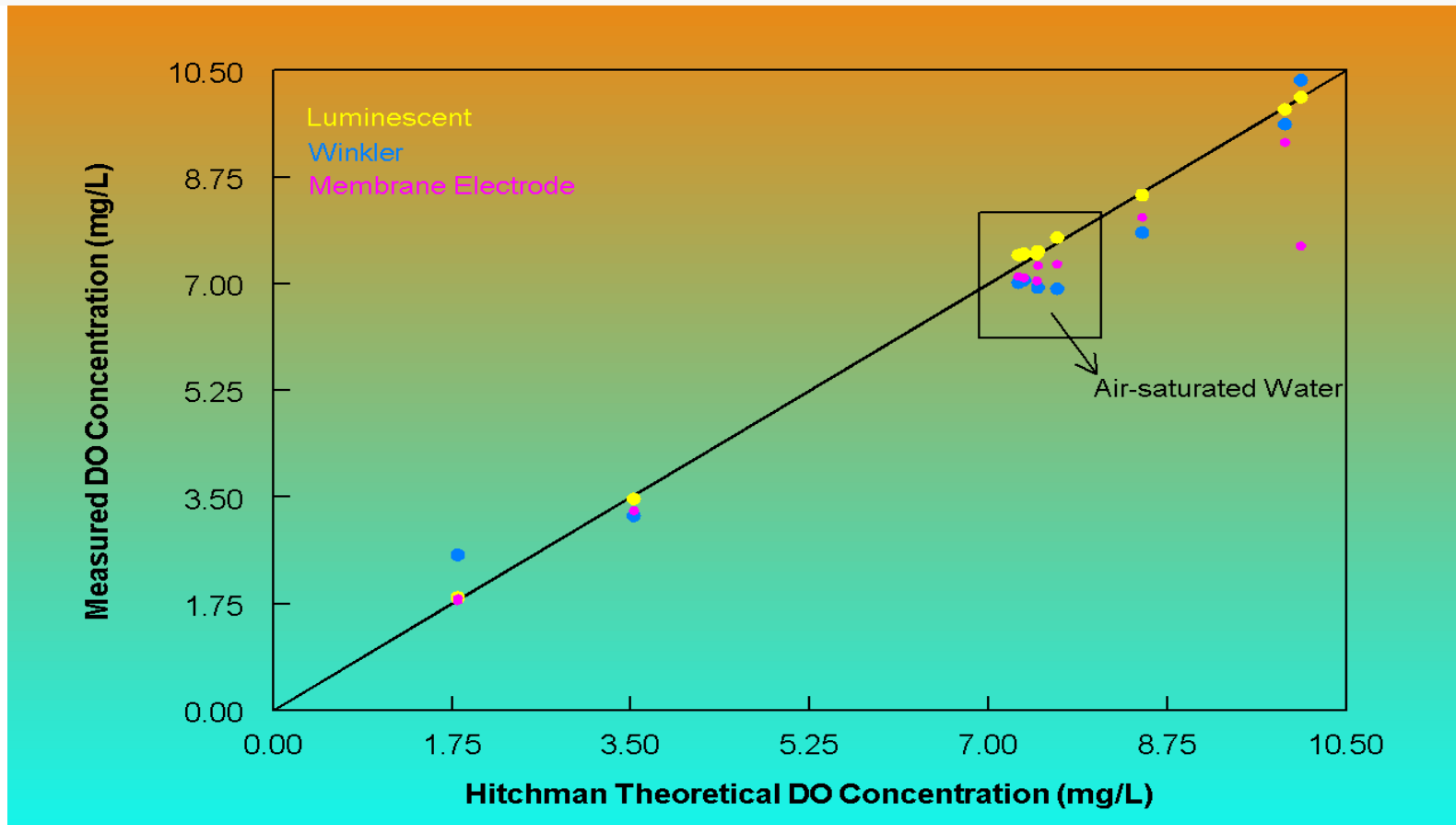


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# Comparative Accuracy of DO Determinants

