

# Measurement of Dissolved Oxygen with a Luminescence-based Oxygen Quenching Sensor



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# Measurement of Dissolved Oxygen

- Introduction

- The measurement of DO is essential in assessing its effects on natural waters, process streams, and control of sewage treatment
- When used to report DO in discharges and to derive the biochemical oxygen demand from wastewater, it becomes a regulatory tool
- Therefore, precision and accuracy is a critical issue of interest in estimating the degree of water quality or purification, and calculating the industrial discharge loading costs

## Dissolved Oxygen Determinants

- Winkler Titration Procedure
  - 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)

## 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
      - Field use impractical
      - Labor Intensive

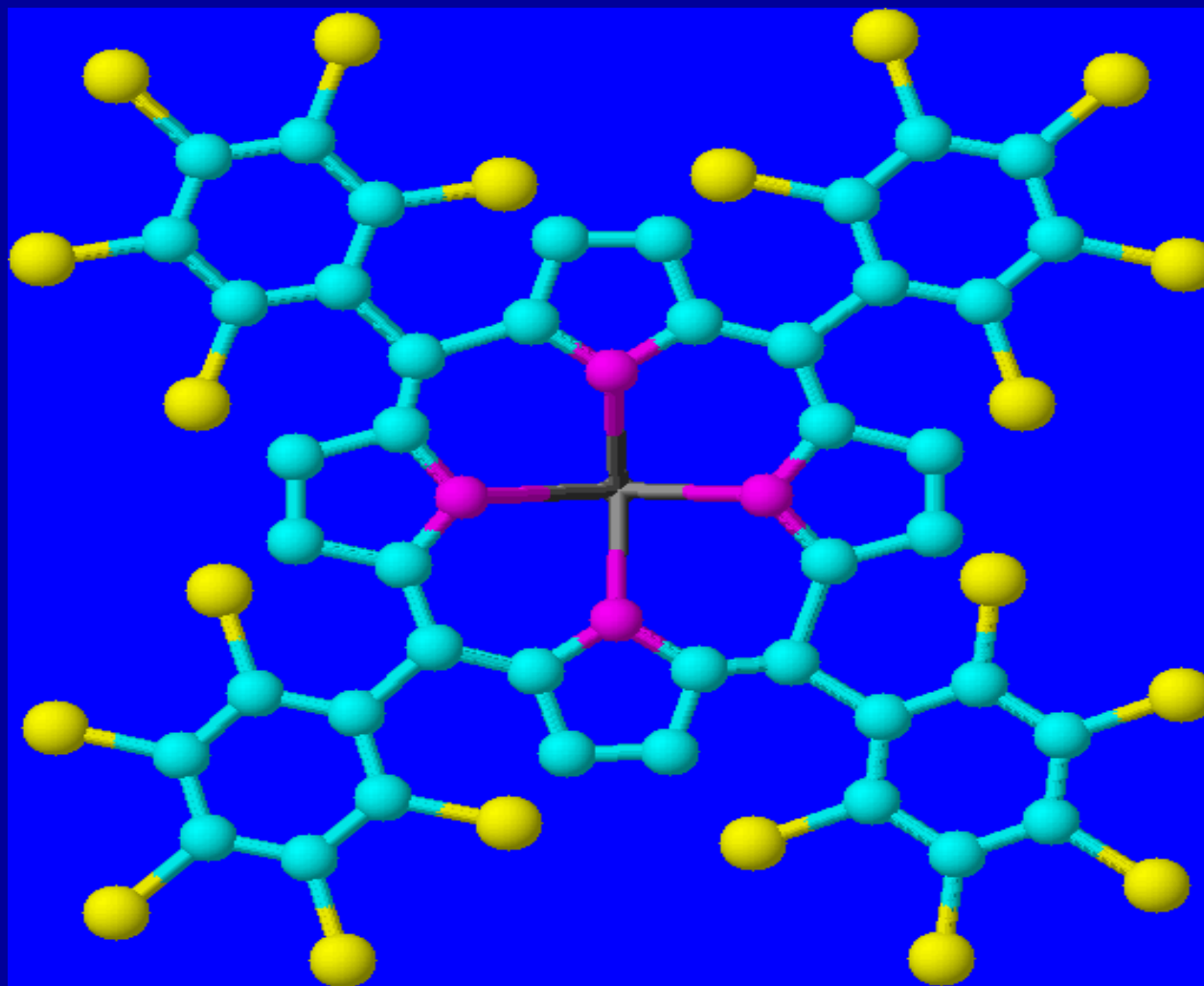
## Luminescence-Based Oxygen Sensors

- Membrane Electrode
  - Oxygen consumptive reduction from 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

