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 it's 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 become 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

- Current Regulatory Approved Methodologies
  - 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)
- Future Methodologies
  - Luminescence
    - Proposed EPA method 360.3
    - ASTM D19.05 subcommittee approval for Standard D888-04 (Method C)

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

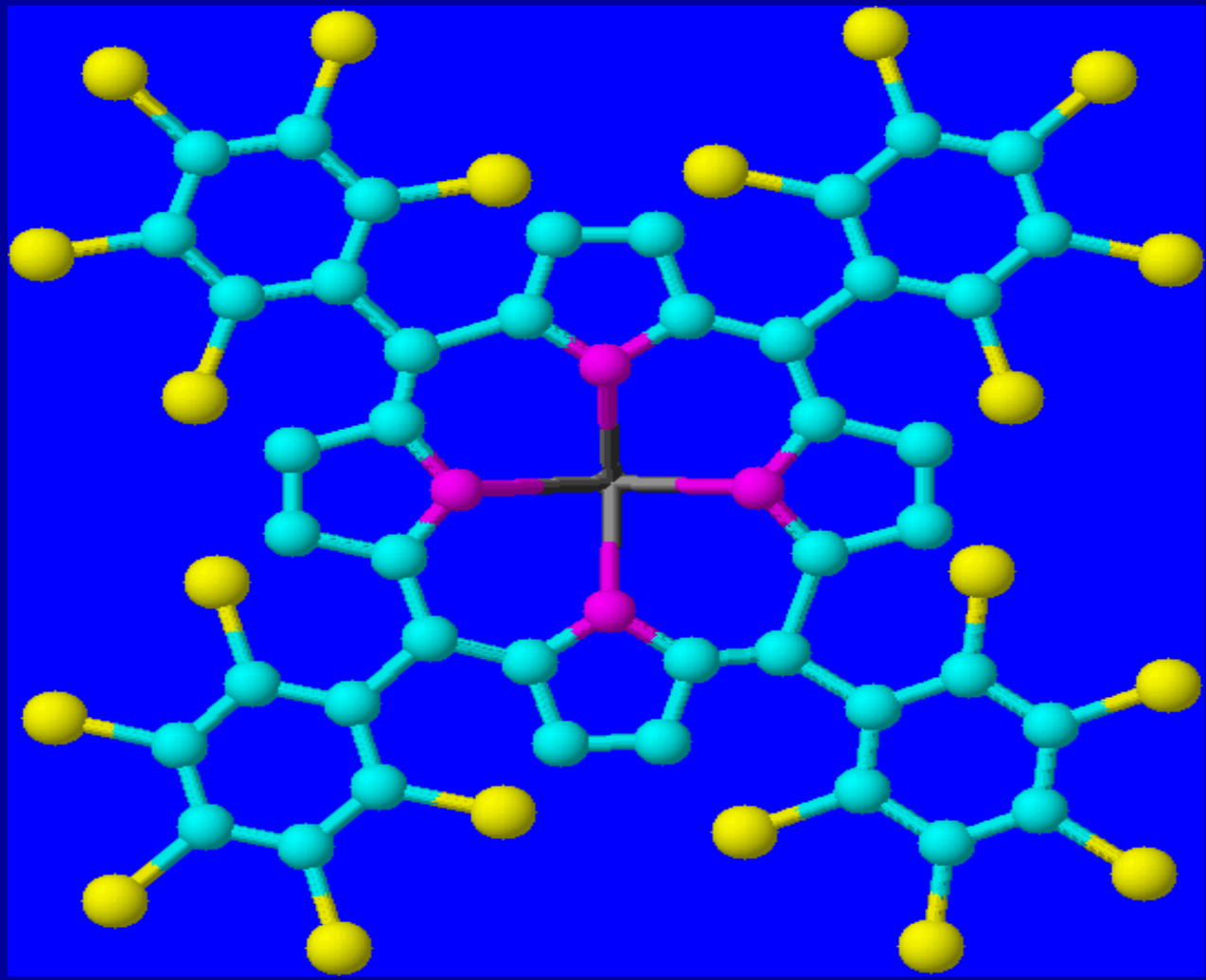
Luminescence-Based Oxygen Sensors

- 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

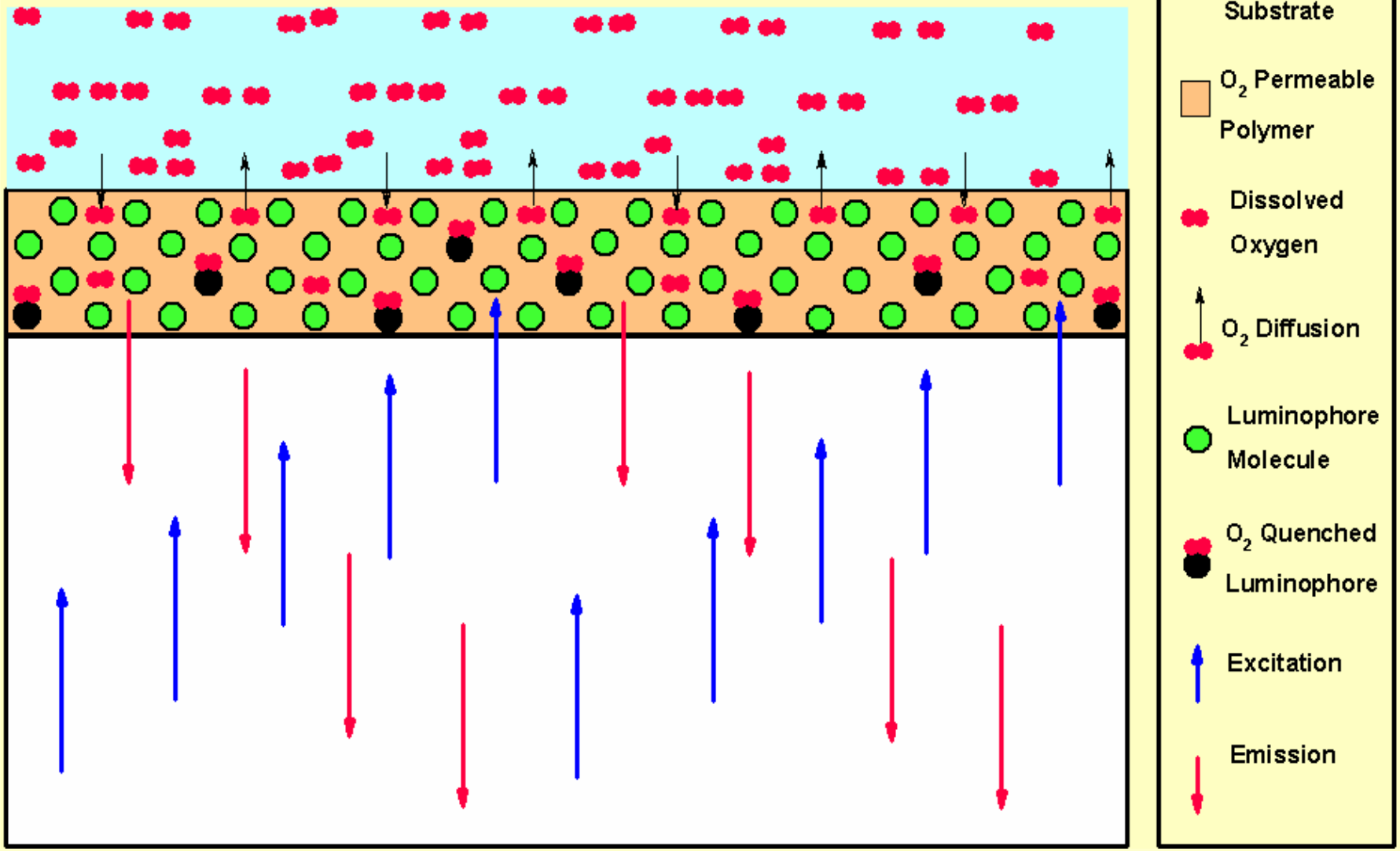
Luminescence-Based Oxygen Sensors

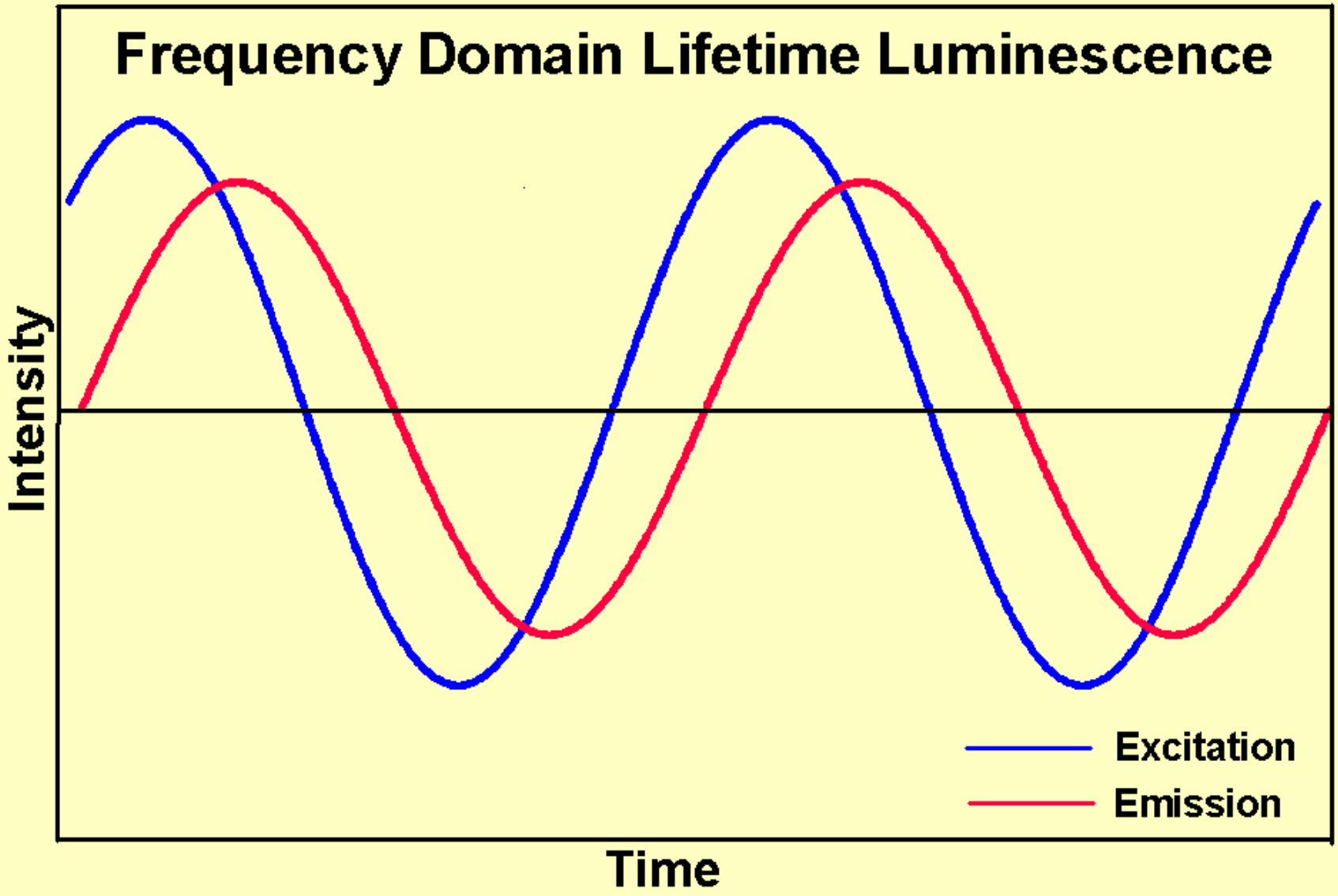
- Luminescence-Based Oxygen Sensors
  - Measures the light emission characteristics of a luminescent reaction
  - In the presence of oxygen the luminescence is quantitatively reduced or quenched
  - Dissolved oxygen concentration is inversely proportional to the luminescence lifetime of the light emitted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

