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PLOA Workshop June 2021

Tips for Accurate pH, ISE, and DO Measurements in Wastewater

Agenda

OHIO WATER ENVIRONMENT ASSOCIATION
EDUCATION. PRESERVATION. DEDICATED TO YOUR WATER ENVIRONMENT.

- Common Wastewater Lab Parameters
- ISE, pH and DO Explained
- Good Laboratory Practice: Tips for Improved Accuracy
  - Calibration
  - Maintenance
  - Storage

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Common Wastewater Lab Parameters

Wastewater: Lab Parameters

Analysis Parameter	Why It's Measured
5-Day Biochemical Oxygen Demand (BOD_5)	Degree of organic load in water
Chemical Oxygen Demand (COD)	Determine amount of organic compounds (indirectly)
Dissolved Oxygen (DO)	Essential for aerobic microorganisms
Total Organic Carbon (TOC)	Measures low concentrations of organic matter (vs BOD/COD)
Alkalinity	Indicates buffer capacity
pH	Neutral pH is required for adequate treatment
Total Nitrogen	Ammonia, Nitrates, Nitrites can be toxic to the environment and human health
Total Phosphorous	High concentrations promote algae blooms

ISE, pH and DO Explained

ISE Electrodes

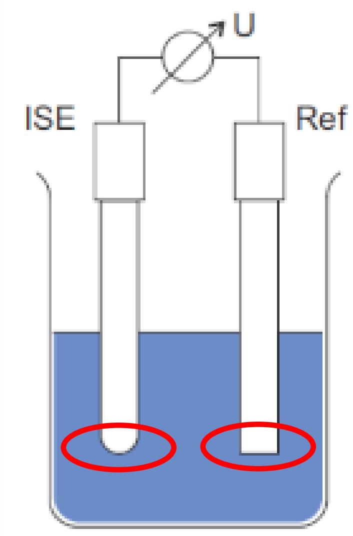
1

Ion Selective Electrode (ISE): Structure

Relies on measurement of a voltage; requires ***two*** points with different electrical potential values

1. **Reference electrode** (i.e. reference half cell)
   - Maintains constant potential (signal) independent of sample

2. **ISE** (i.e. sensing half cell)
   - Electrical potential depends upon the target ion in solution
   - Other ions can interfere

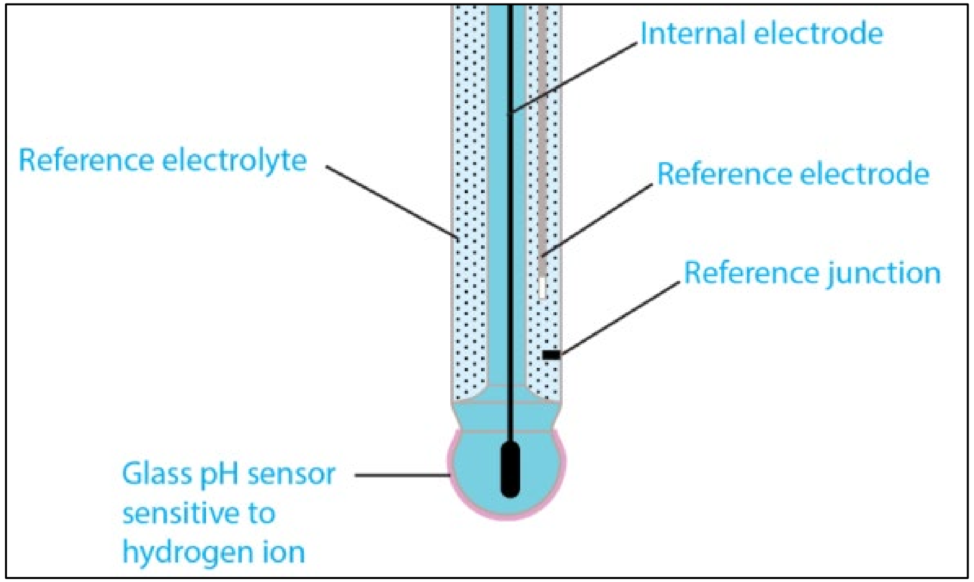


A pH electrode has sensing and reference half-cells

The membrane makes the difference!