HachLDO™ HQ-10



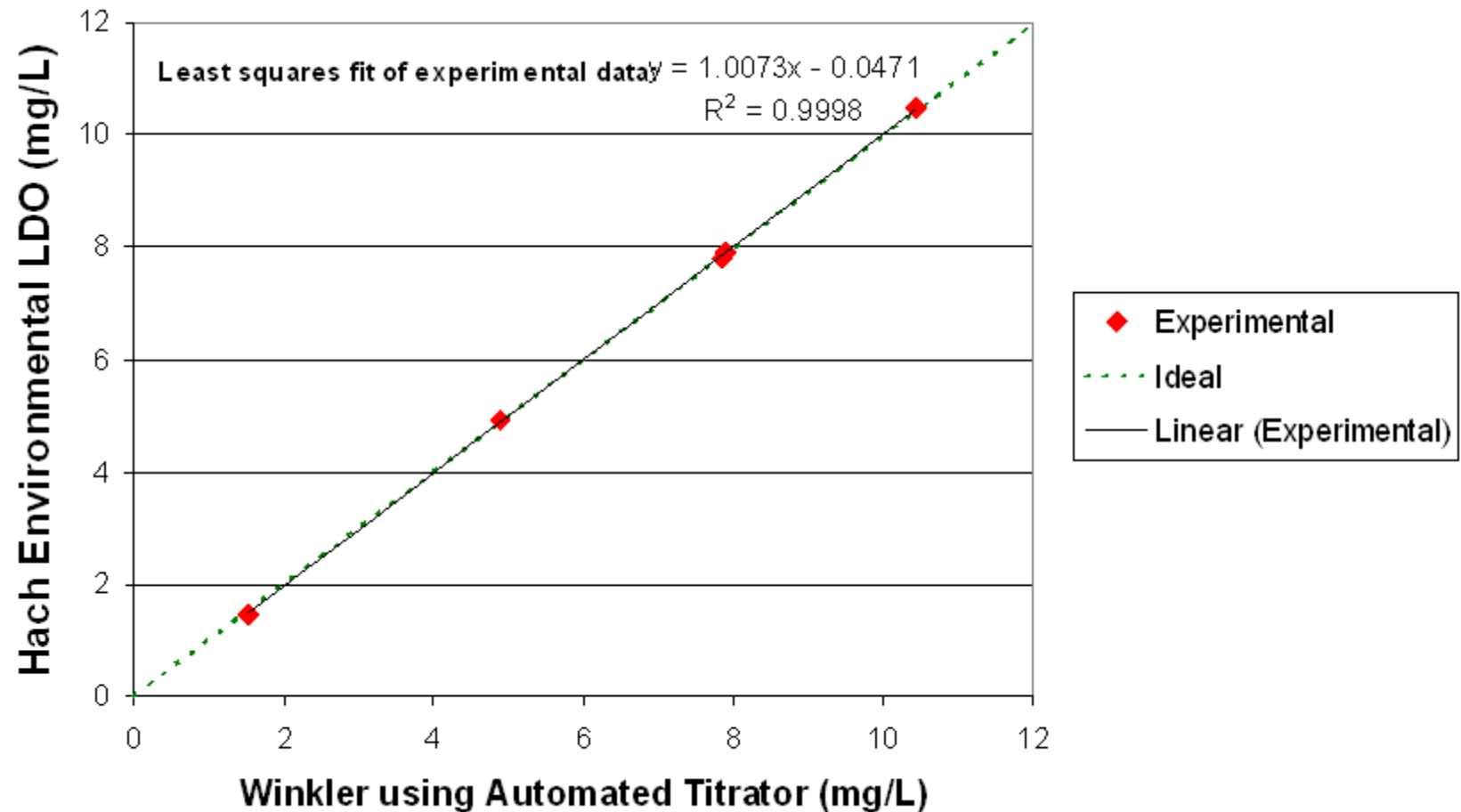


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# Comparative Accuracy of DO Determinants

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Independent testing using automate titrator