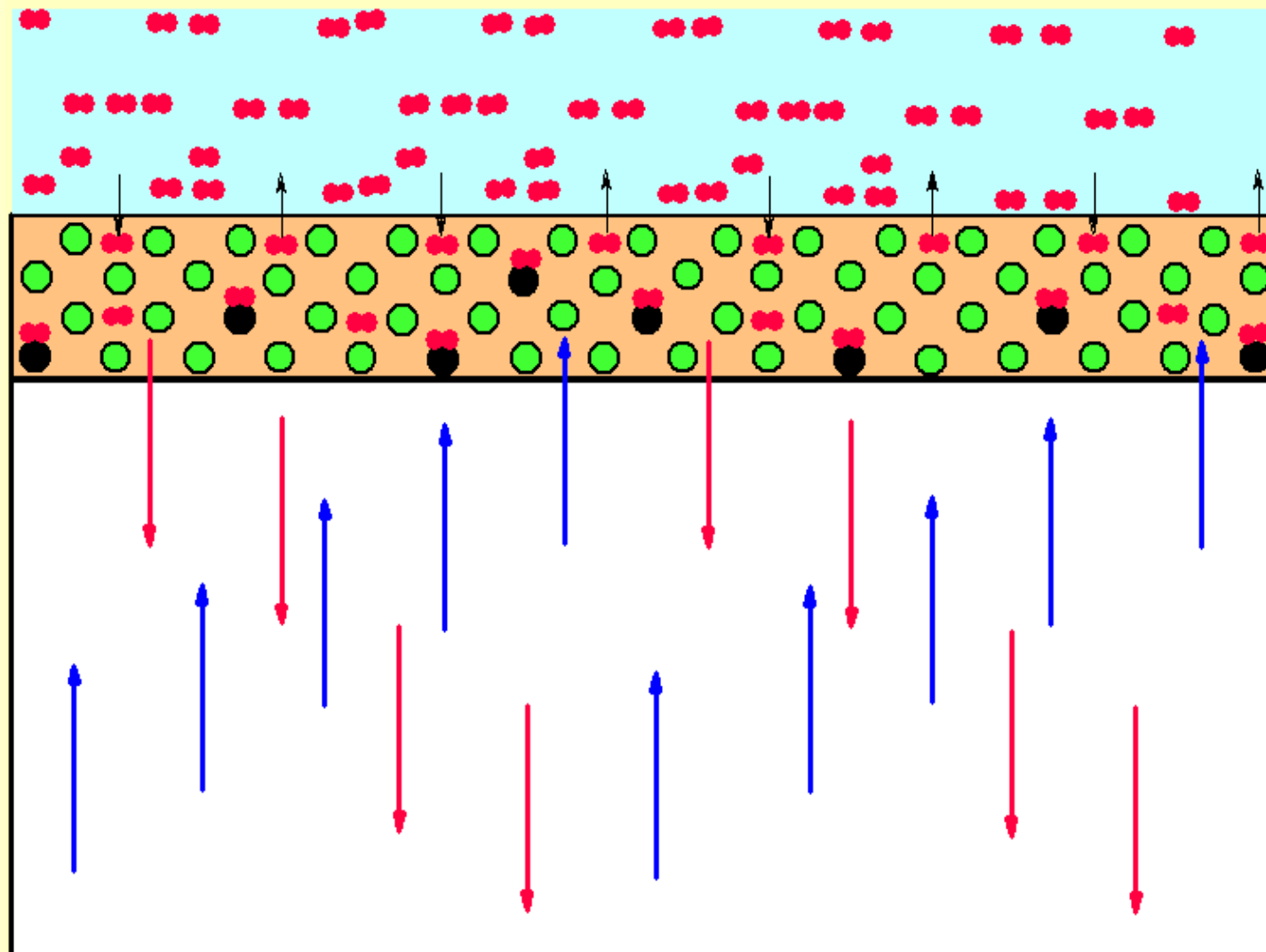
# Luminescence-Based Oxygen Sensors

- Luminescence-Based Oxygen Sensors
  - Measures the light emission characteristics of a reversible 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
    - None known