ISE: How it Works

- Difference between these potentials (mV on display) is correlated to concentration (ion activity) ***based on the result of calibration***
  - Nernst equation establishes relationship between mV output and concentration
- Half cells often combined into one electrode for convenience – ***combination electrode***



ISE: Nernst Equation

$$E = E_0 + (2.303\ RT/nF)\ \log a_{H^+}$$

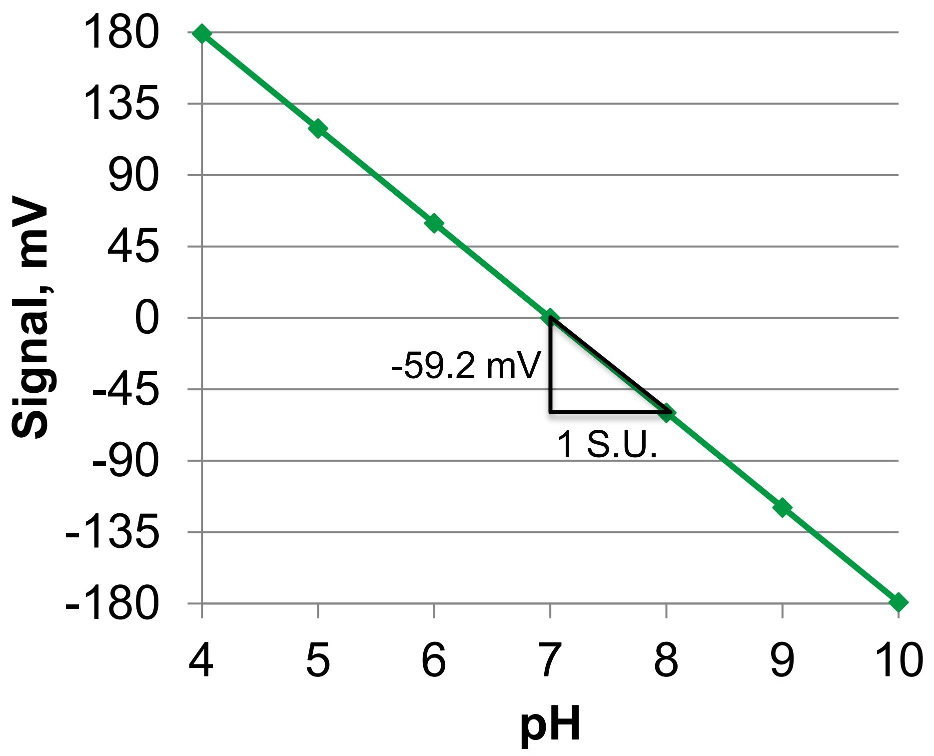


Figure for n = 1 (monovalent)

T = Temperature

n = Valency of the ion

Monovalent ions have slope ~59 mV/decade

pH (H^+)	NH_4^+
NO_3^-	K^+
Cl^-	F^-

Divalent ions have slope ~29 mV/decade

Ca^{2+}	Pb^{2+}

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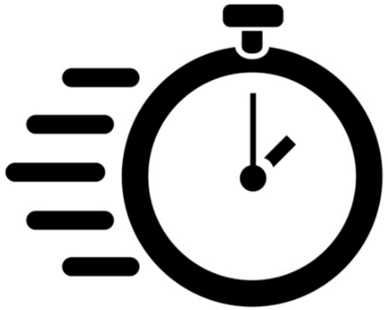
ISE: Pros and Cons

Pros

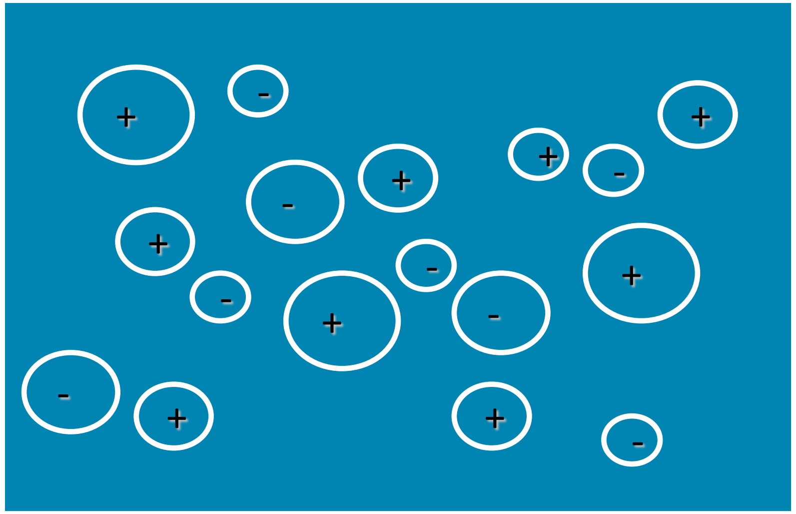
- Wide measuring range
  - e.g., ammonia ISE range is 0.02 to 17,000 mg/L as NH_3
- Fast
- Inexpensive



