How Dissolved Oxygen Sensors Work

Principles and Practice in Water Quality Monitoring

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YSI

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How Sensors Work:
6-Part Series on Water Quality Monitoring

Once a week, we will discuss why it is important to monitor critical water quality parameters.

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Recording available

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June 16th

June 23rd

Recordings Available

Miss the earlier presentations?
Don't Worry!

- How Anti-Fouling Works
- How Algae Sensors Work
- How Turbidity Sensors Work
- How pH + ORP Sensors Work

www.xylem-analytics.asia

Anthony Rohrer

BACKGROUND

BSc Chemistry
University of Illinois

- Associate Product Manager for the WQS product line
- >1 year at YSI
- 6 years in the specialty chemical industry (product management and R&D)

Overview

I. Why Monitor for Dissolved Oxygen?

II. Evolution of Dissolved Oxygen Monitoring

III. Principles: How Dissolved Oxygen Sensors Work

IV. Practice: Real-World Monitoring

Why Monitor for Dissolved Oxygen?

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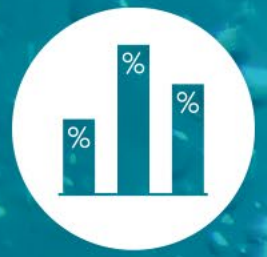
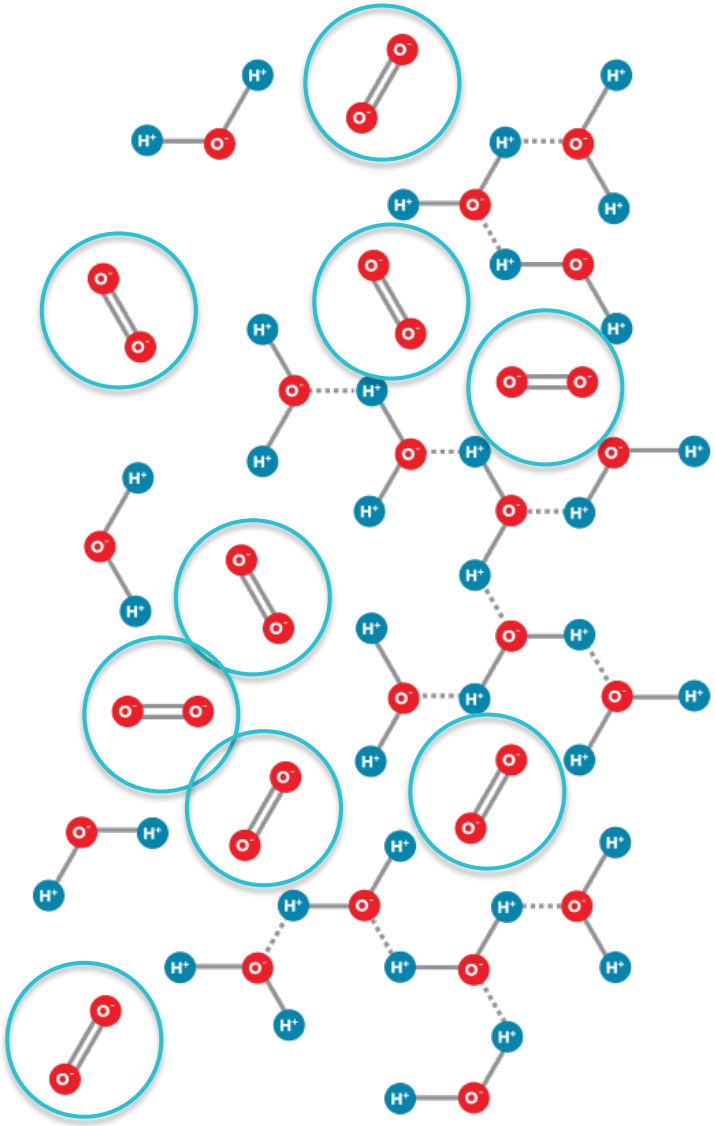


In which application do you typically measure DO levels?

1. Environment monitoring
2. Waste Water monitoring
3. Aquaculture
4. Other

What is Dissolved Oxygen (DO)?

- Required by most aquatic orgs to survive
- Source of oxygen is **NOT** H_2O
- Gaseous, molecular oxygen (O_2) from:
  - Atmosphere
  - Byproduct of photosynthesis
- Once dissolved, it is available for use by living organisms and can play a large role in many chemical processes

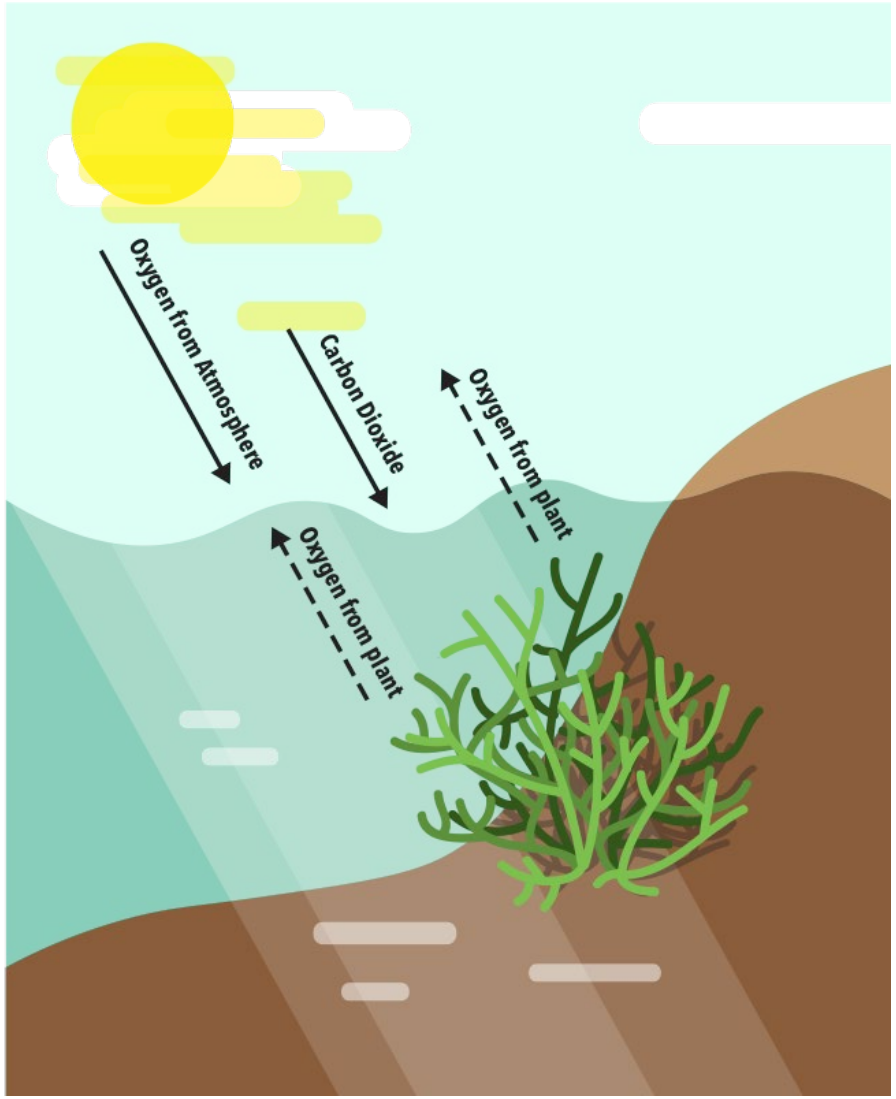


Sources of Dissolved Oxygen (DO)

- **Atmosphere**
  - Oxygen follows concentration gradient
    - Diffuses from air into water until water is completely saturated
    - System is in equilibrium when concentration of oxygen is the same in air and water
  - Aeration = mixture of water and air
    - Mixing causes increased levels of DO in water
    - Occurs anywhere water and air mix – waterfall, air stone, etc.

