Comparing Performance of DO Methods in Water and Seawaters

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Electrochemistry Products

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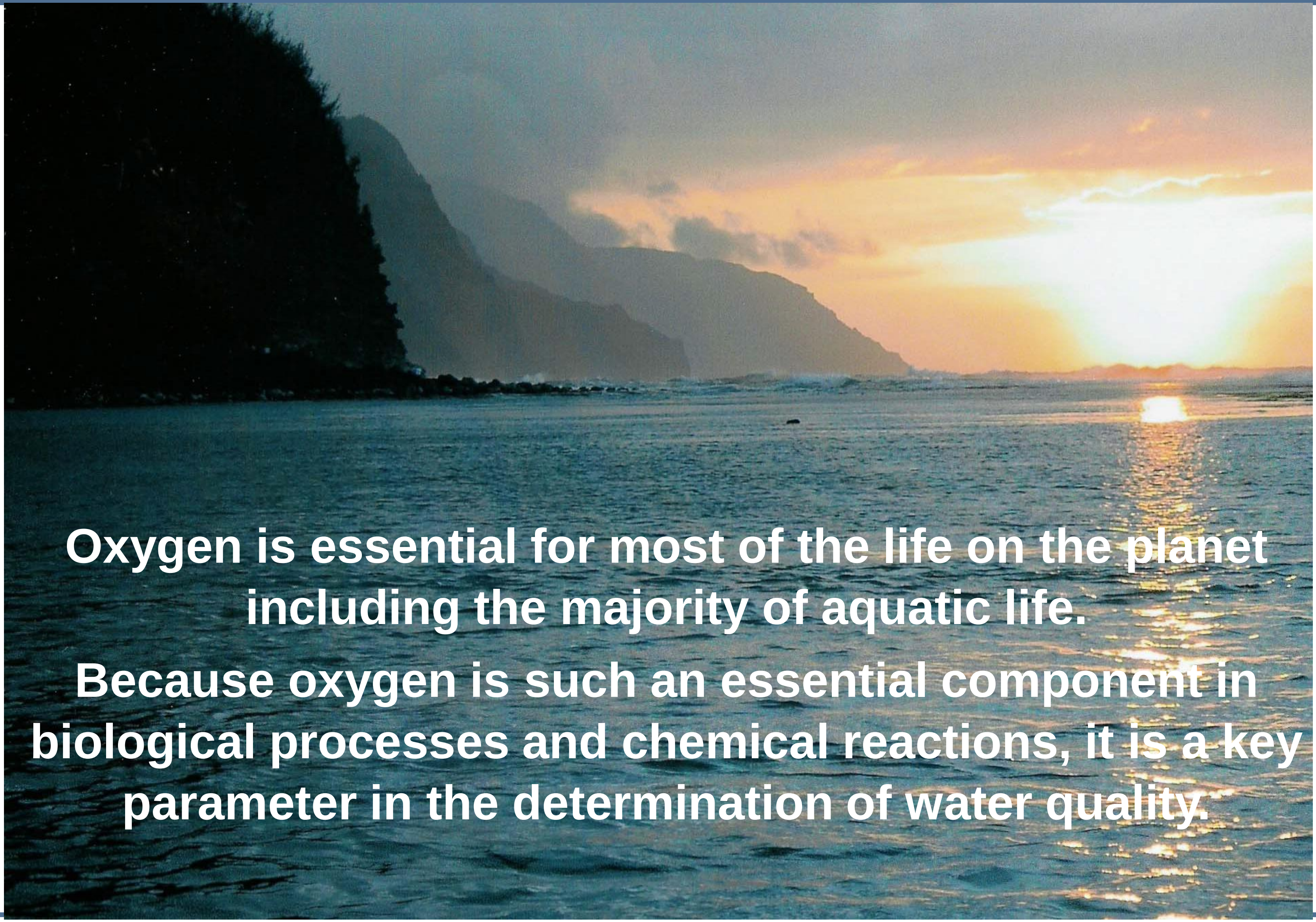
Dissolved Oxygen Measurement



Oxygen is essential for most of the life on the planet including the majority of aquatic life.

Because oxygen is such an essential component in biological processes and chemical reactions, it is a key parameter in the determination of water quality.