Luminophore Structure

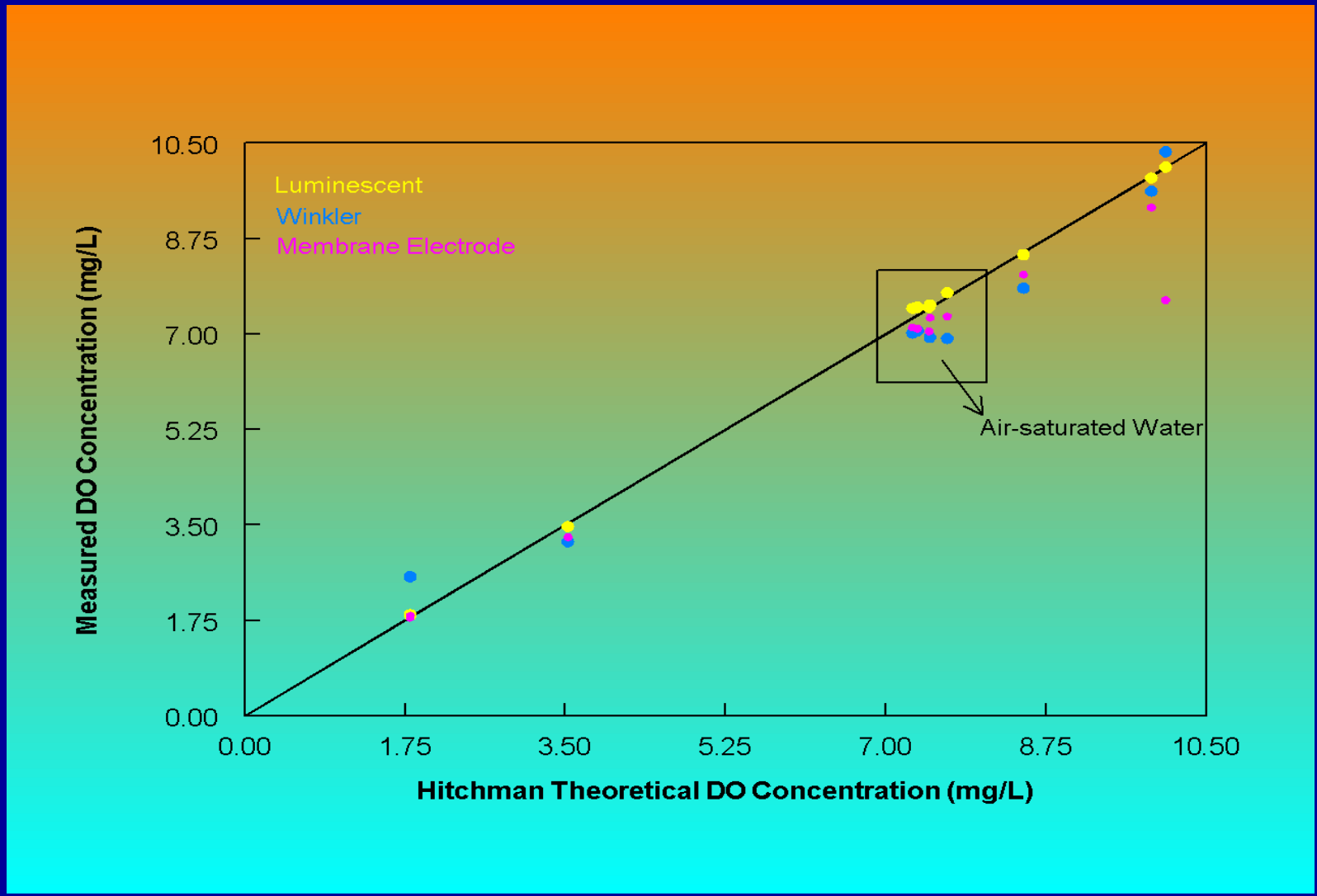


Luminescence Dissolved Oxygen Sensor