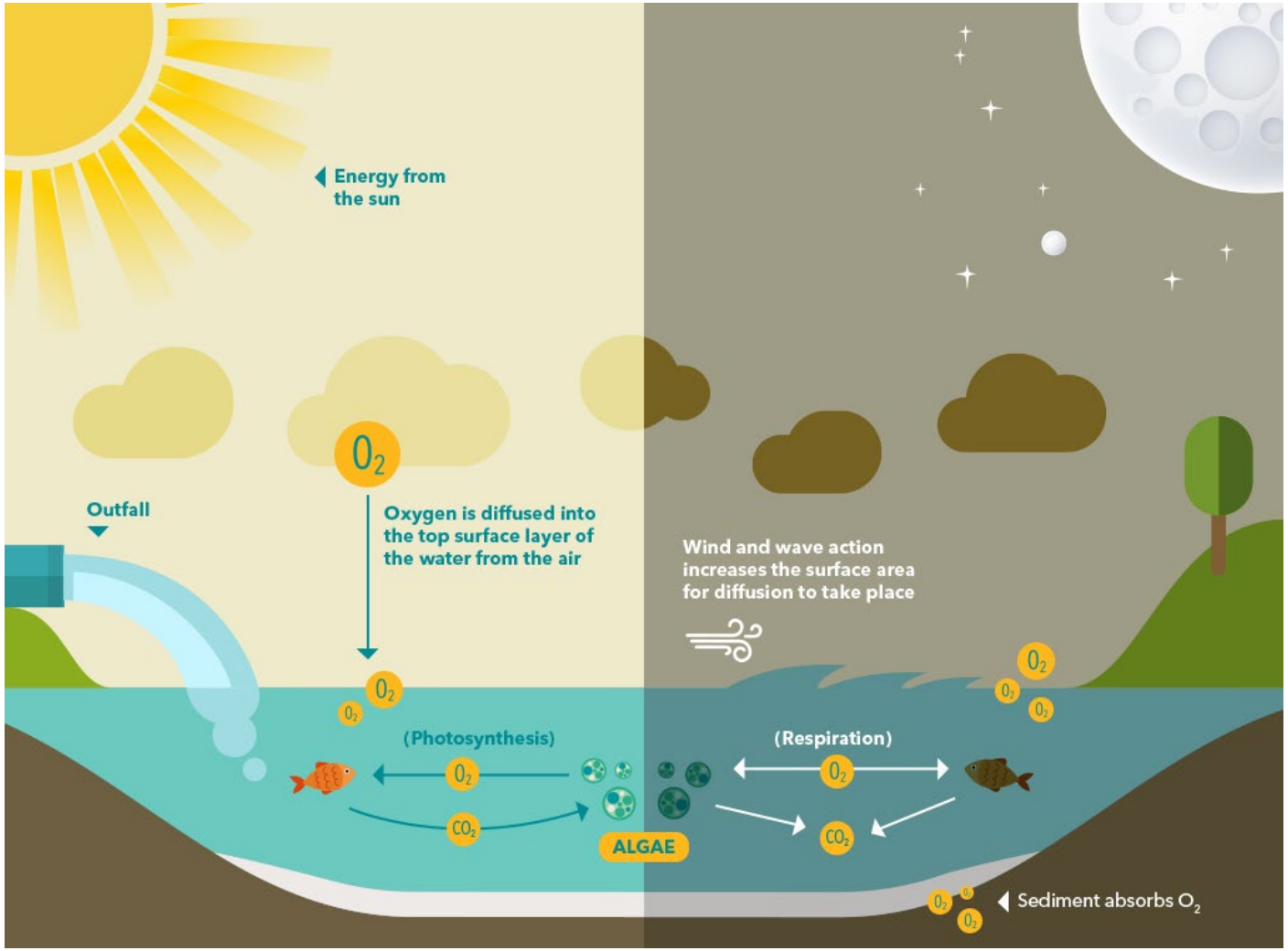
Sources of Dissolved Oxygen (DO)

- **Photosynthesis**
  - Process to generate and repair cells
  - Requires water, light energy, and carbon dioxide
  - Byproduct is gaseous, molecular oxygen



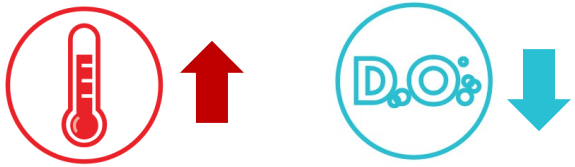
Sources of Dissolved Oxygen (DO)

- **Photosynthesis**
  - Plants & algae produce **and** consume oxygen during the day
    - Cells are performing respiration
  - Plants & algae can't produce oxygen during the night but they continue to consume it
  - Organisms like fish continuously consume oxygen
  - DO levels rise during the day, but fall at night



Environmental Variables

- **Temperature**
  - Most significant variable
  - Always measure temp in addition to DO!

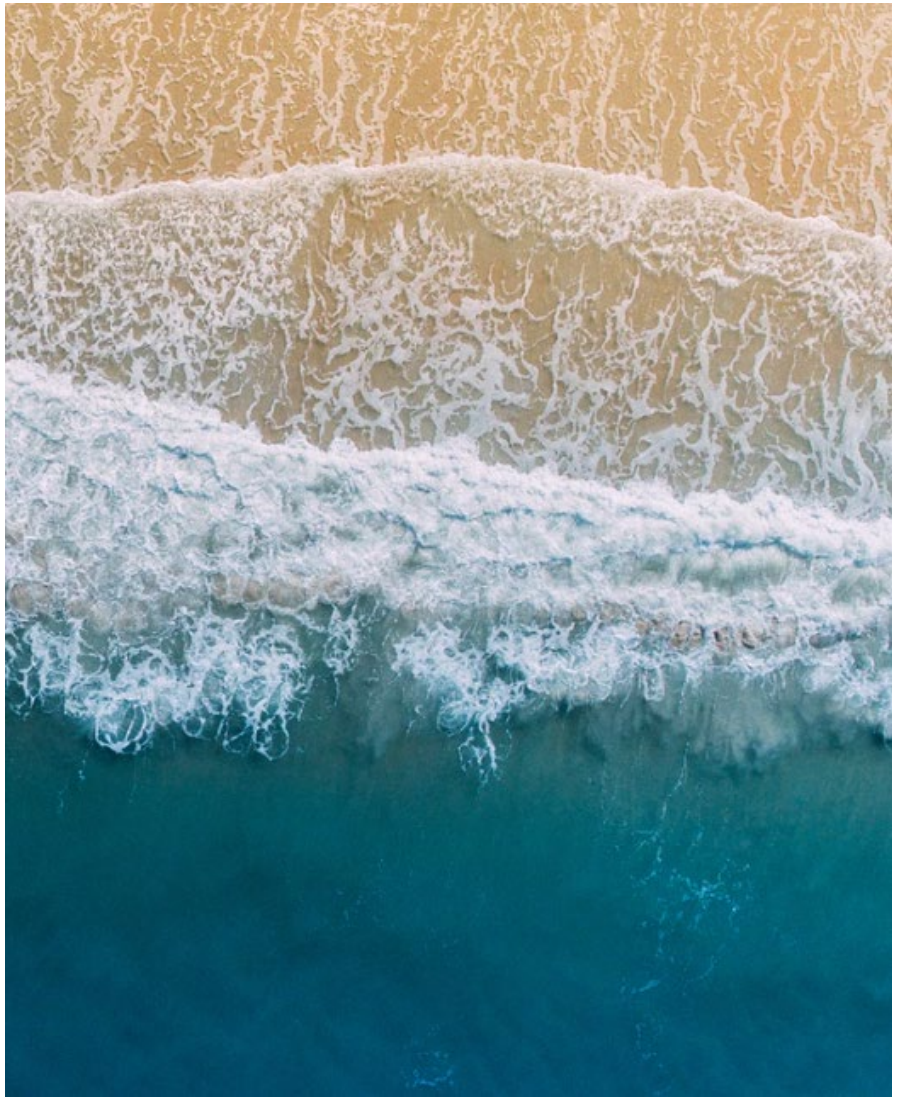


  - Diffusion through sensor membrane changes with temperature

Environmental Variables

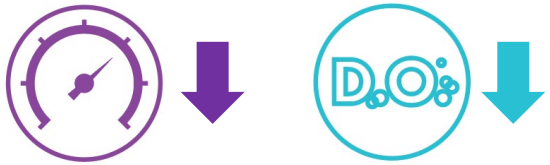
- **Salinity**

  - Seawater can hold about 20% less oxygen than freshwater
  - Measure salinity along with DO when in estuary, wetland, ocean
  - Most DO meters will automatically compensate for changes in salinity



Environmental Variables

- **Barometric pressure**



  - Higher altitude, lower pressure
  - Weather systems also impact pressure
    - Quick drop means a storm is on the way!
  - Most DO meters will automatically compensate for changes in pressure

DO Units

- **mg/L**: milligrams of DO per liter of water

- **DO%**: percent saturation
  - 21% of the atmosphere is oxygen
  - Pressure at sea level = 760 mmHg
  - Overall pressure attributed to oxygen:
    - 760 mmHg * 21% = 160 mmHg
    - Termed **partial pressure**

DO Units

- **DO%**: percent saturation
  - DO probe at sea level (760 mmHg) will calibrate to 100%
  - If not at 760 mmHg, probe will calibrate to DO% value less than 100%
    - Let's say pressure = 750 mmHg
    - 750 / 760 = 98.68%
    - Probe at this pressure will calibrate to 98.68%
  - DO% local function
    - Calibration value = 100% regardless of pressure at time of cal

DO Unit Comparison

- Barometric pressure is the only variable that impacts DO%

Pressure (mmHg)	Altitude (meters)	DO% Calibration Value
760	0	100
654	1254	86
502	3371	66

- mg/L is calculated from DO%, temperature, and salinity

Temp (°C)	DO mg/L when salinity = 0 ppt	DO mg/L when salinity = 18.1 ppt
10	11.29	10.06
25	8.26	7.46
45	5.93	5.41

Causes of Supersaturation

- Photosynthesis
  - Pure oxygen is produced!
  - Account for DO% values up to 500%
- Rapid temperature changes
  - If water temp quickly rises but oxygen can't "escape" quickly enough, DO concentration can be higher than what is expected in equilibrium conditions
- Other sources such as air stones

YSI Tech Note on Supersaturation

Why Monitor for DO in Surface Water?

- Direct indicator of water body's ability to support aquatic life
- DO level needed varies by species
  - Fish grow and thrive b/w 5-12 mg/L
  - **Hypoxia** occurs when DO level can no longer support organisms; 2 mg/L or lower

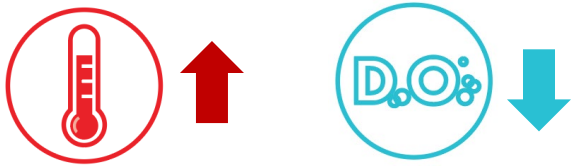
Why Monitor for DO in Surface Water?

- Imbalance of DO occurs in harmful algal blooms (HABs)
  - High photosynthetic activity during the day causes drastic increase in DO
  - Decomposition of algae results in consumption of DO
  - Hypoxia can result

Read about Red Tide monitoring efforts in the latest issue of Mission: Water

Why Monitor for DO in Surface Water?

- Thermal pollution is the dumping of hot or cold water by power plants, industrial manufacturers, etc.