Winkler Method

With this method, dissolved oxygen first oxidizes manganese ions, which in turn react with iodide to produce iodine in an amount equivalent to the oxygen in the sample. The intensity of gold color in the treated sample will be proportional to the amount of iodine liberated in the reaction (and an indication of the amount of dissolved oxygen present).

The reaction is followed by titration with a standard reducing solution to measure of the amount of iodine and therefore the dissolved oxygen concentration.

Winkler Method

- Considered the "Gold Standard" DO measurement method by many agencies and is frequently used to check calibration of other methods.
- Not affected by seawater matrix
- Generally more time consuming, labor intensive, and expensive
- Subject to operator error
- Stability of the reagents is an issue
- Reagents' hazardous classification is an issue
  - Azide: poison
  - Hydroxide and sulfuric acid: corrosive
  - Proper disposal required
- Test is destructive – the sample can not be used for further testing.

Electrochemical or "Clark" Method

A reduction reaction utilizing two metal electrodes (cathode and anode) in contact with supporting electrolyte and separated from the test solution by a gas permeable membrane.

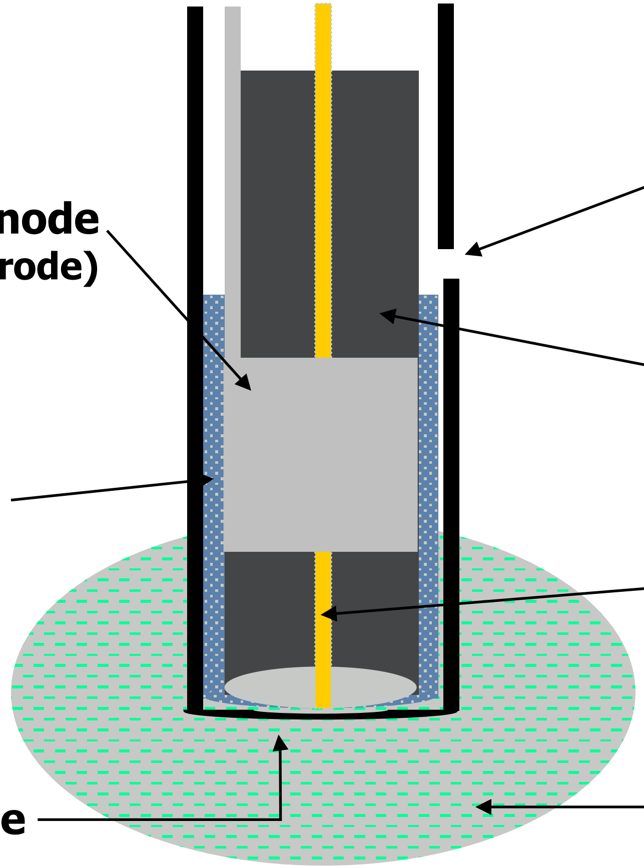
Oxygen diffuses through the gas permeable membrane and is reduced at the cathode by a constant voltage placed across the cathode and anode.

The DO value is determined from the reduction reaction that produces a current flow directly proportional to the dissolved oxygen concentration.

Electrochemical or “Clark” Method

- Saves time, money, and labor
  - No reagents or wet chemistry titration preparation
- Field portable – measurement in situ
- Greater measurement accuracy
- No reagent stability or hazardous classification issues
  - No poisons or corrosives
  - No special disposal required
  - Exception: galvanic probes use hydroxide (corrosive) in small volumes

Overview: Electrochemical or "Clark" Method DO Probe



Oxygen crosses the gas permeable membrane at a rate directly proportional to the dissolved oxygen concentration.
The higher the dissolved oxygen concentration, the higher the current.