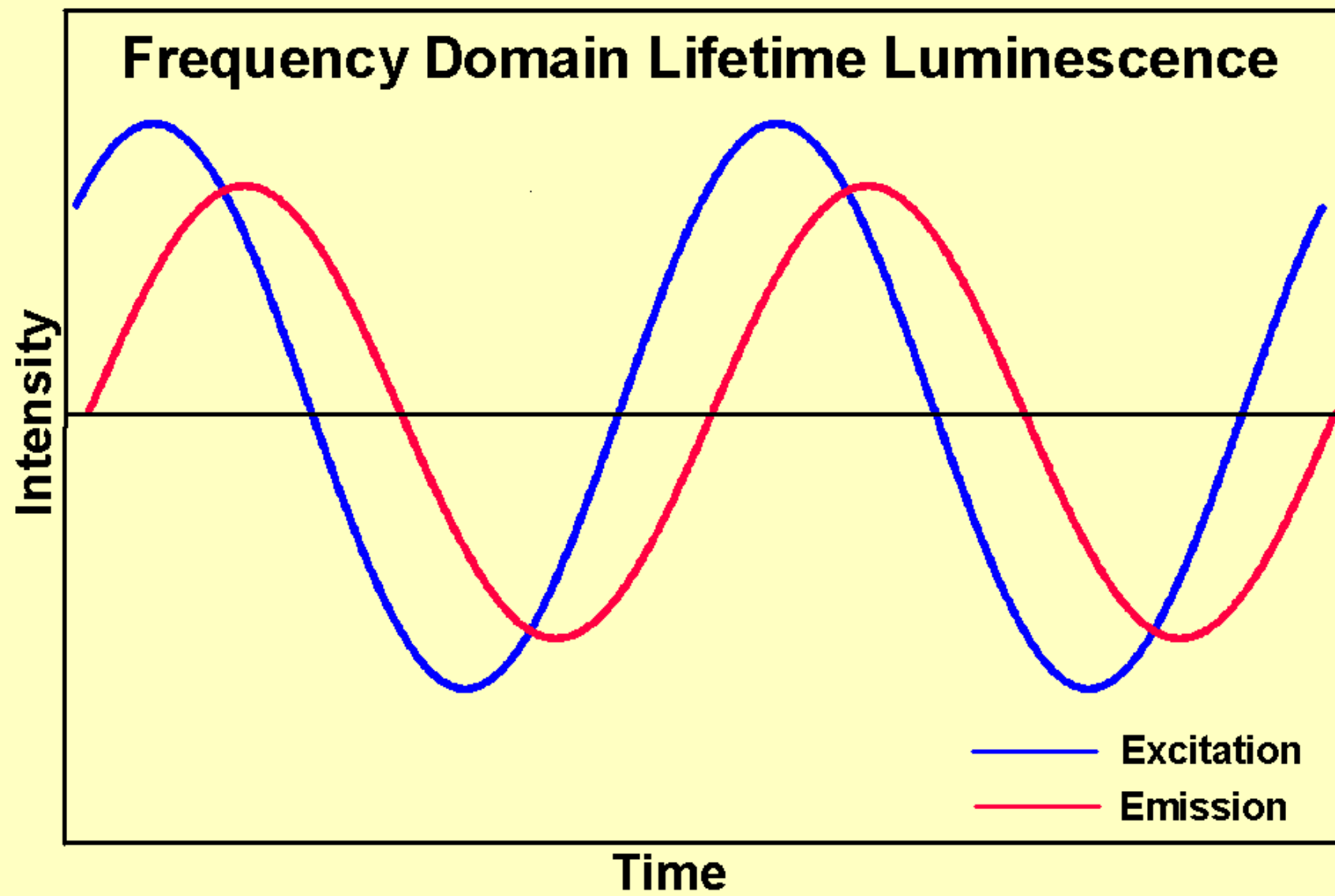
# Luminophore Structure



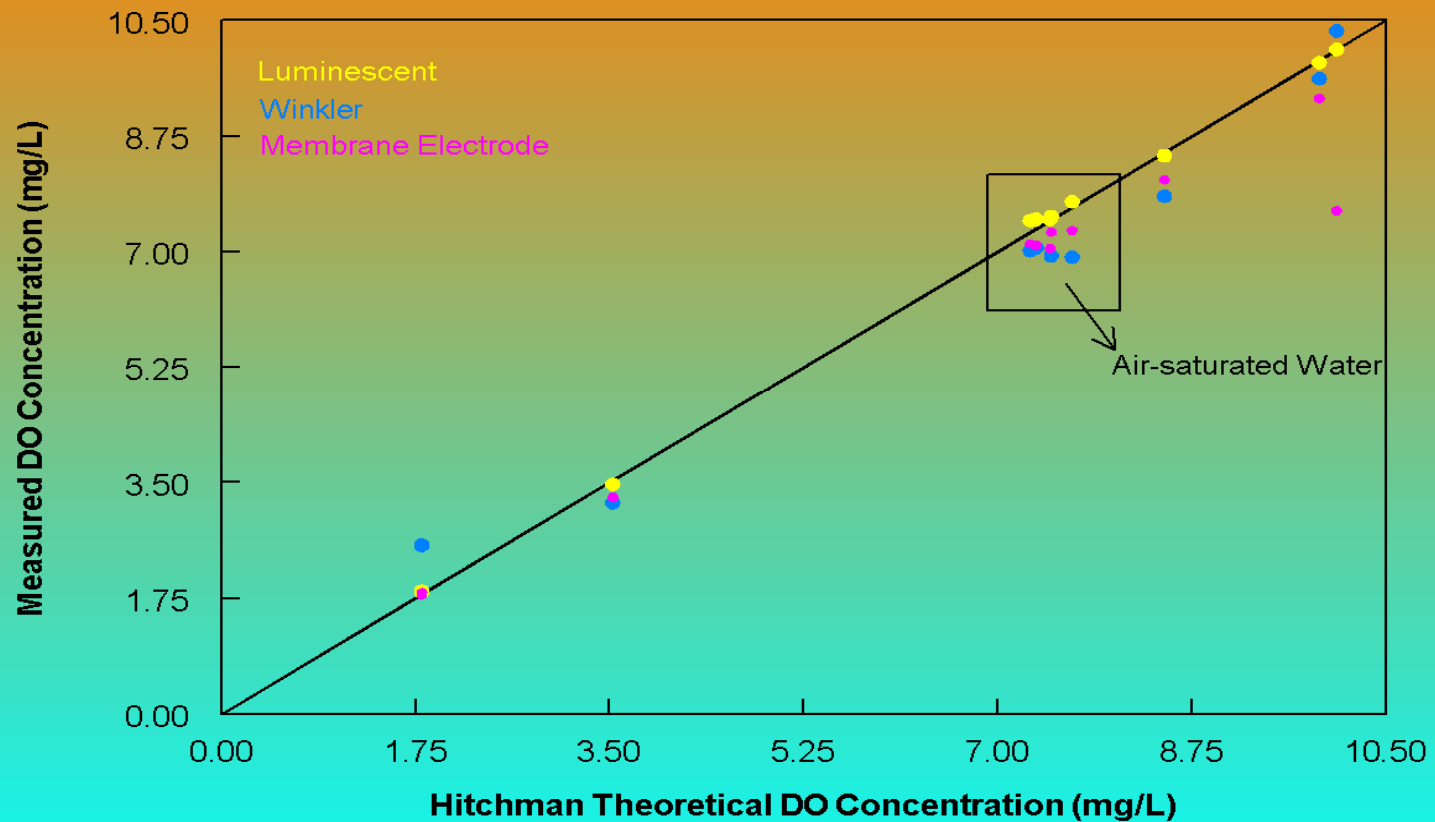
# Luminescence Dissolved