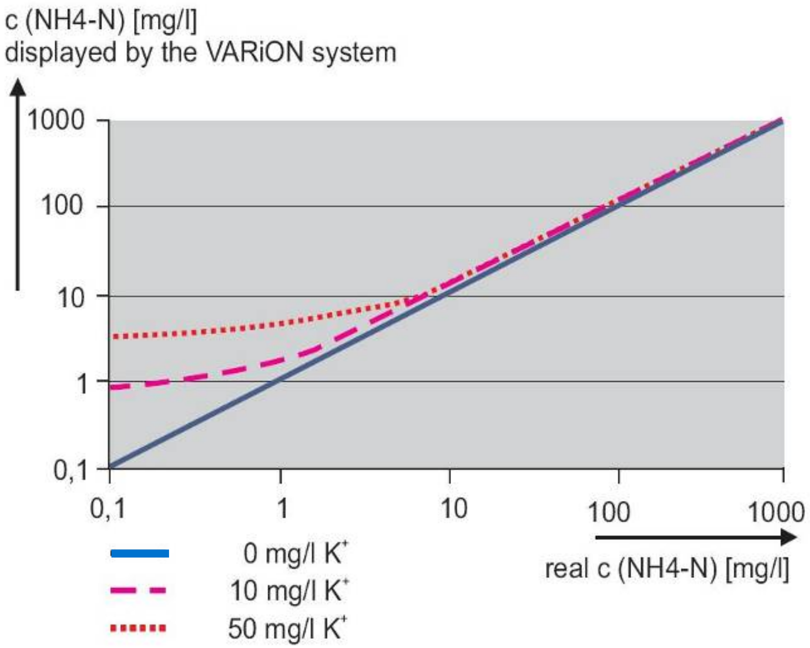
Cons

- Lower stability – esp. at low concentrations
- Operation & Maintenance

ISE: The Matrix Effect



- **Interaction of ions**
  - "Matrix effects" can result in false readings
    - Potassium impact on ammonium
- **Mitigation of Matrix Effect**
  - **Field**: Use of a compensating electrode
  - **Lab**: Use of ionic strength adjuster
    - Ensures same ionic strength
    - "Masks" impact of interfering ions