- Fish kills due to suffocation as a result of influx of hot water

Why Monitor for DO in Surface Water?

- Road salt runoff increases salinity

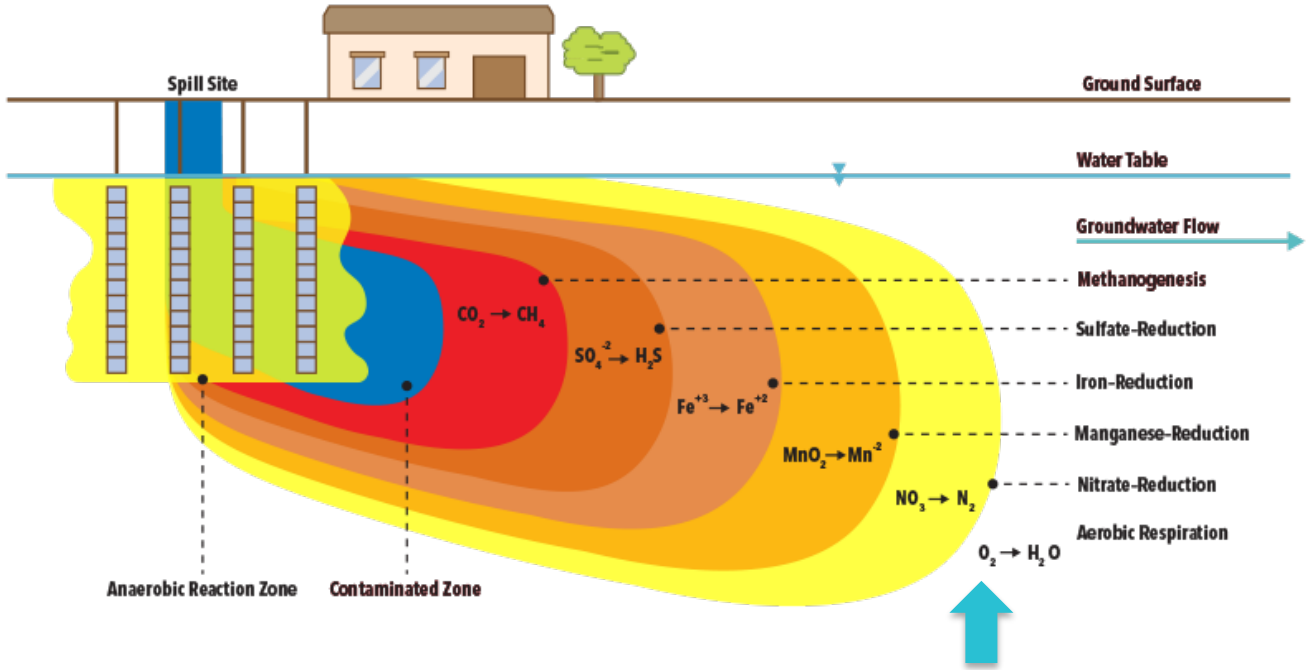
- Fish kills due to suffocation as a result of too much salt runoff

Why Monitor for DO in Groundwater?

- Helps determine when stable conditions are met during purging
- Monitor for artificial aeration when sampling
- Plays role in chemical reactions in the subsurface
  - Regulates valence state of trace metals
  - Constrains bacterial metabolism of dissolved organic species

Why Monitor for DO in Groundwater?

- Microbes use DO when degrading oil contamination
  - Microbes need to respire (breathe); requires an electron acceptor
  - Oxygen is the most preferred electron acceptor, carbon dioxide is the least
    - Oxygen is used up first! DO present only where there is no contamination
  - Distinct redox zones form as electron acceptors are used up by microbes
  - Process can occur in other environments, such as marine ecosystems



Adapted from Parsons, 2004

Why Monitor for DO in Wastewater?

- Waste is transformed into harmless end products by microbes
  - Microbes in process rely on DO to survive
  - In activated sludge process (ASP), air is pumped into aeration tanks that are filled with microbes suspended in water

Why Monitor for DO in Wastewater?

- Effluent must contain limited amount of nutrients
  - Biological Nutrient Removal (BNR) processes remove nutrients
  - BNR requires VERY strict conditions; anerobic, anoxic, and aerated zones

Evolution of Dissolved Oxygen Monitoring

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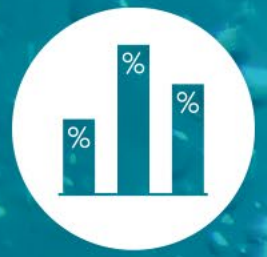
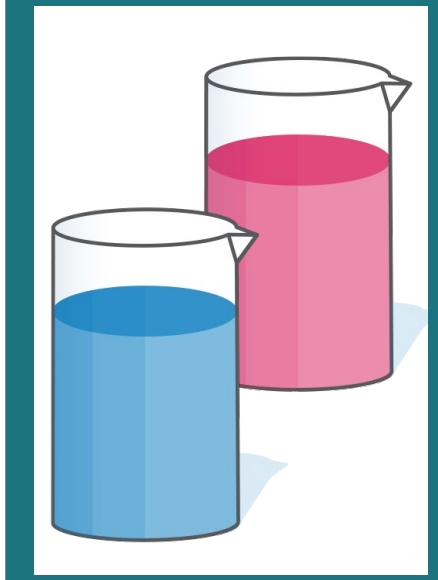


What method you preferably use to measure DO?

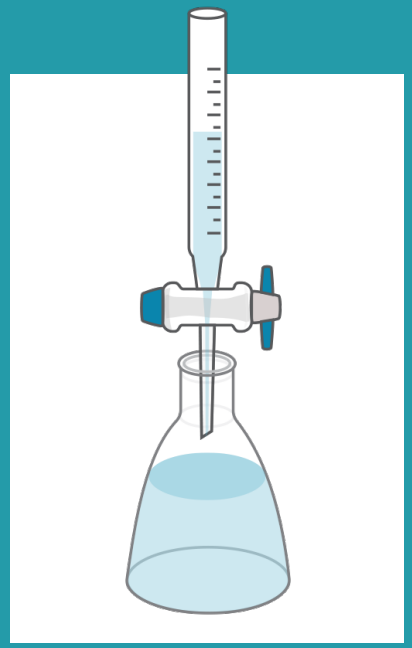
1. Wrinkler Titration
2. Colormetric
3. Diaphragm electrode
   (Galvanic or Pologra phic sensor)
4. Optical or Luminescent sensors

Measurement Methods

Colorimetric



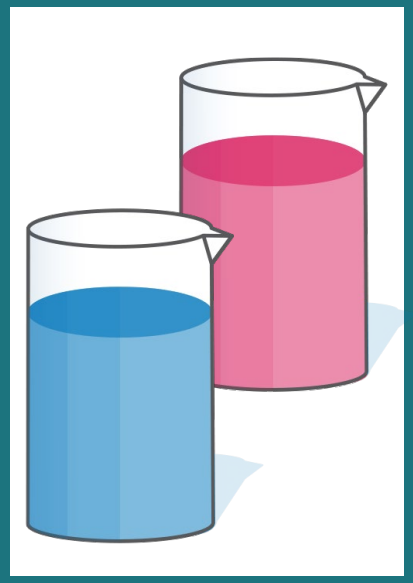
Winkler Titration



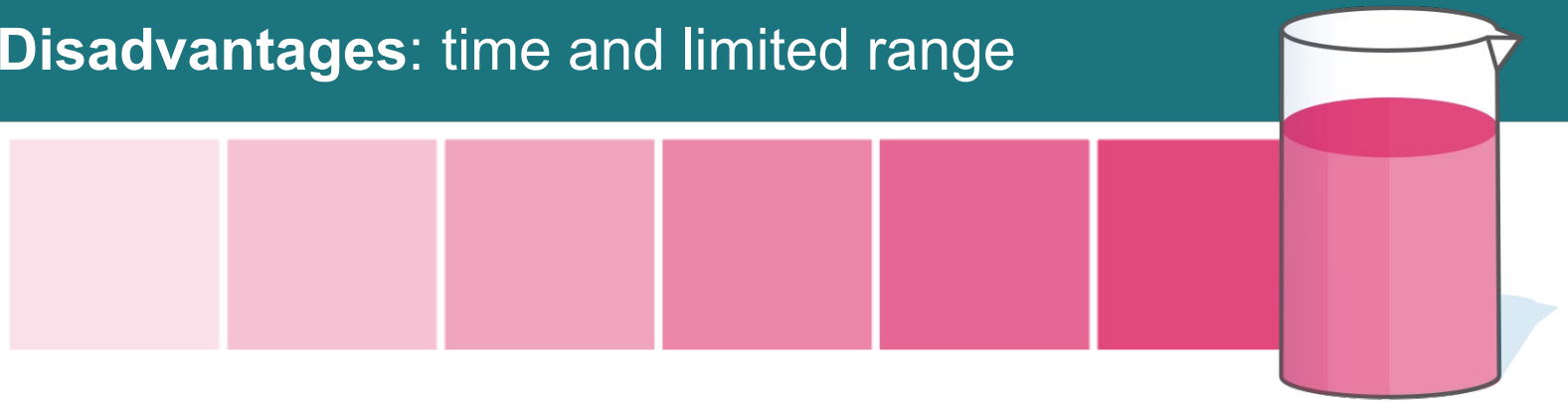
Electrochemical Sensors

Optical Sensors

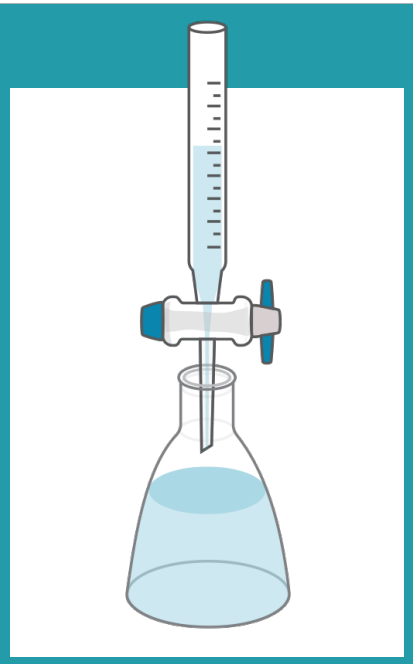
Colorimetric



- Colorimeters = filter photometers
- Sample and reagent are mixed
- Light passes through solution and a colored filter onto a photodetector
  - Filters are for a specific wavelength
  - Light is absorbed if target species present
- Two colorimetric methods - Indigo Carmine and Rhodazine D
- **Disadvantages**: time and limited range