Oxygen Sensor



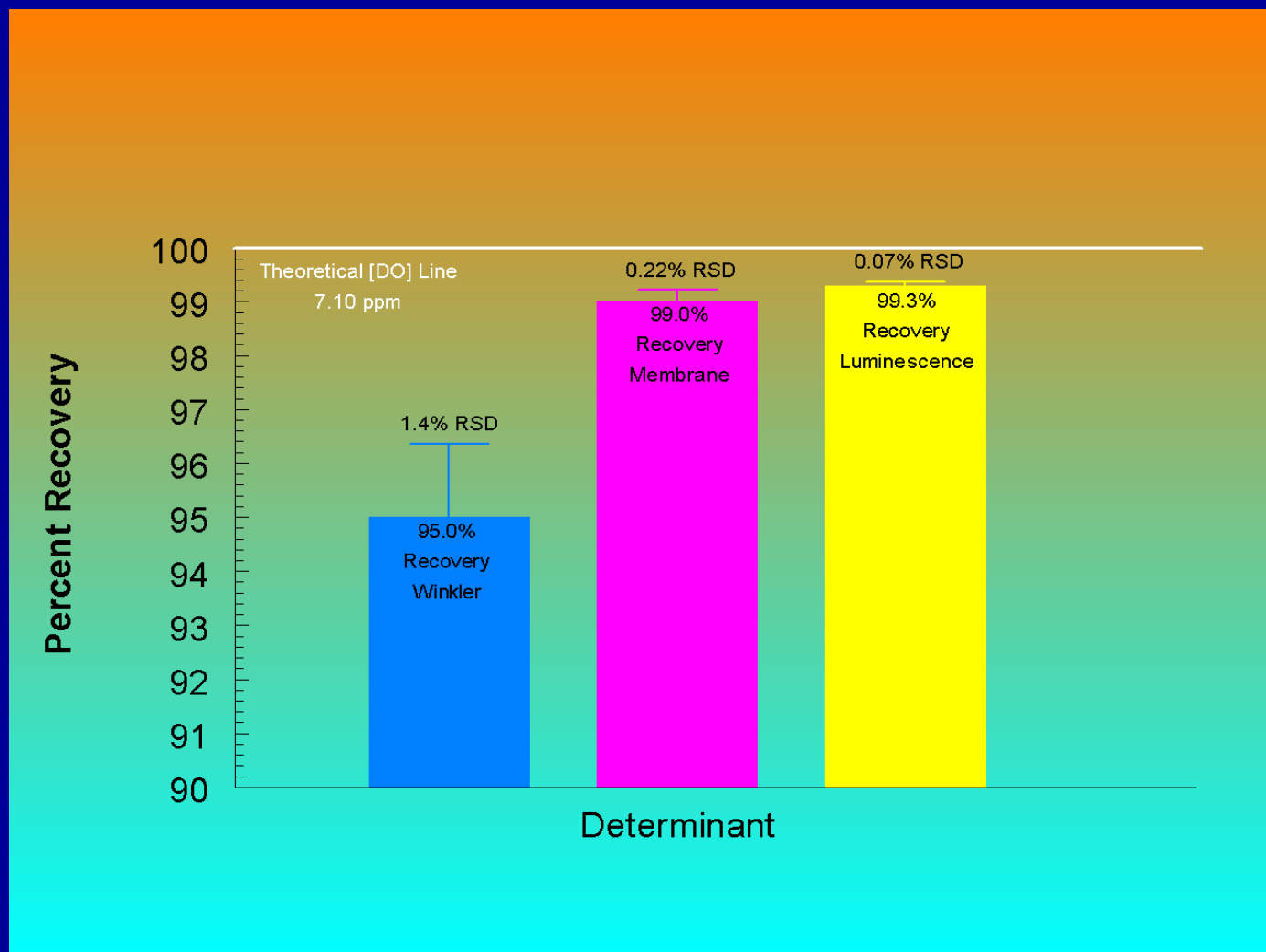
- O<sub>2</sub> Permeable Substrate
- O<sub>2</sub> Permeable Polymer
- Dissolved Oxygen
- O<sub>2</sub> Diffusion
- Luminophore Molecule
- O<sub>2</sub> Quenched Luminophore
- Excitation
- Emission