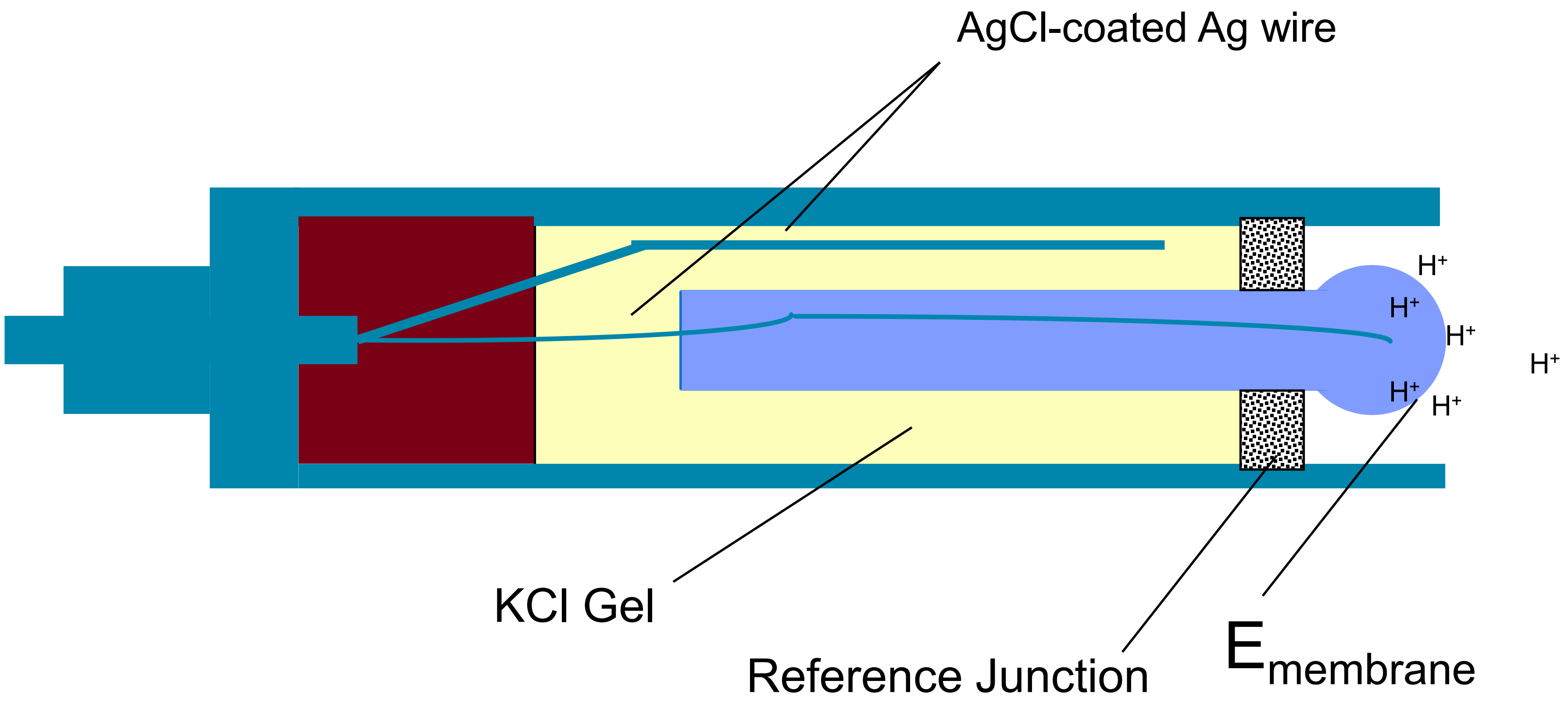


pH Electrodes

1

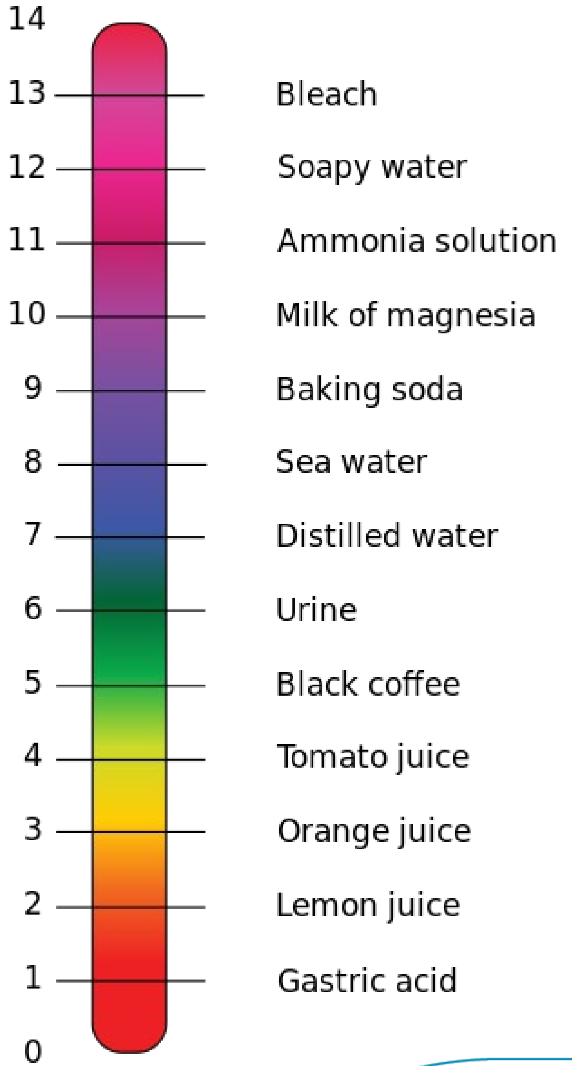
pH: Combination Electrode

1. Glass membrane senses H^+ and a voltage is generated
2. A fill solution picks up the signal from the membrane
3. A pure silver wire coated with silver chloride passes the signal to the electrode's cable or connector



pH: How it's Measured? – Glass Electrode

- Glass sensing bulb is filled with solution of stable pH (usually 7) so inside of glass surface experiences constant binding of H+ ions
- Outside of bulb is exposed to sample where H+ varies
- Differential of H+ creates a potential which is read versus the stable potential of the reference electrode
- Signal is in mV which is related to pH by the Nernst Equation