Winkler Titration



- DO in sample is “fixed” by adding a series of reagents
- Endpoint is where a color change occurs
- Many SOPs still call for a Winkler Titration
- Often requires three samples; results are averaged
- **Advantage**: Accurate at low concentrations
- **Disadvantages**: Time-consuming and VERY easy to mess up

Electrochemical Sensors

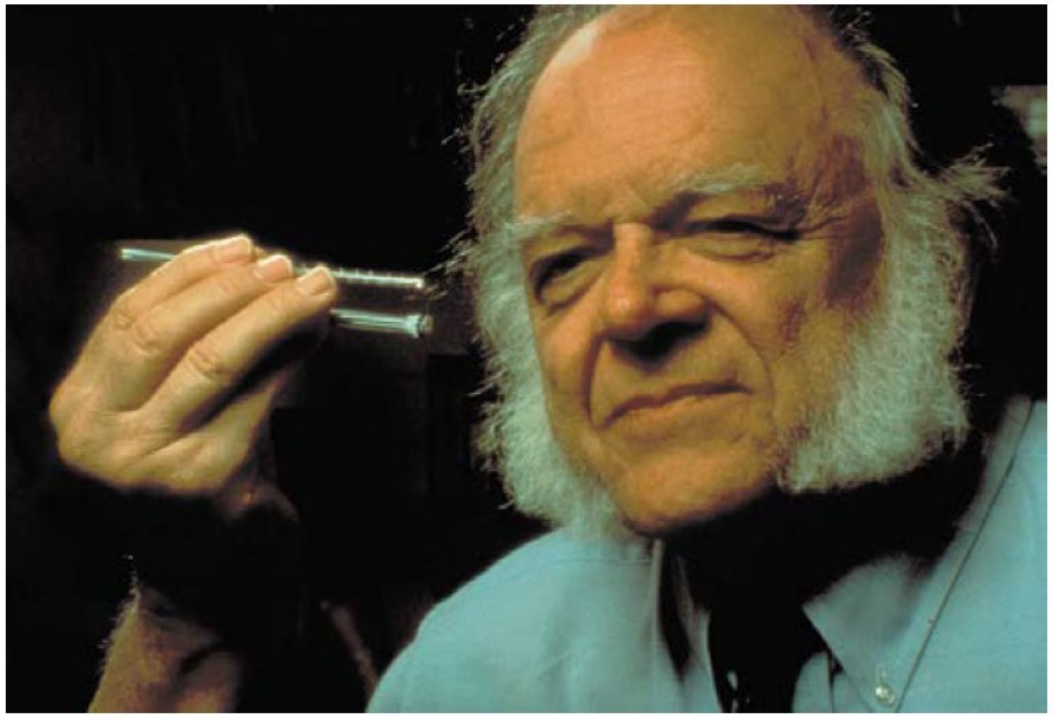
- Sensor submerged directly in water or larger sample aliquot
- Oxygen diffuses through membrane and is consumed during measurement
- **Advantages**: Very fast response, wide measurement range
- **Disadvantage**: Requires sample movement over membrane!

Optical Sensors

- Sensor submerged directly in water or larger sample aliquot
- Light causes sensing element to glow
- Oxygen affects lifetime and intensity of luminescence
- **Advantages**: No stirring required, very little maintenance, high accuracy, stable
- **Disadvantage**: Slightly slower response time

Evolution of Dissolved Oxygen Monitoring: Summary

- Photometers require mixing of a reagent and have limited range
- Winker Titrations are difficult; it doesn't take much to mess them up!
- Electrochemical sensors have been around for a long time and are still used
- Most modern instruments feature optical sensors



How Dissolved Oxygen Sensors Work: Principles

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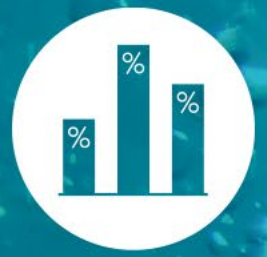
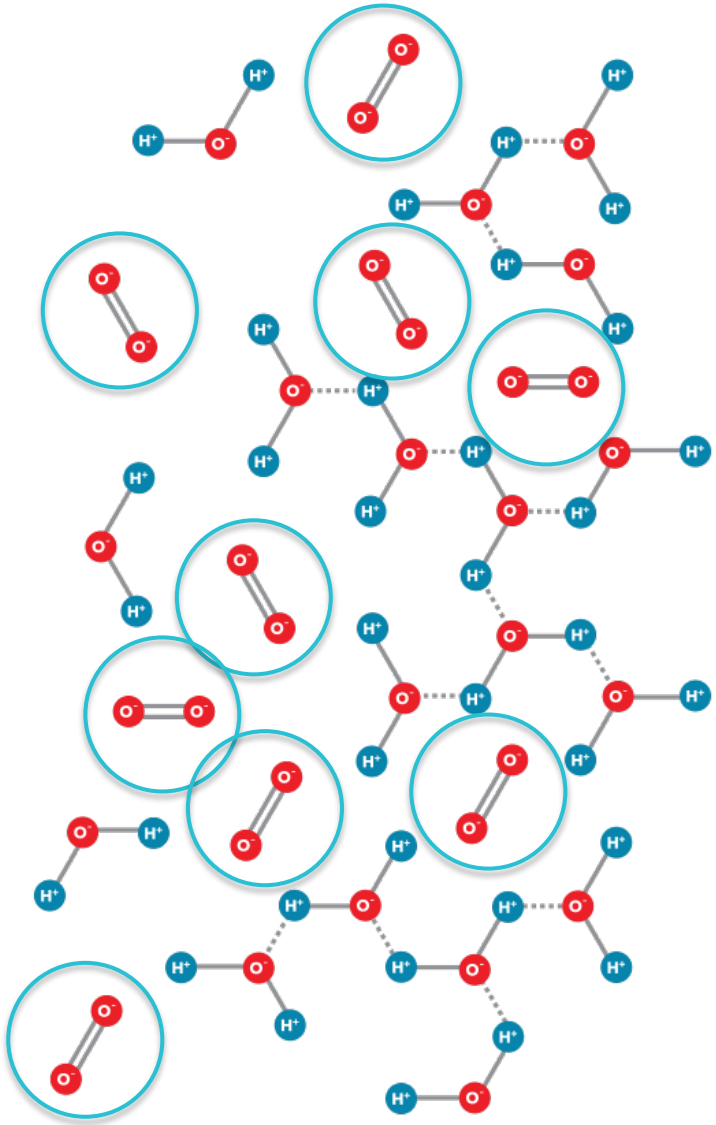


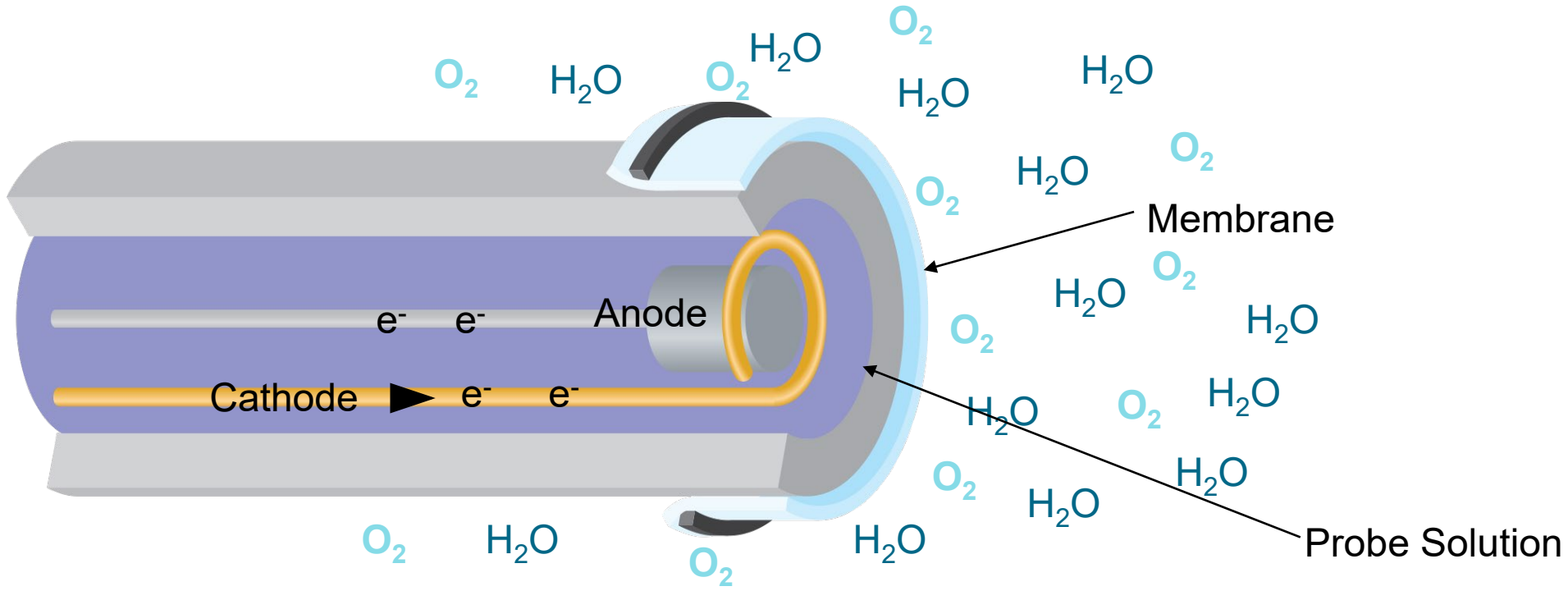
Which webinars in this series have you watched besides this one? Select all that apply.