## Comparative Accuracy of DO Determinants



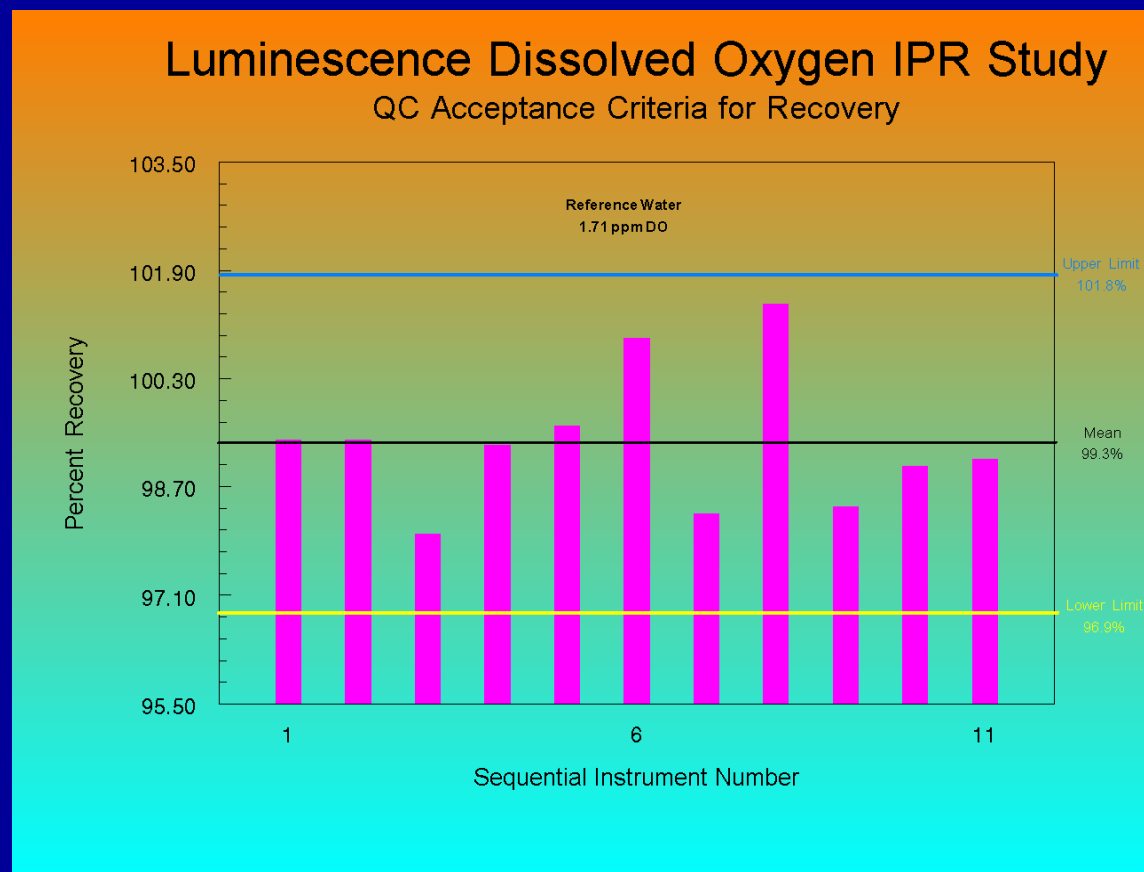
## Comparative Precision and Accuracy of DO Determinants