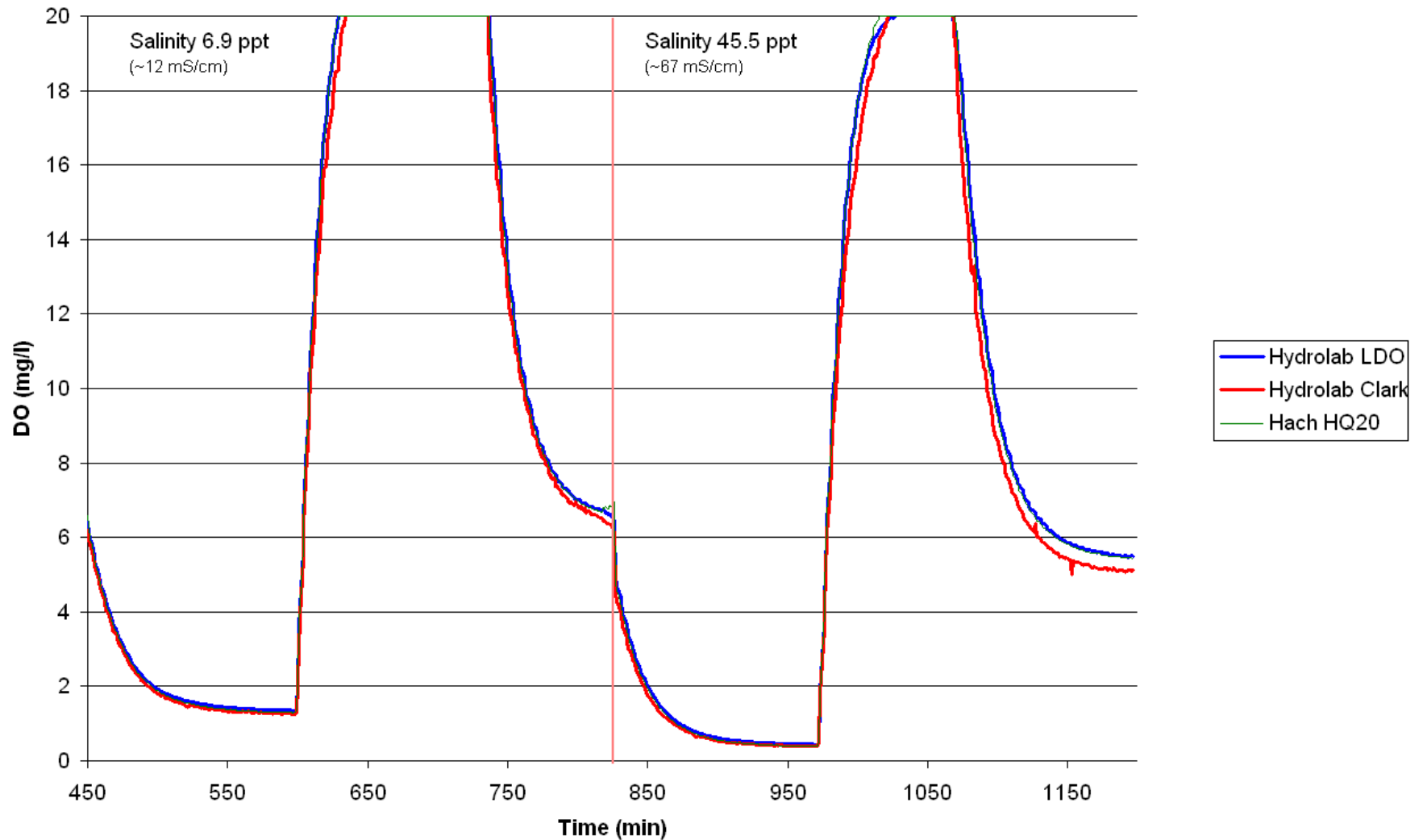


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# Comparative Accuracy of DO Determinants

DO measurements using Hach LDO and Clark DO in water with Salinity > 1 ppt





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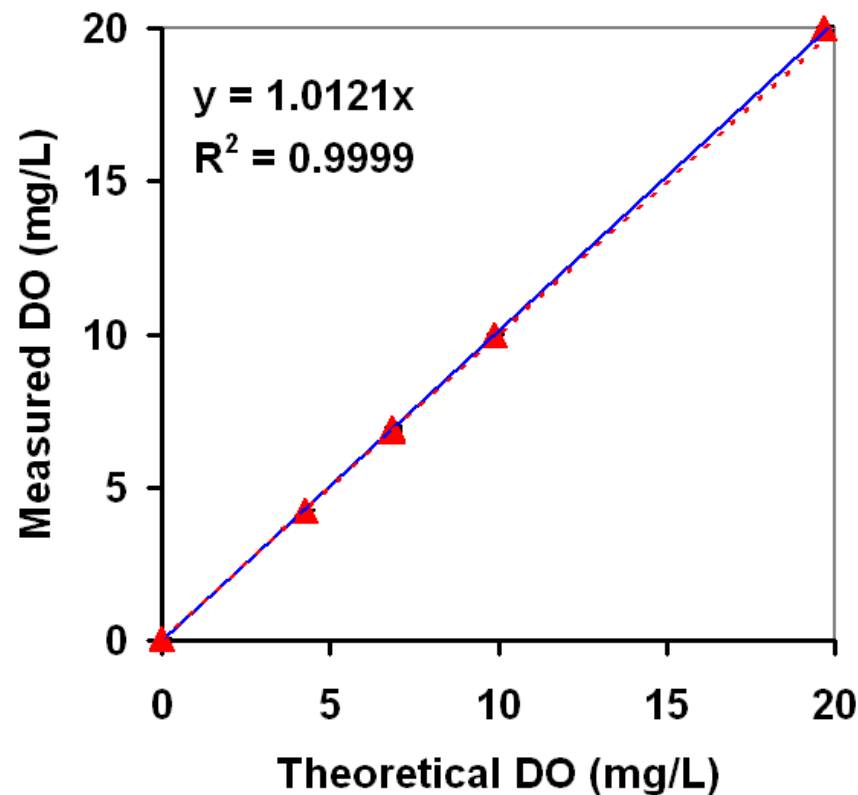


# Comparative Accuracy of DO Determinants

## HachLDO™

### Validation of Measurement Range for LDO Portable

(Dec. 21, 2004; Dashed Line is the Theoretical Response)





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# Questions