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Overview: Two Types of Clark Electrodes

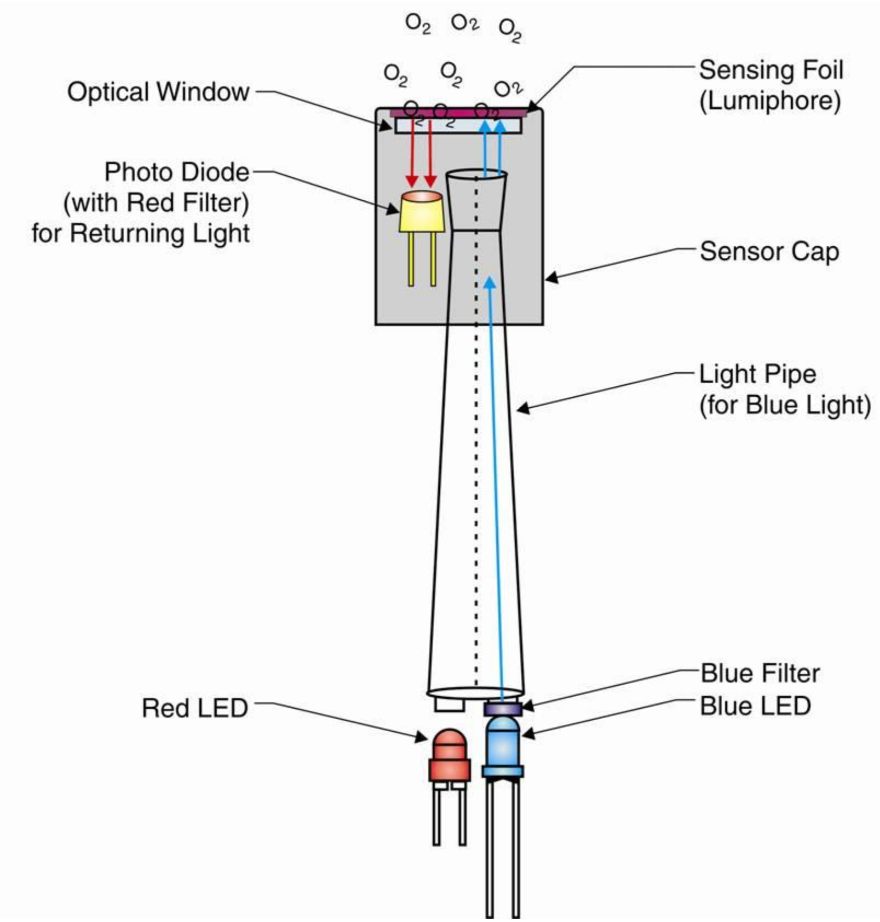
- Polarographic probe
  - Typically composed of a silver anode and a noble metal cathode (gold or platinum).
  - The electrolyte used as a bridge is KCl.
  - This electrode requires an outside power source to provide a voltage of 0.65 - 0.80 V for the oxygen reduction.
- Galvanic probe
  - Typically composed of a lead anode and a silver cathode.
  - The electrolyte used as a bridge is KOH.
  - Due to the dissimilar metals used for the anode and cathode, this electrode produces its own voltage.

Polarographic and Galvanic probes are not cross-compatible between meters.

Considerations When Using the “Clark” Method DO Probe

- **Barometric pressure**
  - Dissolved oxygen concentration affected by barometric pressure change
  - Potential error with weather fluctuation and elevation change -Reduced to <0.5% when automatic correction sensor is built into meter
- **Sample Stirring**
  - Oxygen is consumed at the cathode and must arrive at the sensor faster than it can be consumed
  - Stirring is necessary to avoid oxygen depletion at the membrane
- **Temperature**
  - DO levels and diffusion rates change with temperature
  - Temperature compensated probe design will correct for temperature effects
- **Salinity**
  - Presence of salts diminish the potential of water to hold oxygen
  - Potential error is reduced by automatic or manual salinity correction factor
- **Interfering gases**
  - Sulfide, sulfite (galvanic), chlorine, nitrous oxide
- **Probe maintenance**
  - Membranes and Electrolyte; as well as Cathode and Anode Cleaning

Optical / Luminescence Method



A blue LED in the RDO® emits a light that causes the lumiphore molecules embedded in the gas-permeable sensing foil to react, emitting red photons.