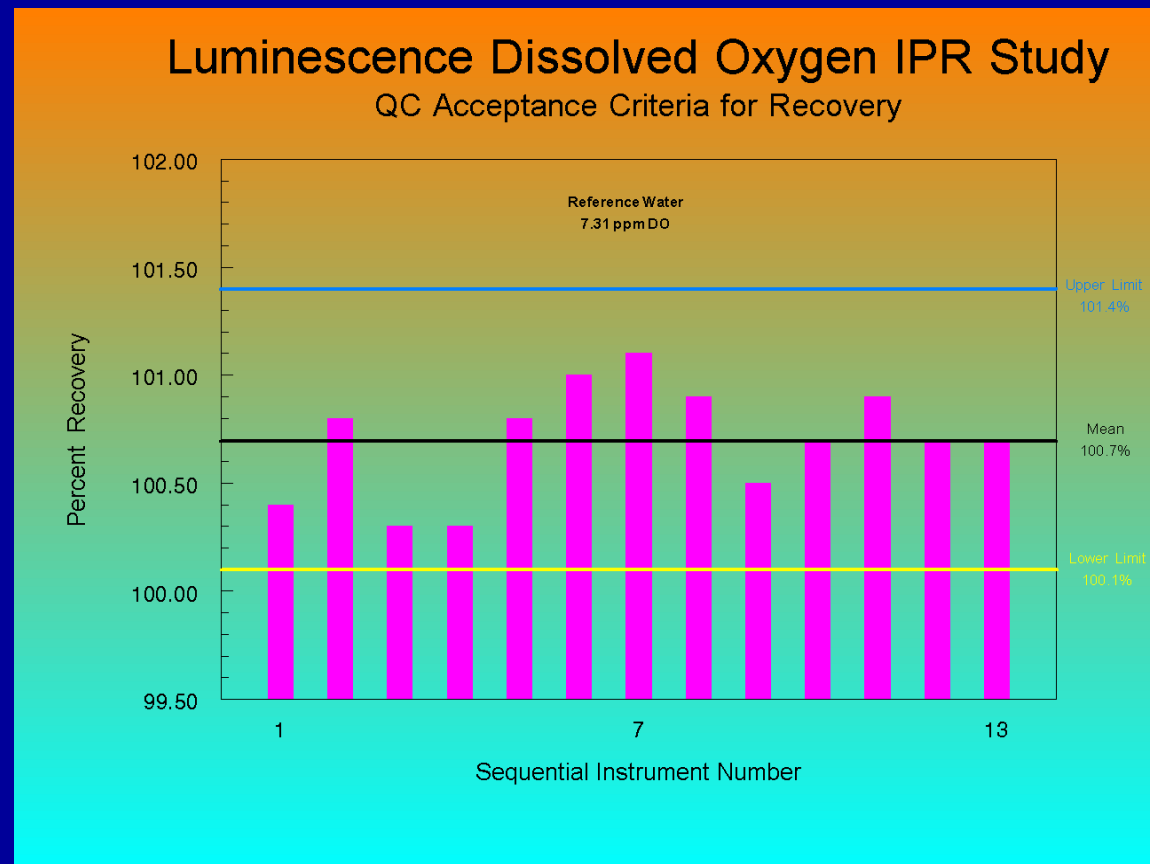
## EPA Quality Assurance Acceptance Criteria for Precision and Recovery

- Theoretical [DO] – 1.71 ppm
- Mean
  - 99.3%
- 95% Confidence Interval
  - 0.024
- % Lower Limit
  - 96.9%
- % Upper Limit
  - 101.8%