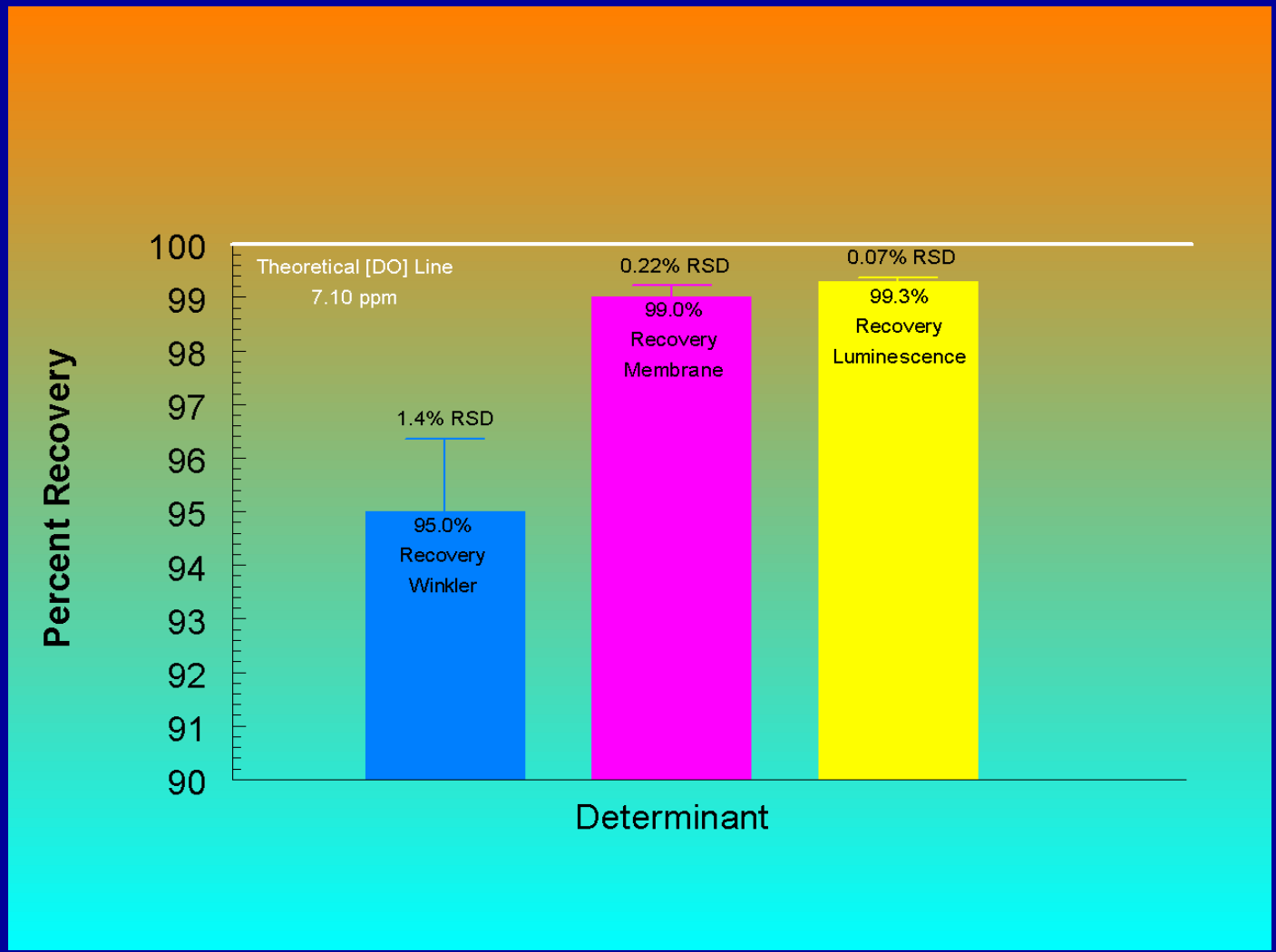



Frequency Domain Lifetime Luminescence
Intensity
Time
Excitation
Emission