What Does a DO Sensor Measure?

- Measure the pressure of oxygen that is dissolved in the sample
  - Expressed in DO%
- Barometric pressure is the only variable that impacts DO%
- mg/L is calculated from DO%, temperature, and salinity



Electrochemical Sensors



- Oxygen diffuses through membrane
- Oxygen reduced (consumed) at cathode
- Electrons flow = electrical signal
- Oxygen conc. proportional to signal level (mA)

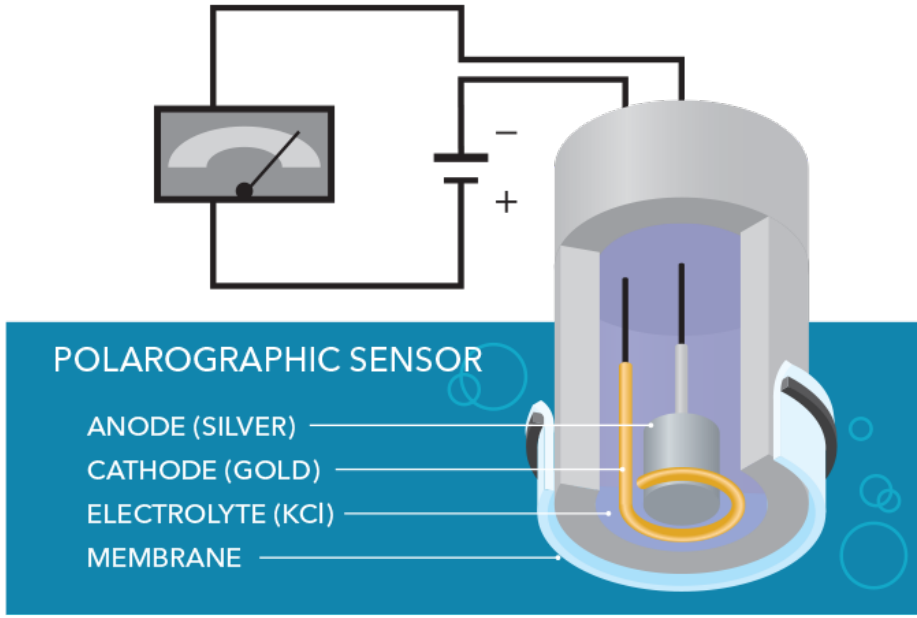
Comparison of Electrochemical Sensors

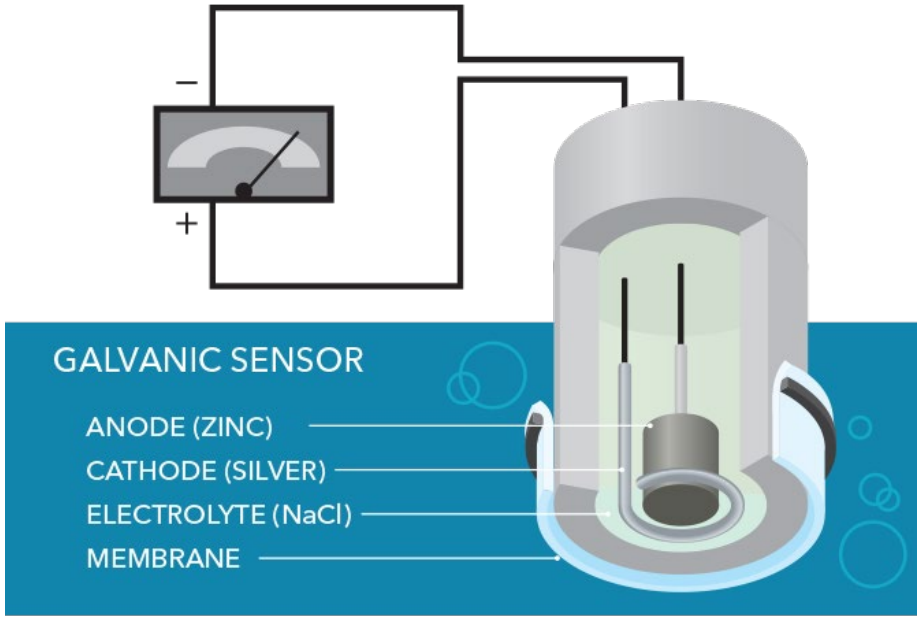
Polarographic

- Silver anode and gold cathode
- These materials require the probe to polarize (warm up) before use
- Probe is not “used up” when the meter is off

Galvanic

- Zinc anode and silver cathode
- These materials allow the probe to always be on
- No warm up required, but it also means the probe is “used up” faster

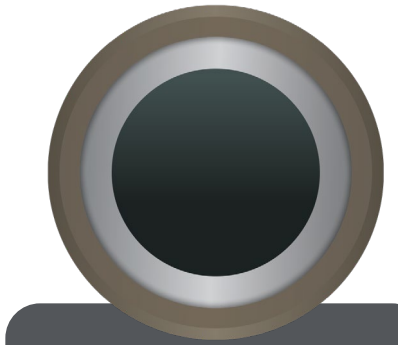




Available Sensors

EXO™
Continuous Monitoring

ProDSS
Spot Sampling



ODO
Sensor

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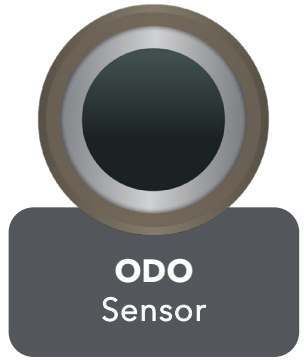
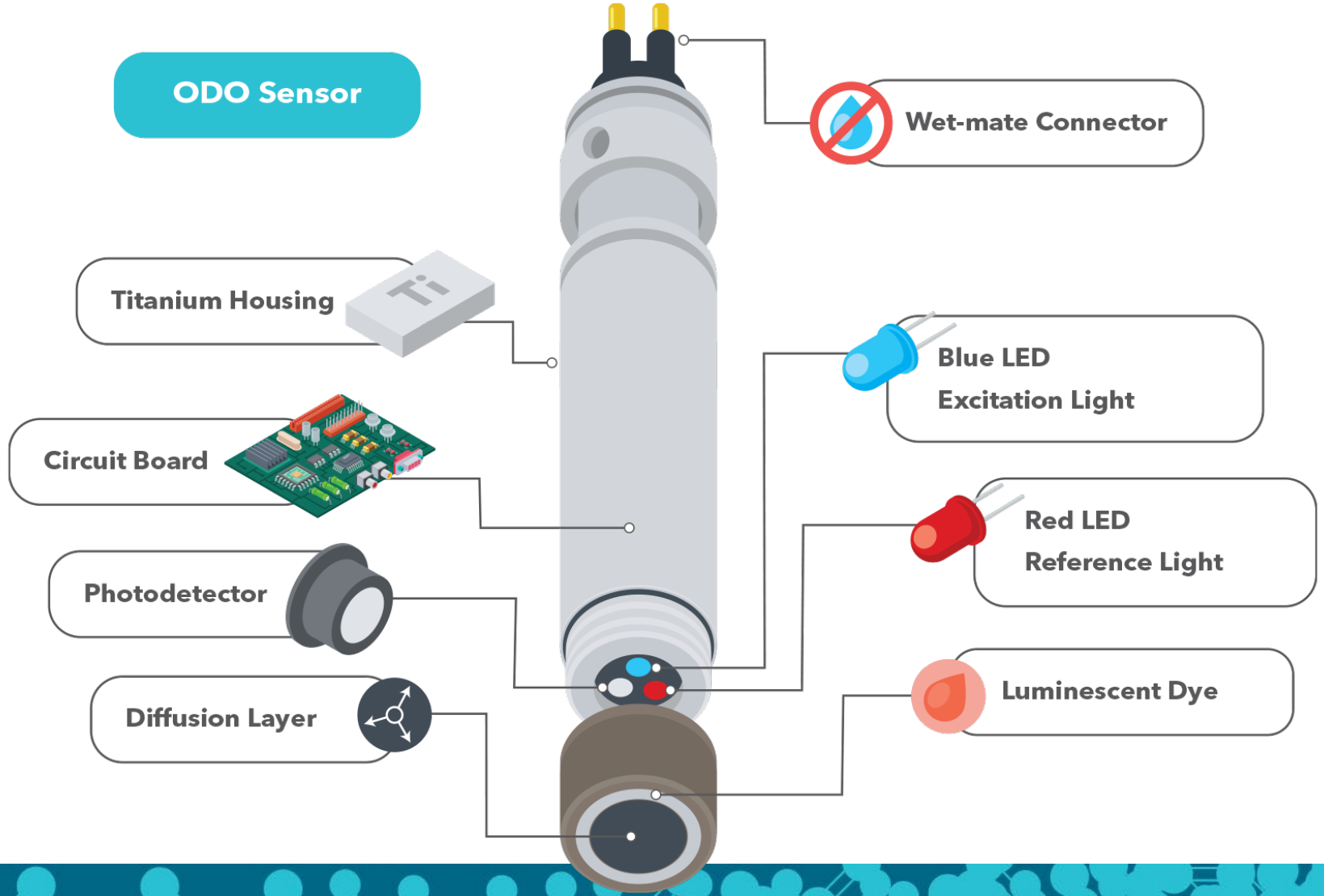
Anatomy of YSI's Optical DO Sensor