## EPA Quality Assurance Acceptance Criteria for Precision and Recovery

- Theoretical [DO] – 7.31 ppm
- Mean
  - 100.7%
- 95% Confidence Interval
  - 0.003
- % Lower Limit
  - 101.1%
- % Upper Limit
  - 101.4%





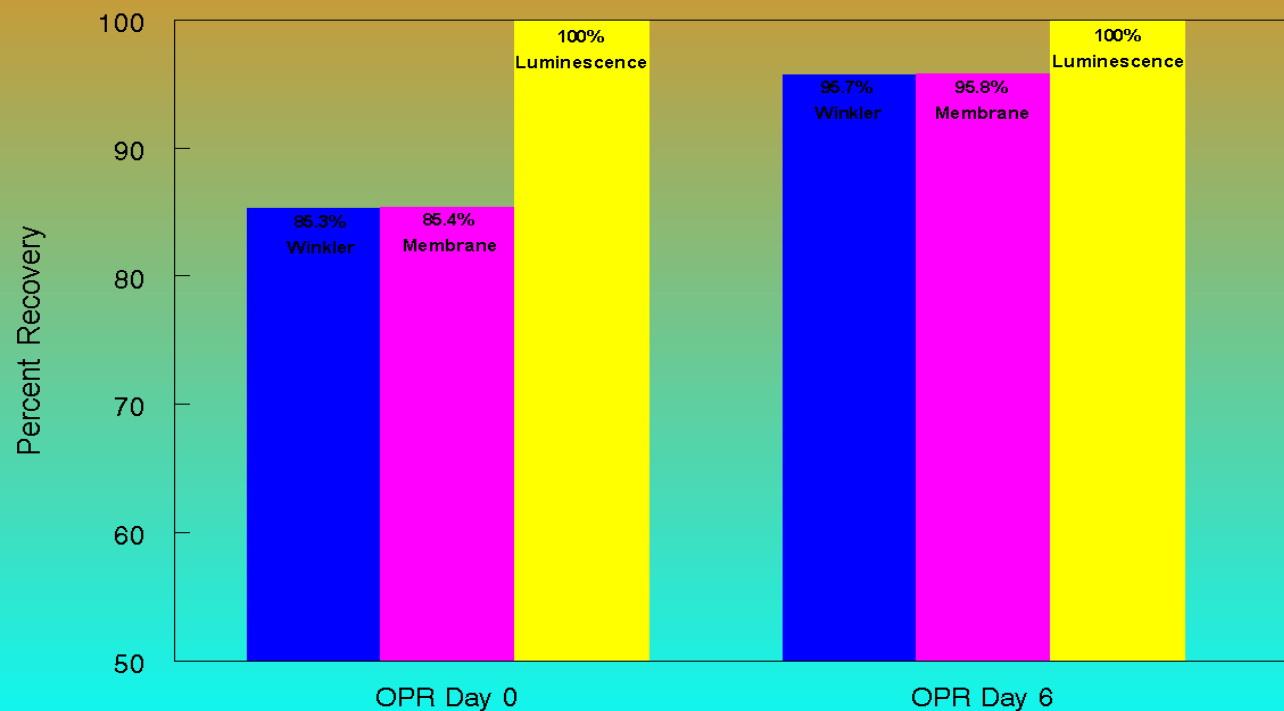
## EPA Quality Assurance Acceptance Criteria for Method Detection and Method Limit

- Method Statistics
  - Single laboratory
  - 9 different instruments
  - 7 replicates
  - Theoretical [DO] = 0.07 ppm
  
- Mean Recovery
  - 98%
  
- Method Detection Limit
  - 0.02 mg/L
  
- Method Limit
  - 0.06 mg/L



# Standard Methods Quality Control Results for Biochemical Oxygen Demand

## Air-saturated Water Calibration Verification



# Standard Methods Quality Control Results for Biochemical Oxygen Demand

5-Day Incubated Glucose & Glutamic Acid  
Check Sample Recovery