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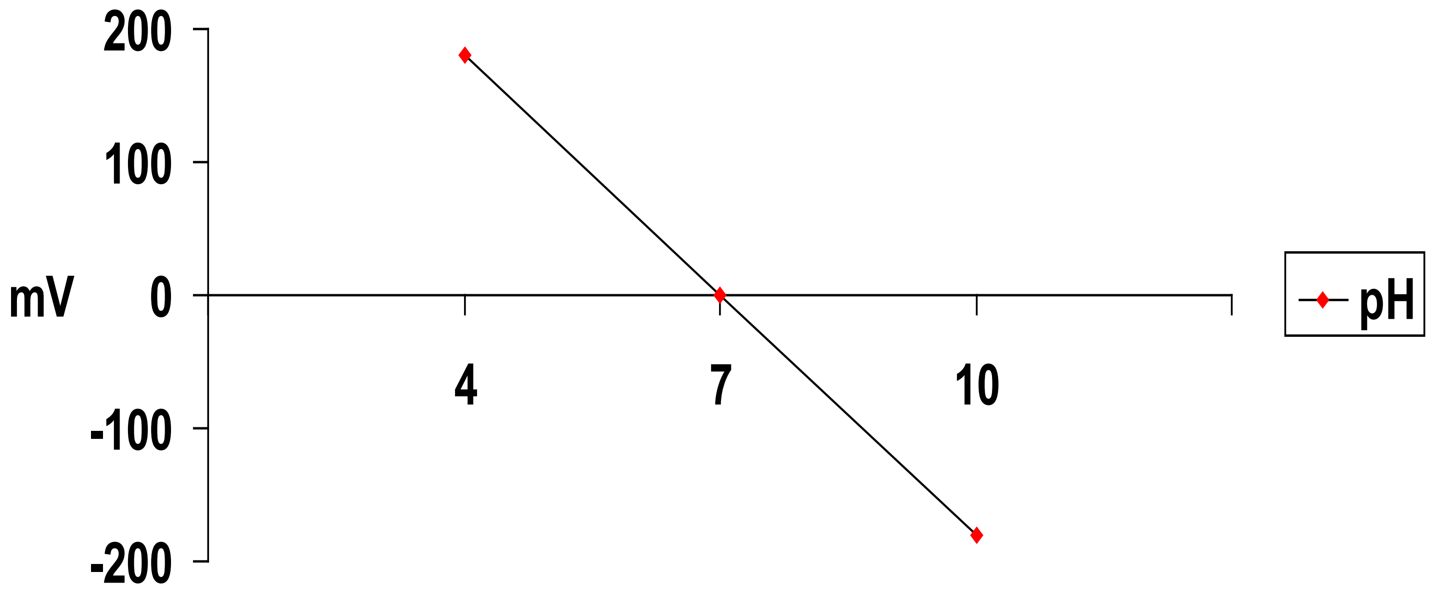
pH: Nernst Equation

The potential is related to the pH by a form of the Nernst Equation



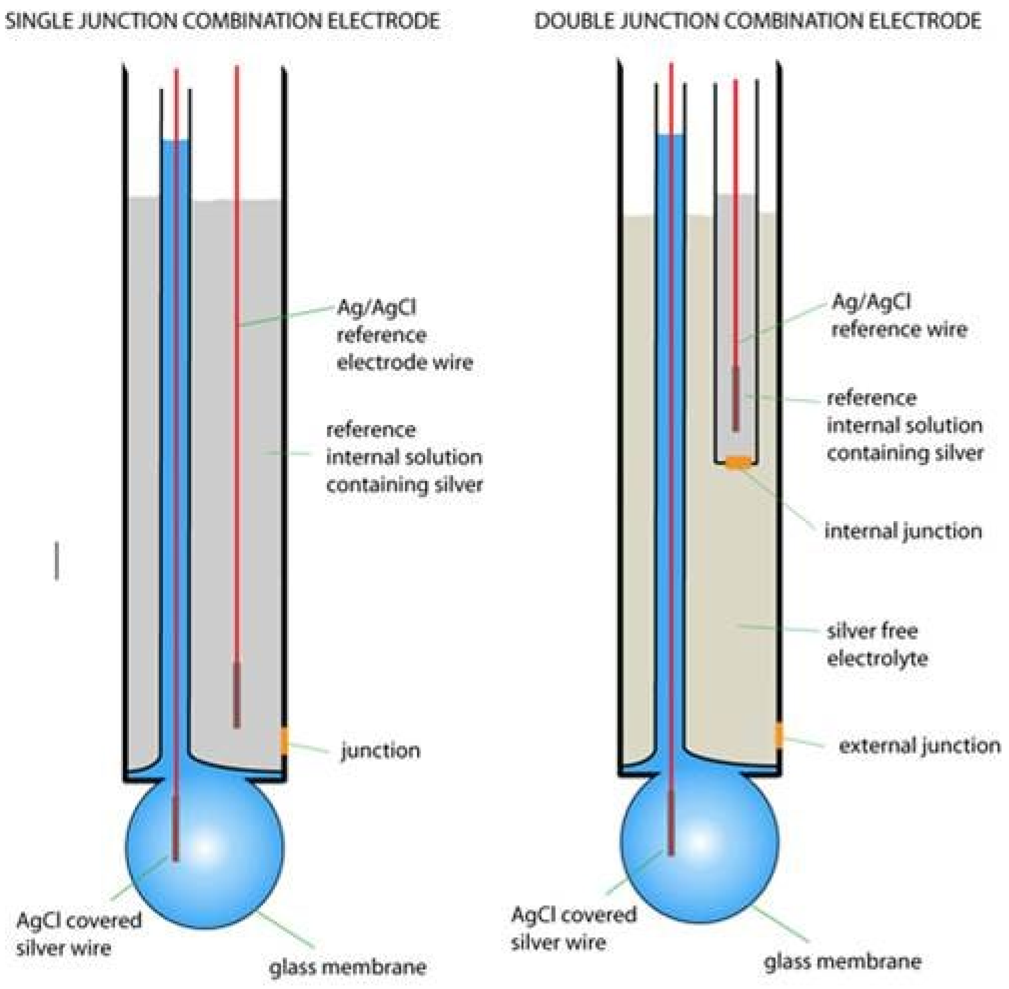
pH 4 meter should read 150 to 210 mV
pH 7 meter should read -50 to +50 mV
pH 10 meter should read -150 to -210 mV

pH: Selecting a Sensor

Select a combination sensor that includes the reference

Single or Double Junction

- Single Junction
  - satisfactory for most application
- Double Junction
  - recommended for use in solutions containing heavy metals, sulfides, proteins and other materials that interact with silver
  - double junction design provides additional protection against contamination.