Comparative Accuracy of DO Determinants

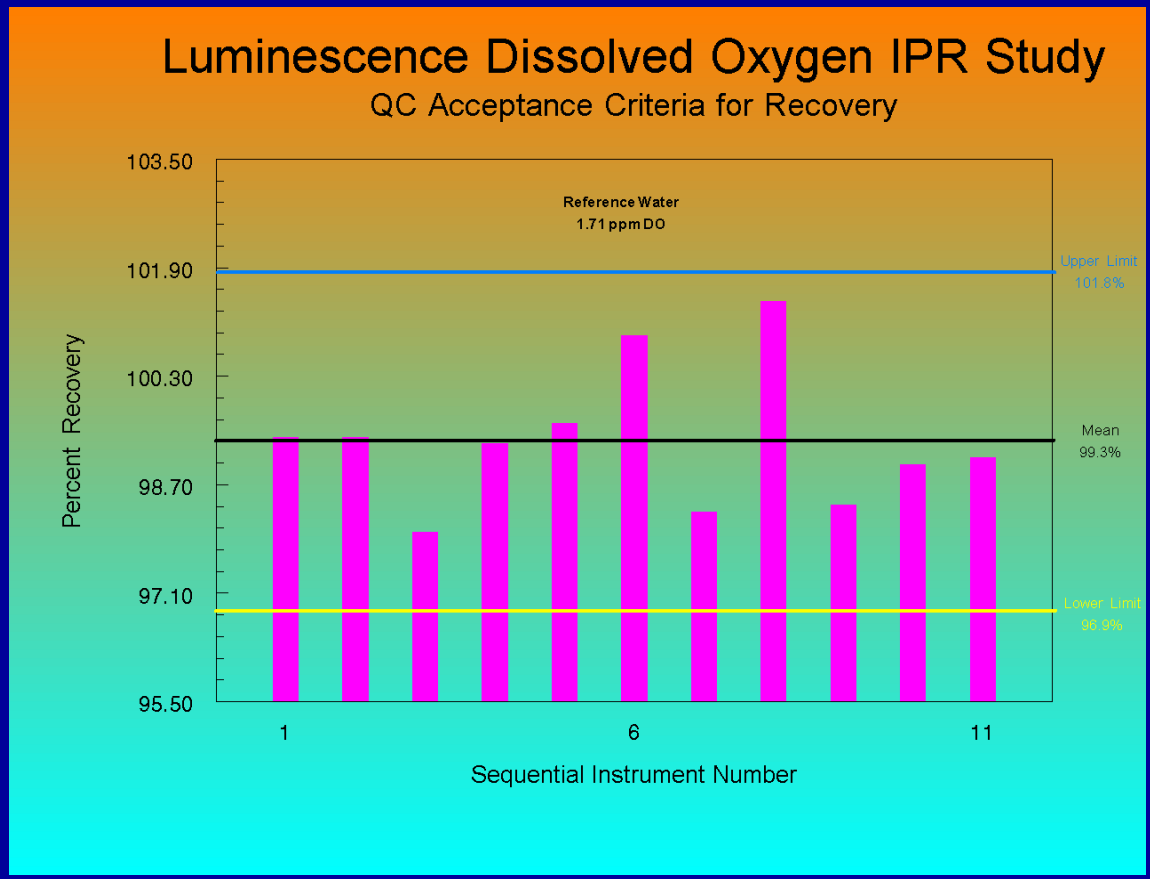


Comparative Precision and Accuracy of DO Determinants