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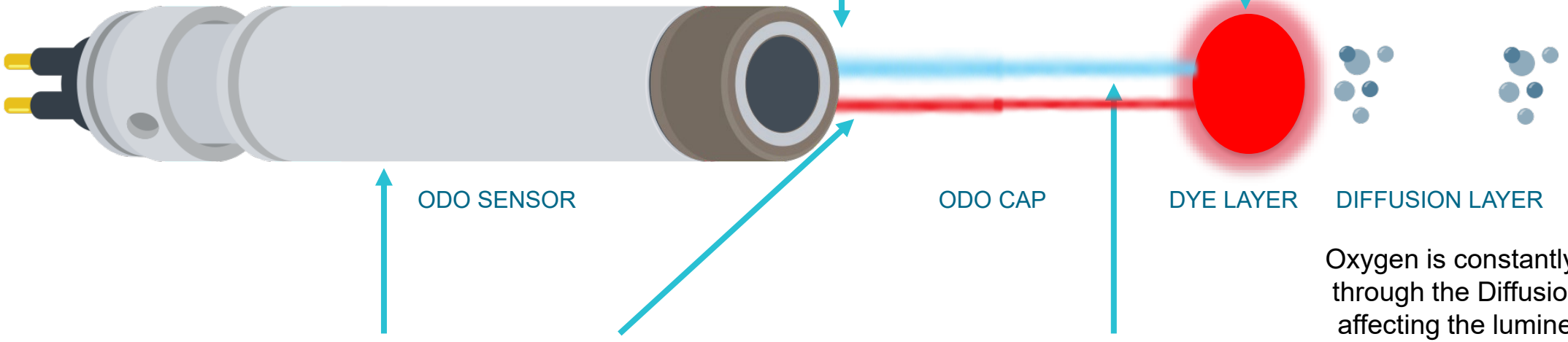
Optical Dissolved Oxygen Sensors



The lifetime of the luminescence is measured by the sensor and compared against the reference and a stable dissolved oxygen concentration is calculated.

The amount of oxygen passing through the sensing layer is inversely proportional to the lifetime of the luminescence in the sensing layer.

Oxygen is constantly moving through the Diffusion Layer, affecting the luminescence of the sensing layer.

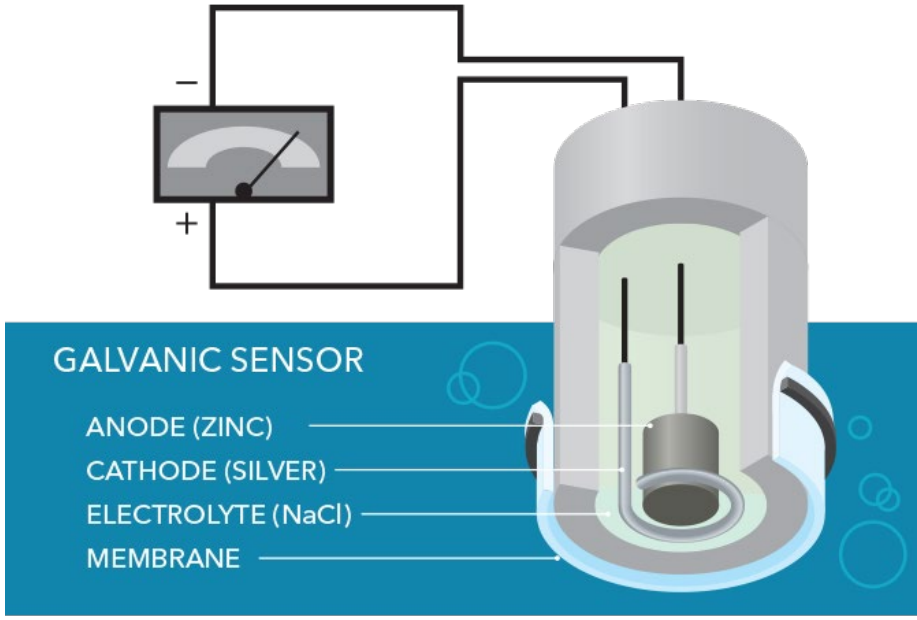
Sensor Cap Coefficients

- Sensor firmware stores coefficients for the sensor cap
- Coefficients allow for linear output from the sensor
- These coefficients are what allow YSI to give you the highest-accuracy sensor
  - Always update coefficients when changing a cap

Comparison of Electrochemical and Optical

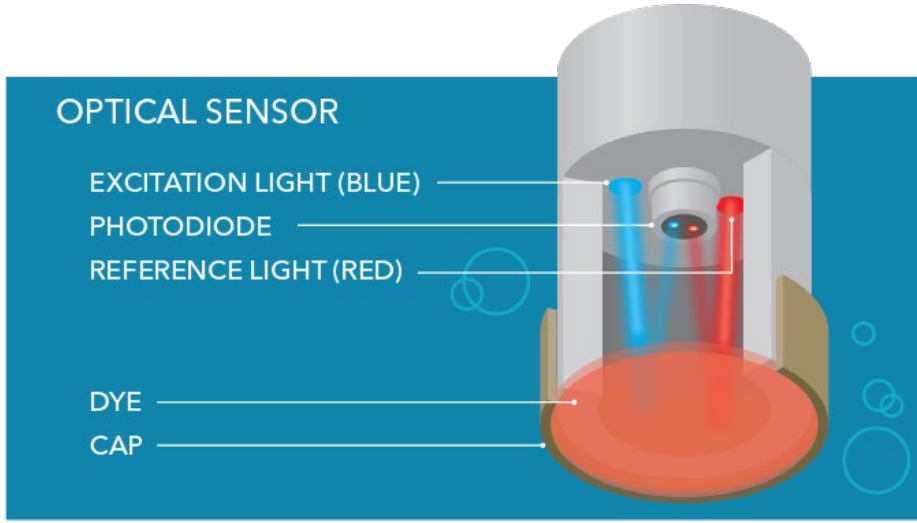
Electrochemical (Polarographic or Galvanic)

- Consumes oxygen; sample movement across membrane is required
- Membranes need to be changed every ~6 weeks
- Fast response (stabilization) time
- Calibrate every day
- Some gases (hydrogen sulfide) can interfere



Optical

- No stirring required
- Less maintenance; change cap every 12-24 months
- Slower response (stabilization) time
- Better accuracy in typical DO range
- Calibration is much more stable; they drift less
- Alcohol and organic solvents can damage materials in the cap



How Dissolved Oxygen Sensors Work: Best Practices

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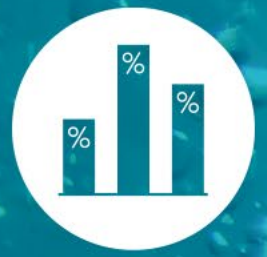


Dissolved Oxygen in water is most strongly affected by

1. Temperature
2. Atmospheric pressure
3. Salinity
4. All of the above
5. None of the above

Best Practice

I. Calibration

II. Membranes & Optical Caps

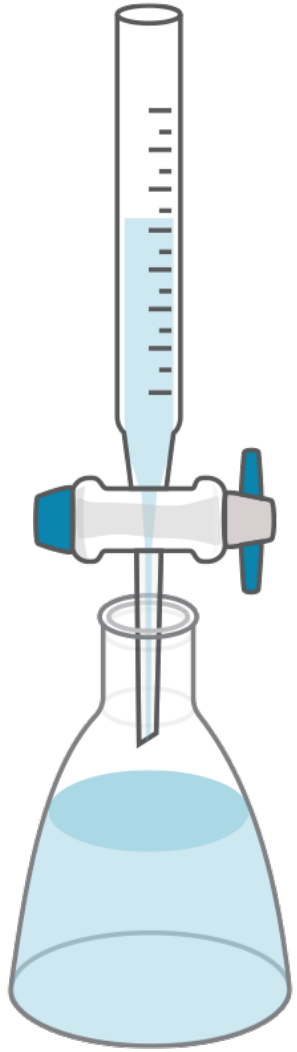
III. Maintenance

IV. Preventing Biofouling

Calibration Options

- Calibration against a Winkler Titration

1. Sample of water divided into four parts
2. Titrate three of the samples
3. If any one of the samples' titrated value varies more than +/- 0.5 mg/L, it should be discarded.
4. Average the results
5. Place the DO sensor in the fourth solution, start calibration, enter the averaged value