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Dissolved Oxygen Sensors

1

Disolved Oxygen (DO): Sensor Technologies

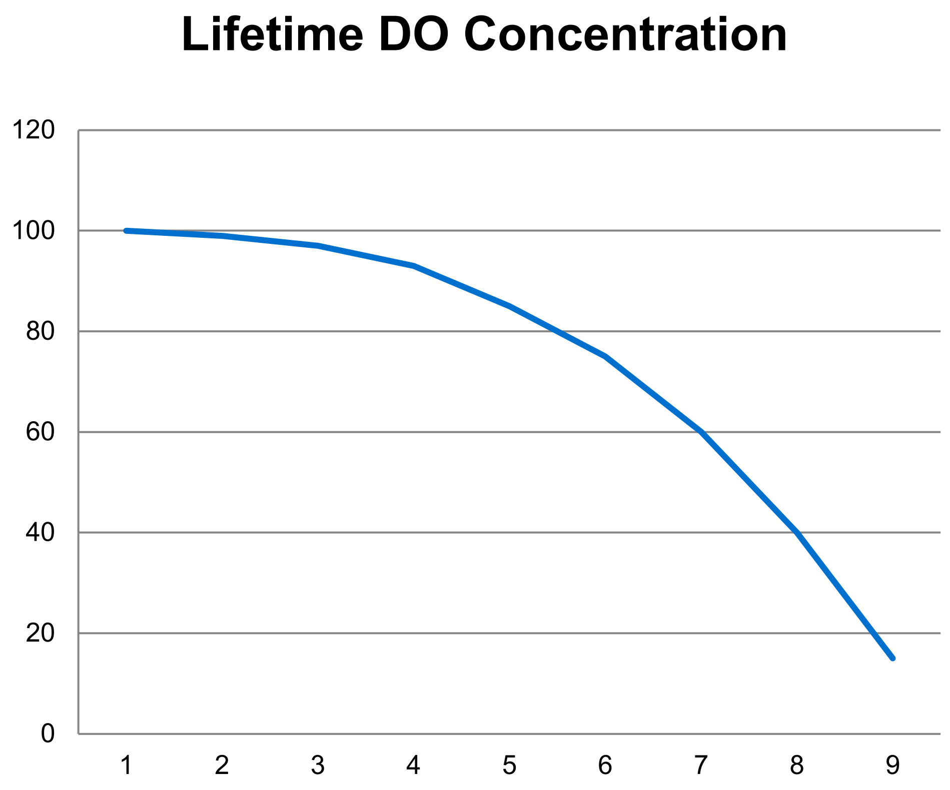
Primary sensor types:

- Optical/Luminescent
  - Life Time
  - Intensity
- Clark Electrochemical (membrane covered, steady state)
  - Polarographic: steady state and rapid pulse
  - Galvanic: steady state