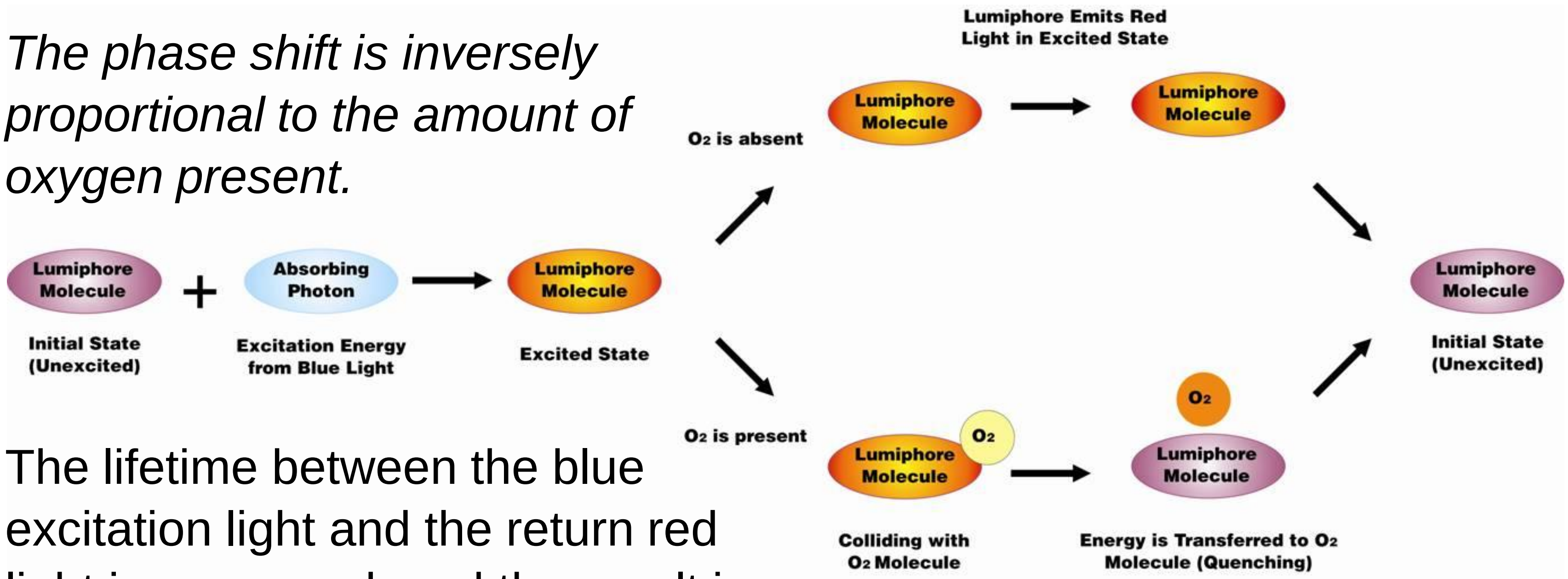
The sensor then measures the "phase", or delay, of the returned signal compared to the excitation signal.

This dissolved oxygen measurement is based on luminescence "lifetime" rather than "intensity".

Optical / Luminescence Method

The presence of oxygen in the foil quenches luminescence (blue light photons) and causes a phase shift in the return signal, detected by the photodiode.

The phase shift is inversely proportional to the amount of oxygen present.



The lifetime between the blue excitation light and the return red light is measured, and the result is used to quantify the dissolved oxygen present.