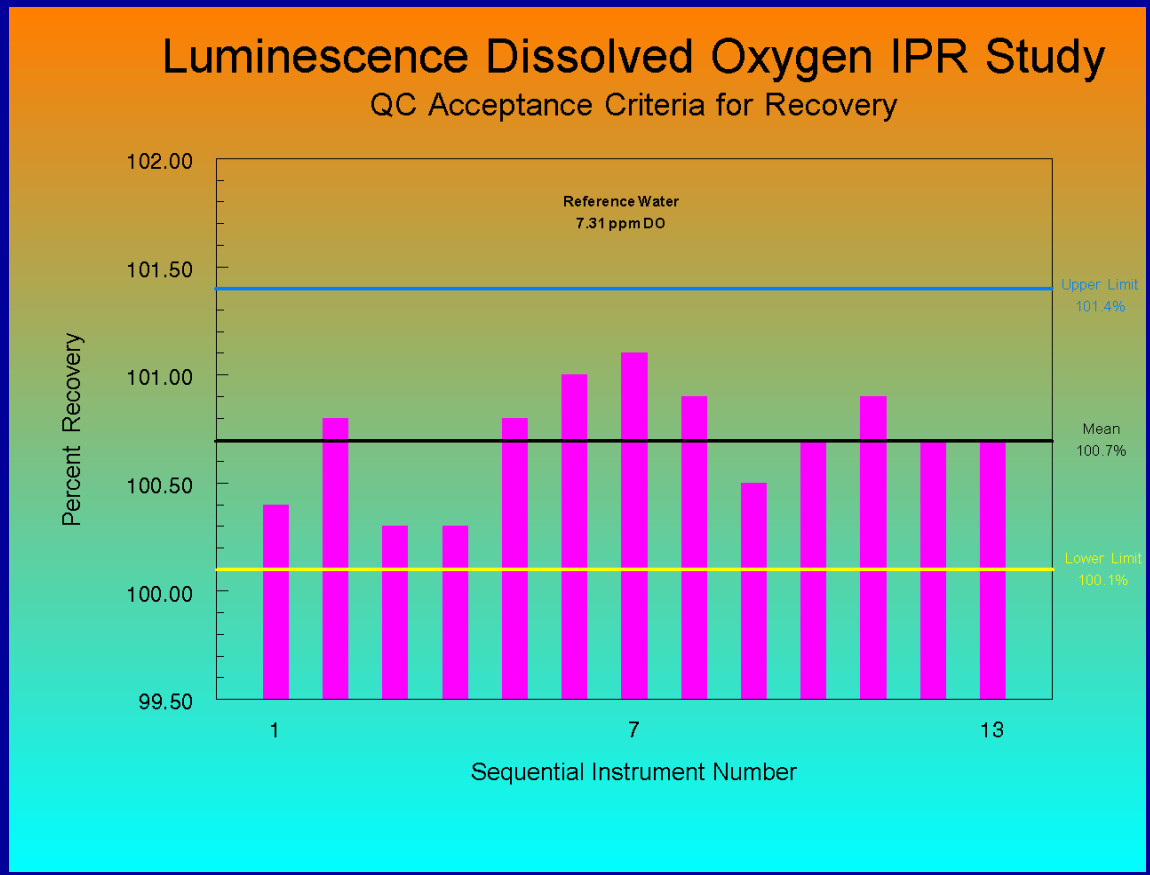
EPA Quality Assurance Acceptance Criteria for Precision and Recovery