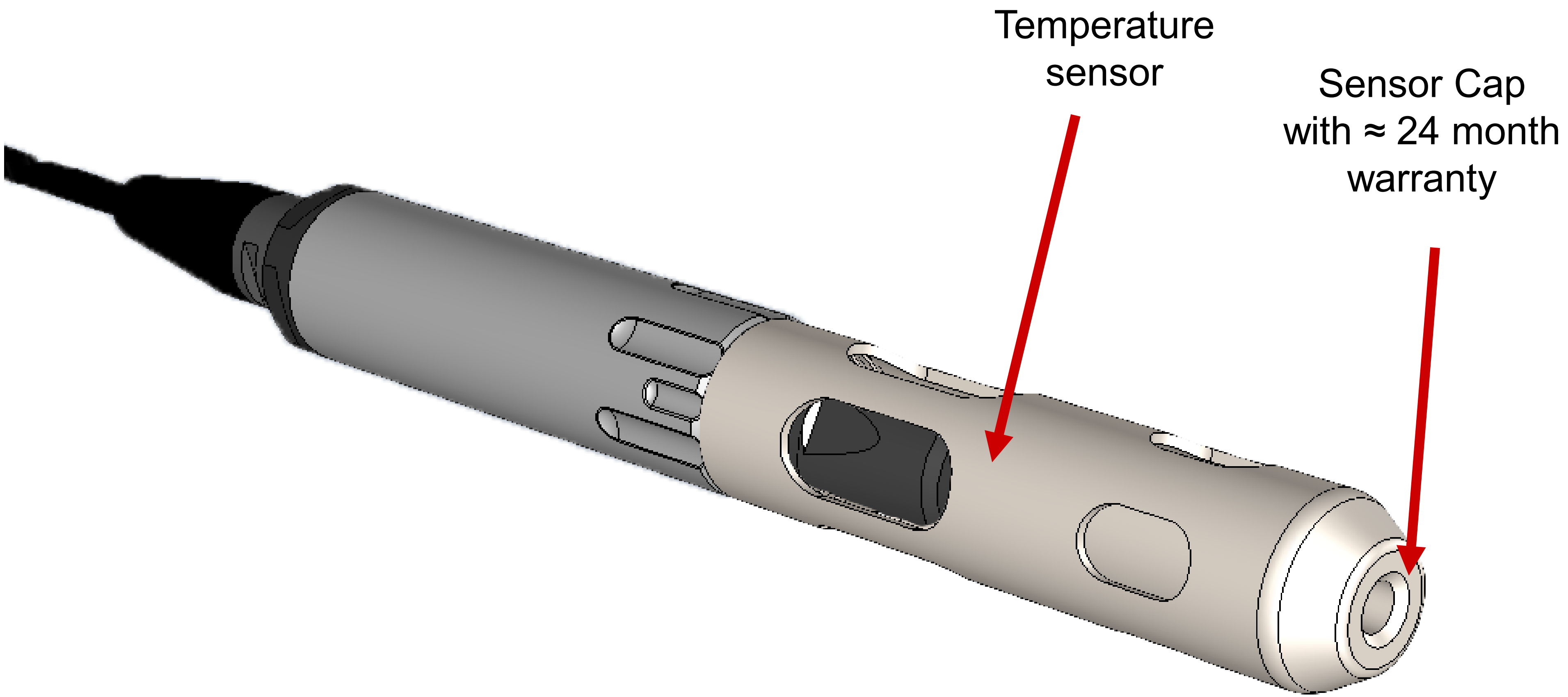
DO: Optical Technology

Life Time Optical Technology:

- The quenching relationship has an inverse, non-linear relationship with the dissolved oxygen concentration.
- The primary advantage of lifetime is that the lifetime sensor has greater long-term stability.
  - Dye degradation has less effect on lifetime based measurements
  - This method will require less frequent calibrations.