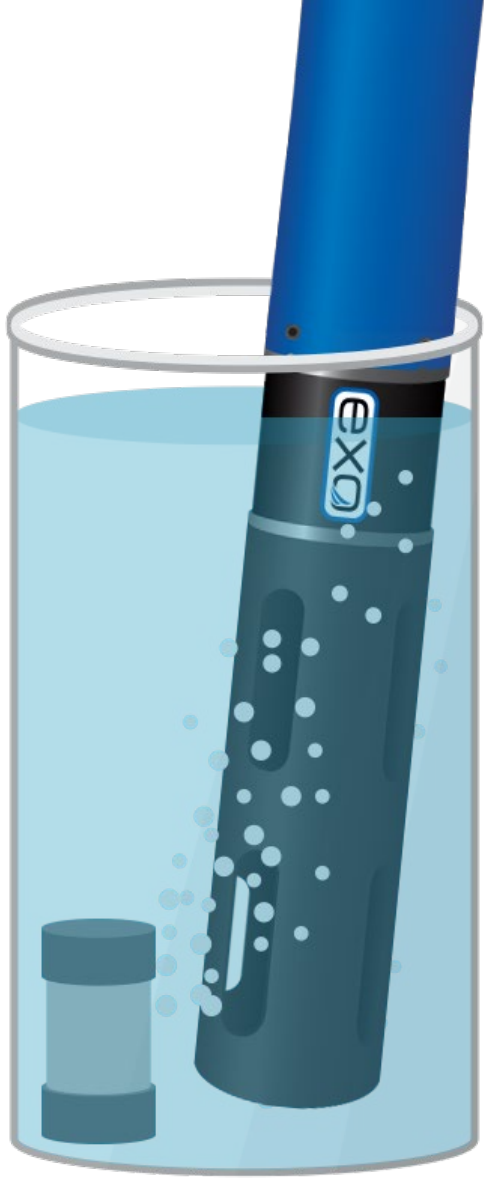
Calibration Options

- Air-saturated water

1. Use an air pump and air stone to aerate tap water for 1 hour

2. Place sensor in solution and calibrate

   - Value will be 100% only if pressure = 760 mmHg



Calibration Options

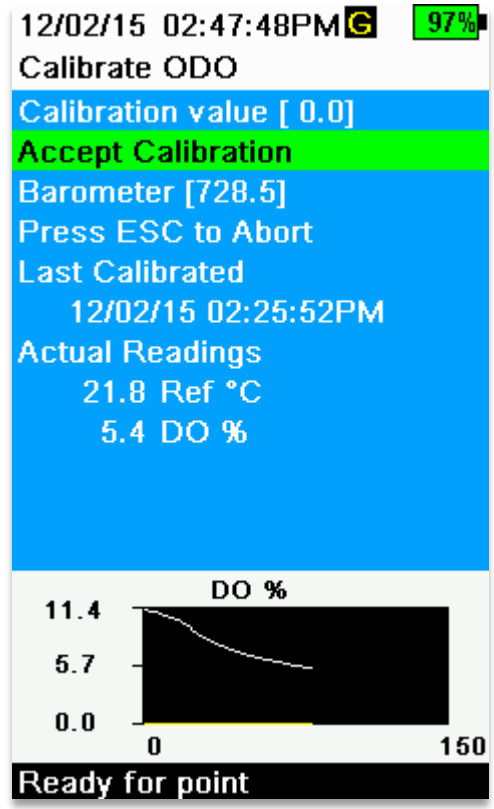
- Water-saturated air

1. Dry the thermistor and the membrane (e-chem) or sensor cap (optical)
2. Place probe in water-saturated air environment (100% humidity)
3. Wait 10 minutes for the calibration chamber to become completely saturated
4. Complete calibration

- Easy, accurate calibration method!

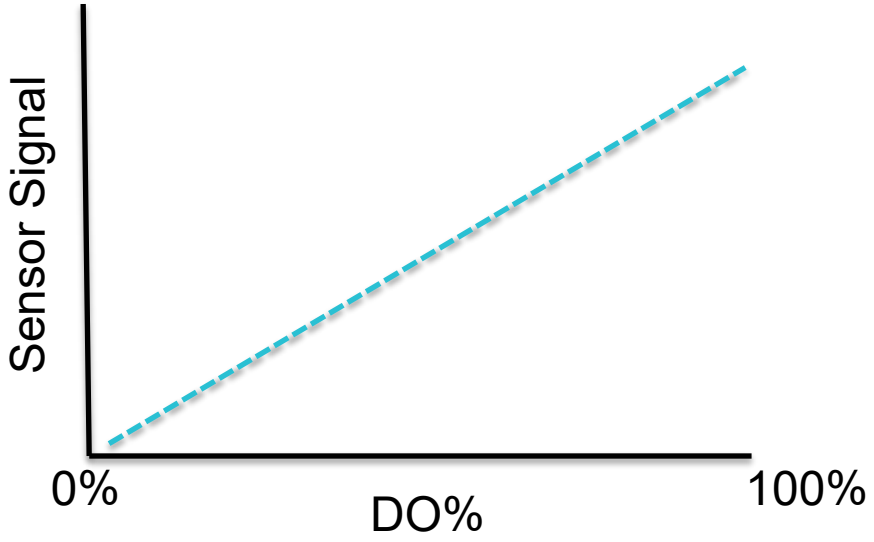
Calibration Options

- Zero DO Cal
  - Only recommended if measuring in low DO or to verify operation across entire range
  - One calibration point completed in environment with no DO, second point is typical DO% cal
  - Sodium sulfite solution or nitrogen gas
  - Don’t do it every time you calibrate!
    - Perform check before actually calibrating
  - Remove wiper and rinse VERY well



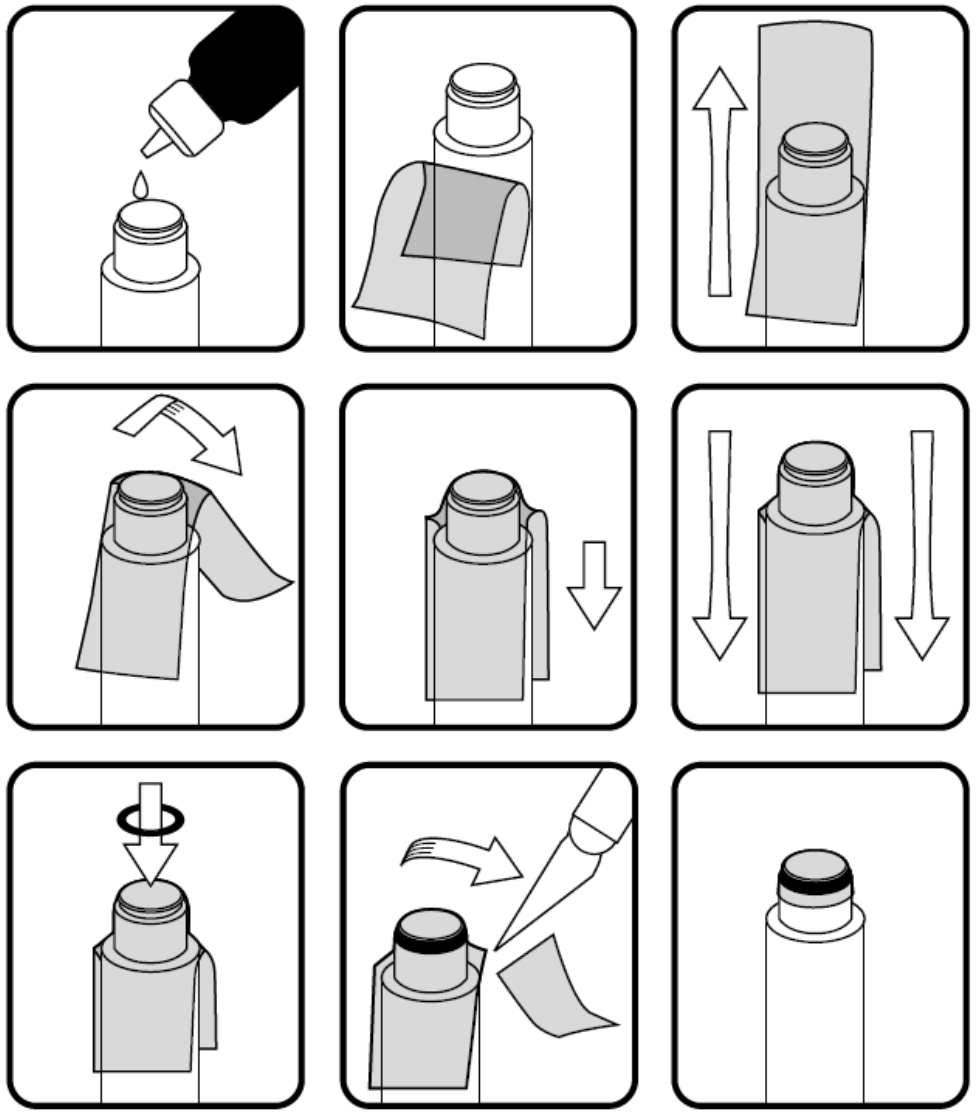
Why Calibration Matters

- 1-point calibration is a slope correction
- 2-point calibration adjusts the slope and zero point
  - Adjusts everything to be perfectly linear between zero and DO% calibration point
- How frequently should I calibrate?
  - Optical sensors drift less than electrochemical sensors and are therefore better for monitoring applications
  - Calibrate when possible