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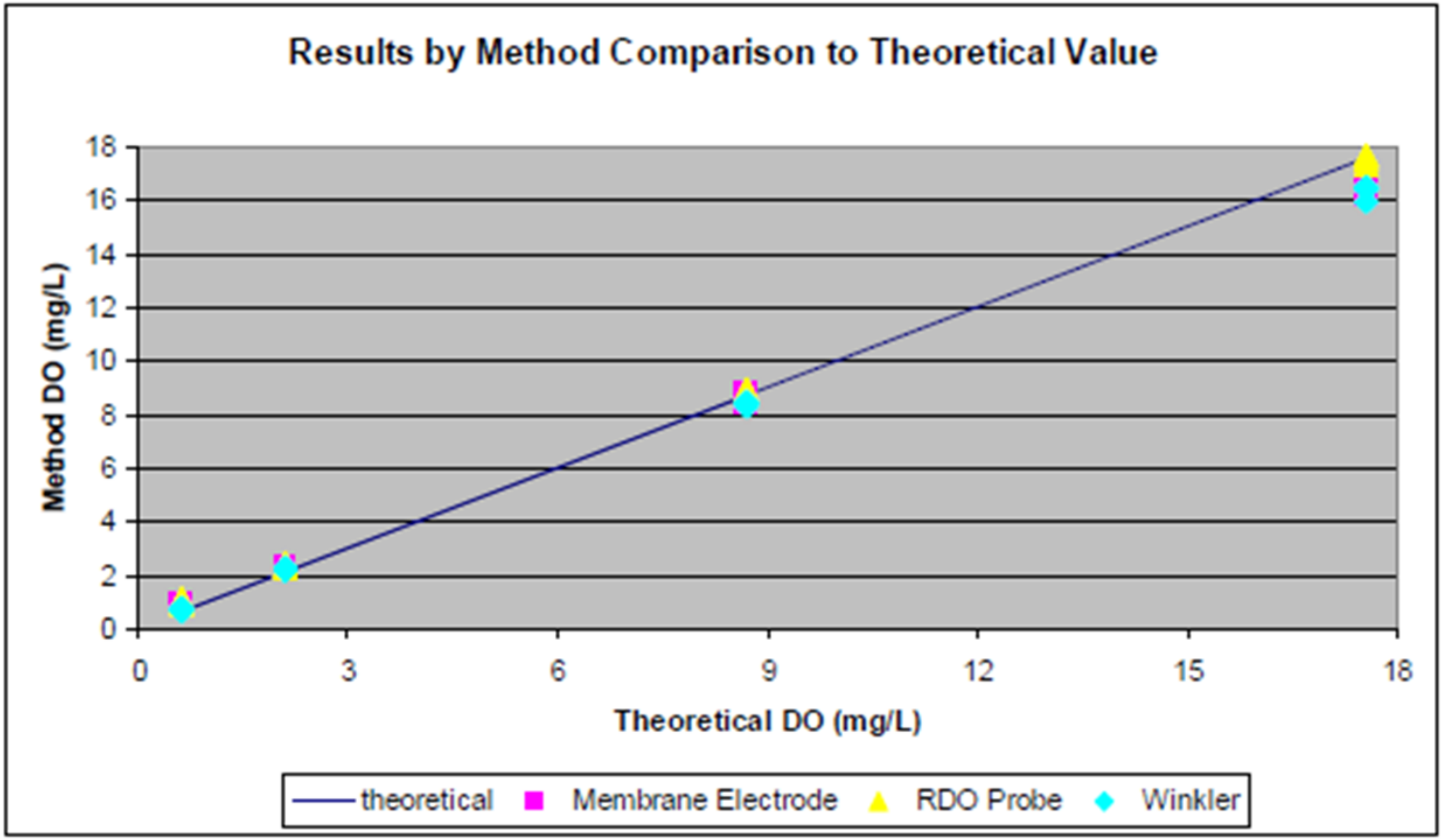
Optical / Luminescence DO Method

- **Accuracy and Precision equal to or better than Winkler or Clark DO Methods**
- **Fast Response**
  - **Polarization or warm-up time not required… is ready to take readings immediately**
  - **Highly sensitive lumiphore obtains readings quickly**
- **Improved Accuracy for Low Level Oxygen Measurements**
- **Elimination of Stirring for oxygen flow across sensor**
  - **Oxygen is not consumed by a measurement reaction**
- **Reduced Measurement Interference**
  - **Lumiphore Sensing Technology is specific to Oxygen**
  - **Measurement Unaffected by Color, Turbidity, Sulfides**
- **Elimination of Electrical Interference Issue**
  - **Works well in electrically busy areas-Cable length does not affect performance**
- **Reduced maintenance costs and time commitment**
  - **No membranes to change-No electrolyte solution**

Comparing Results by the Various DO Methods



There is good agreement between the three test methods and all results agree well with the expected DO concentration.

Method Performance in Seawater

	Surface			
	Dissolved Oxygen			Temperature
	Average (mg/L)	Standard Deviation	% CV	Average (oC)
Polarographic Probe	8.49	0.155	1.80%	12.9
RDO Probe	8.78	0.093	1.10%	13.5
Winkler Titration	8.57	0.067	0.80%	n/a

All method results are in agreement and are within 2% of the average DO measurement.


Thank you.