- 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

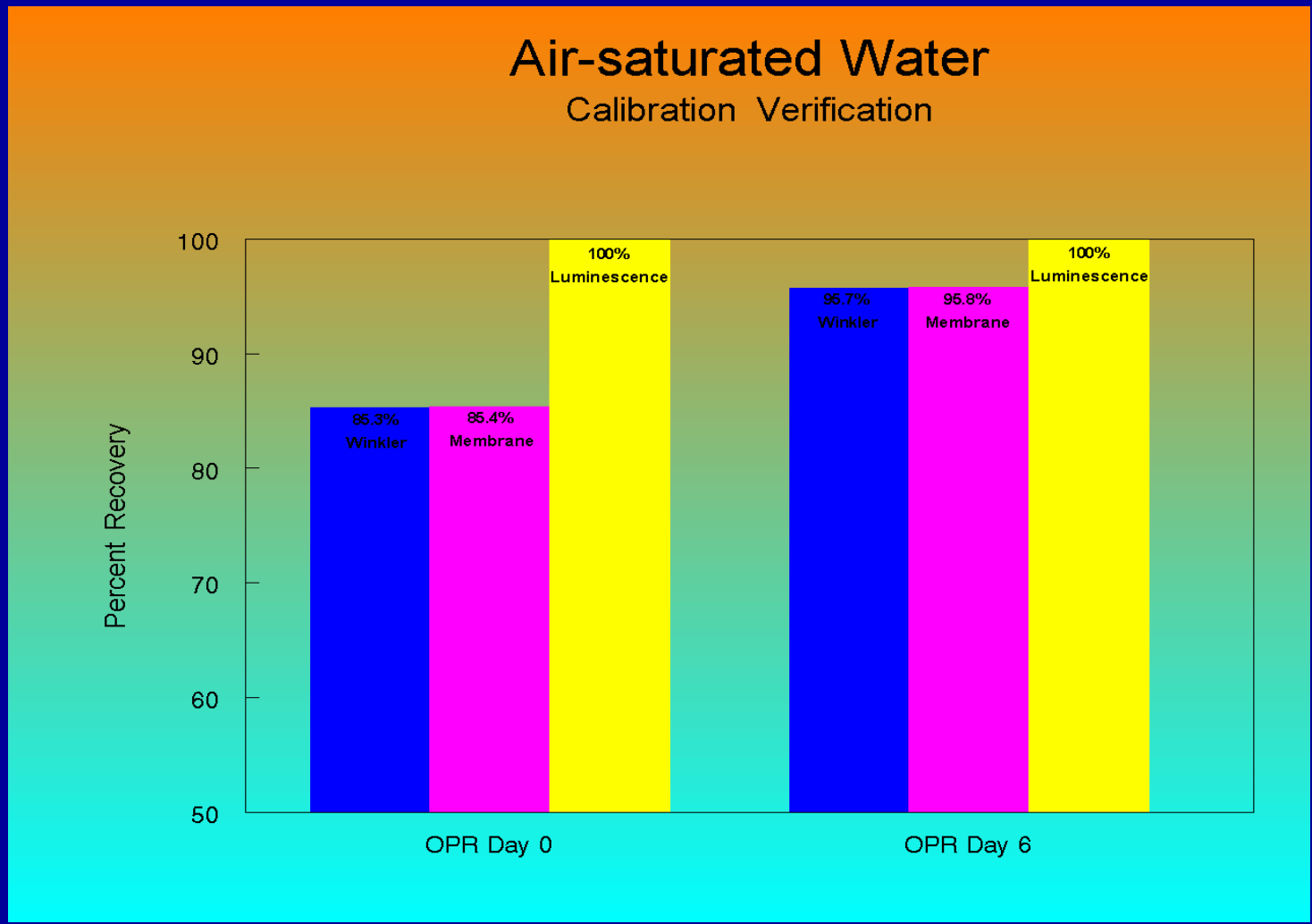
- Theoretical [DO] – 7.31 ppm
- Mean
  - 100.7%
- 95% Confidence Interval
  - 0.003
- % Lower Limit
  - 101.1%
- % Upper Limit
  - 101.4%



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



Standard Methods Quality Control Results for Biochemical Oxygen Demand