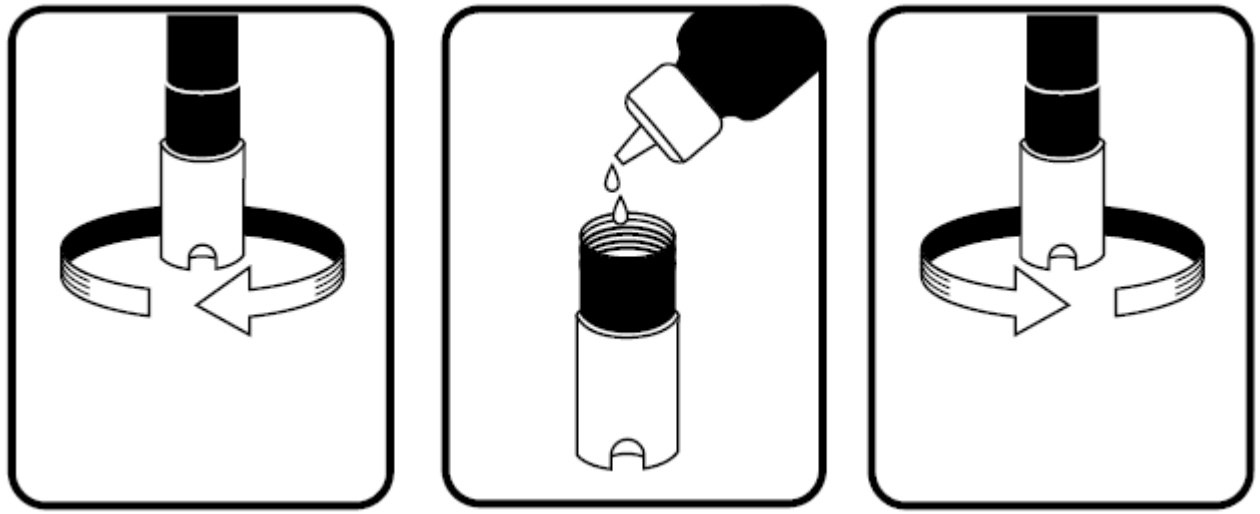
Stretch Membrane Replacement

- Older electrochemical probes often have a stretch membrane
- Change every 2-8 weeks
- Stretch membranes are difficult!
  - Easy to wrinkle and trap air bubbles



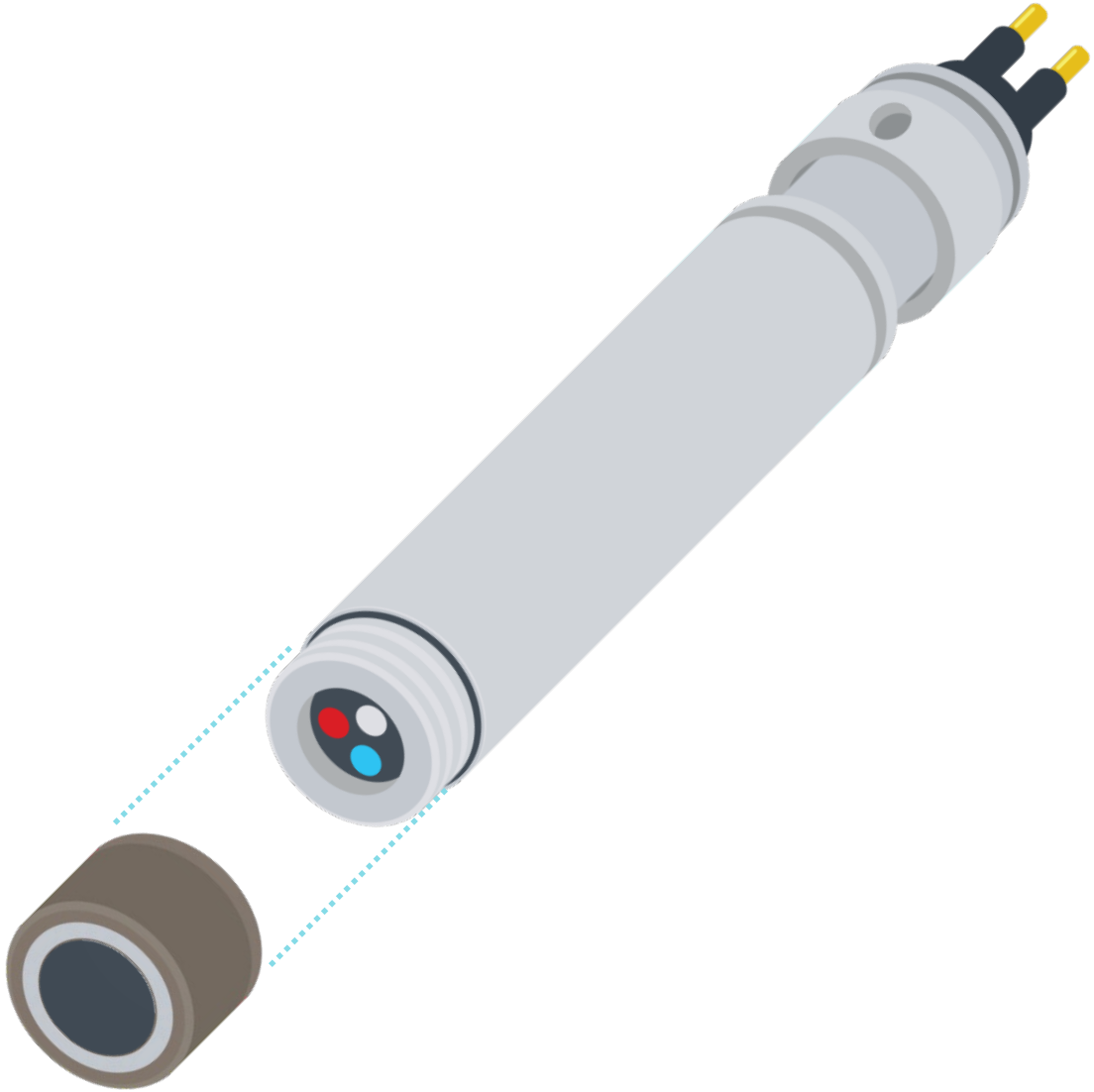
Cap-Style Membrane Replacement

- Newer electrochemical probes have a cap membrane
- Change every 2-8 weeks
- Membrane already installed
- Simply fill with electrolyte and install!
  - Ensure there are no tears or air bubbles



Optical Sensor Cap Replacement

- Optical sensors have a sensor cap rather than a membrane
- Change every 12-24 months
- No electrolyte!
- Install cap
  - Should be no large scratches in the paint layer
- Update sensor cap coefficients for highest accuracy



Polarographic Sensor Maintenance

- Error message during calibration could be due to anode fouling
- Soak overnight in 3% household ammonia cleaner
- Wet sand with 400 grit sand paper after soak
- Rinse thoroughly with DI water and install a new membrane
- Don’t clean unless necessary

Galvanic Sensor Maintenance

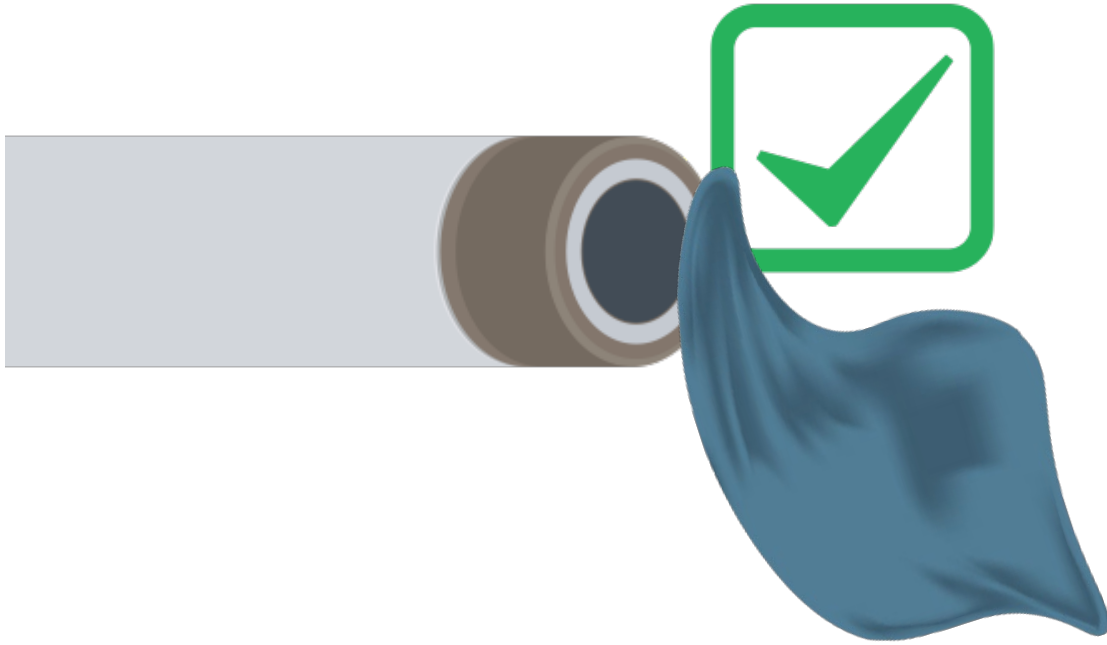
- Sand anode and cathode using 400 grit wet/dry paper to remove white deposits
- Rinse with DI water
- Allow probe to stabilize before calibration
- Don’t soak galvanic probe in ammonia
  - NOTE: YSI polarographic sensors have a black body, galvanic sensors have a grey body

Before

After

Optical Sensor Maintenance

- Clean sensor cap using clean water, a lint-free cloth and mild detergent (if necessary)
- Don’t scratch paint layer
- Don’t use abrasives, alcohol or organic solvents
- Replace cap if damage to paint layer as this impacts sensor accuracy (confirmed with failed calibration)
- Don’t let the sensor cap dry out

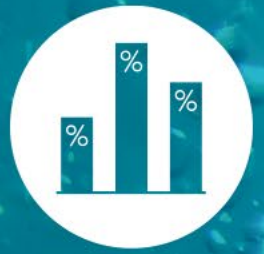


Optical Sensor Cap Rehydration

- If left dry for longer than 8 hours, it must be rehydrated
- Soak the ODO sensor in room temperature tap water for 24 hours
- Recalibrate the sensor after soaking

Prevent Fouling - Sonde

- Anti-fouling accessories
  - Copper components
  - Sonde sleeves
  - C-Spray
- Central Wiper



Do you want someone from YSI to contact you to discuss dissolved oxygen sensors?

Questions?

Contact us:

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June 23rd / www.xylem-analytics.asia

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