ProODO® Probe

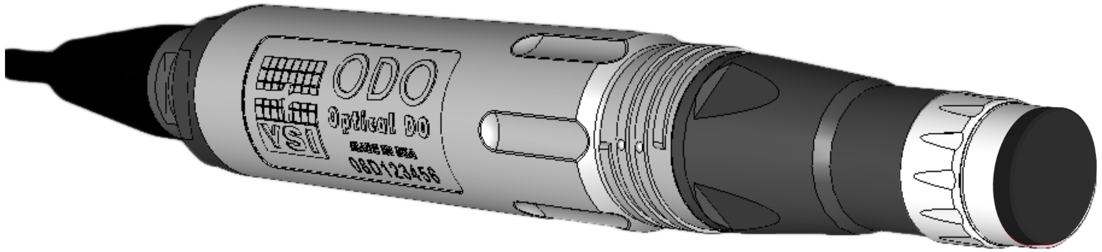


Dissecting the Sensor Cap

Oxygen Permeable Diffusion Layer

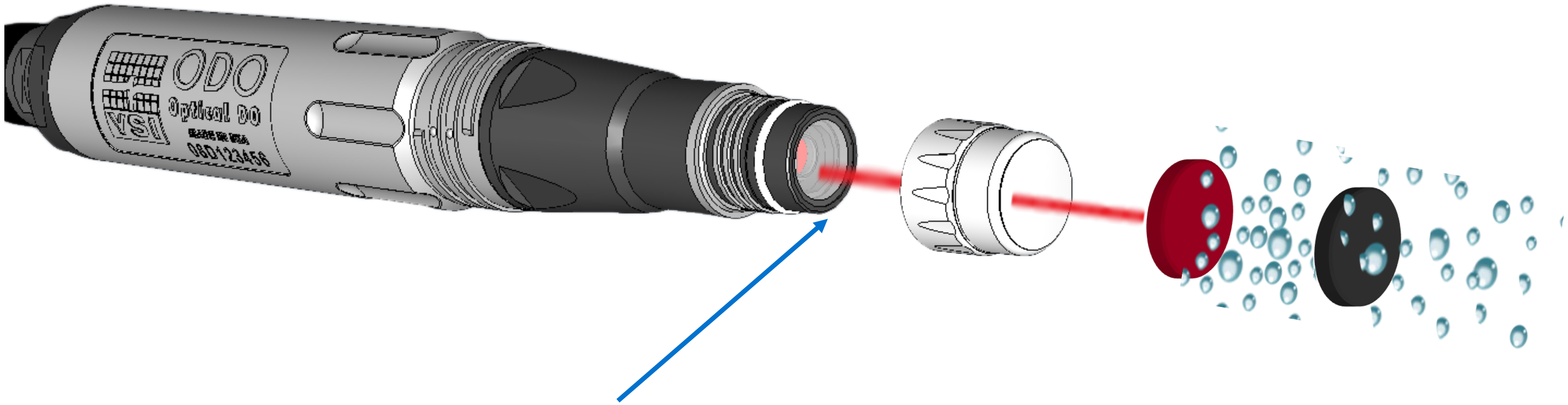
Allows oxygen through

Protects Sensing Element



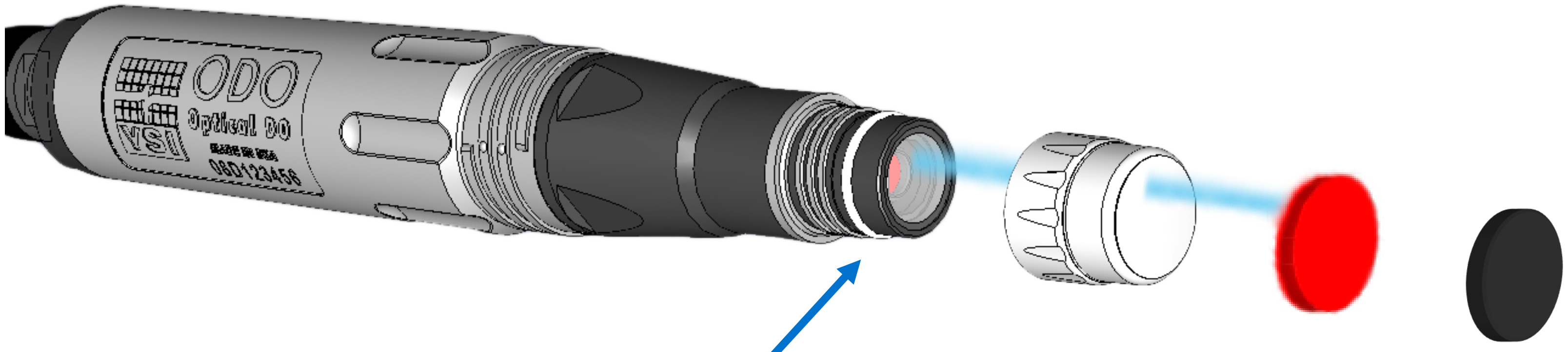
Sensing Element –
dye layer

The Reference



The sensor emits a red light, which is reflected by the sensing element (dye layer) in the sensor cap. The sensor measures the reflected light and uses it as the reference value.

Measuring Dissolved Oxygen

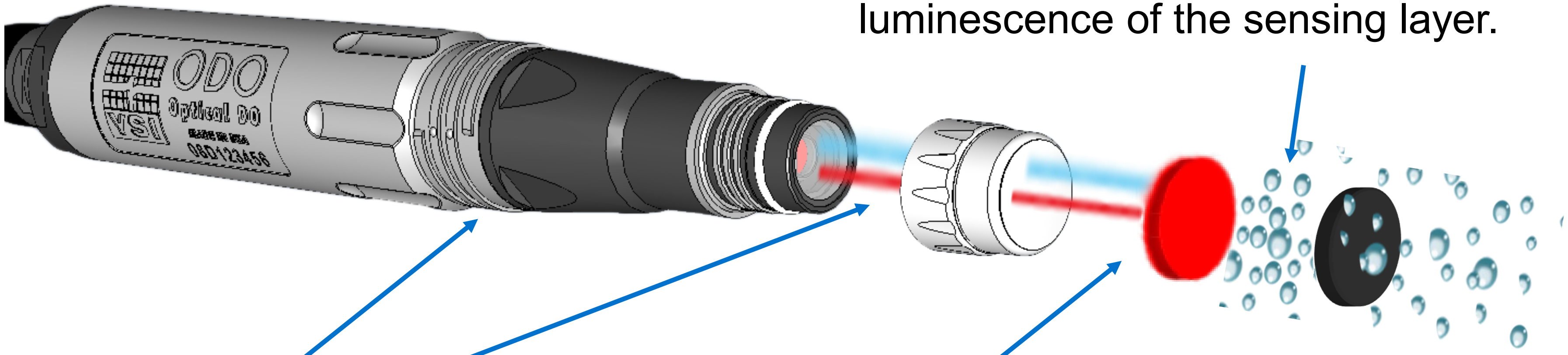


The excitation fiber
in the sensor emits
a blue light

causing the sensing element to glow,
or luminesce red.

Measuring Dissolved Oxygen

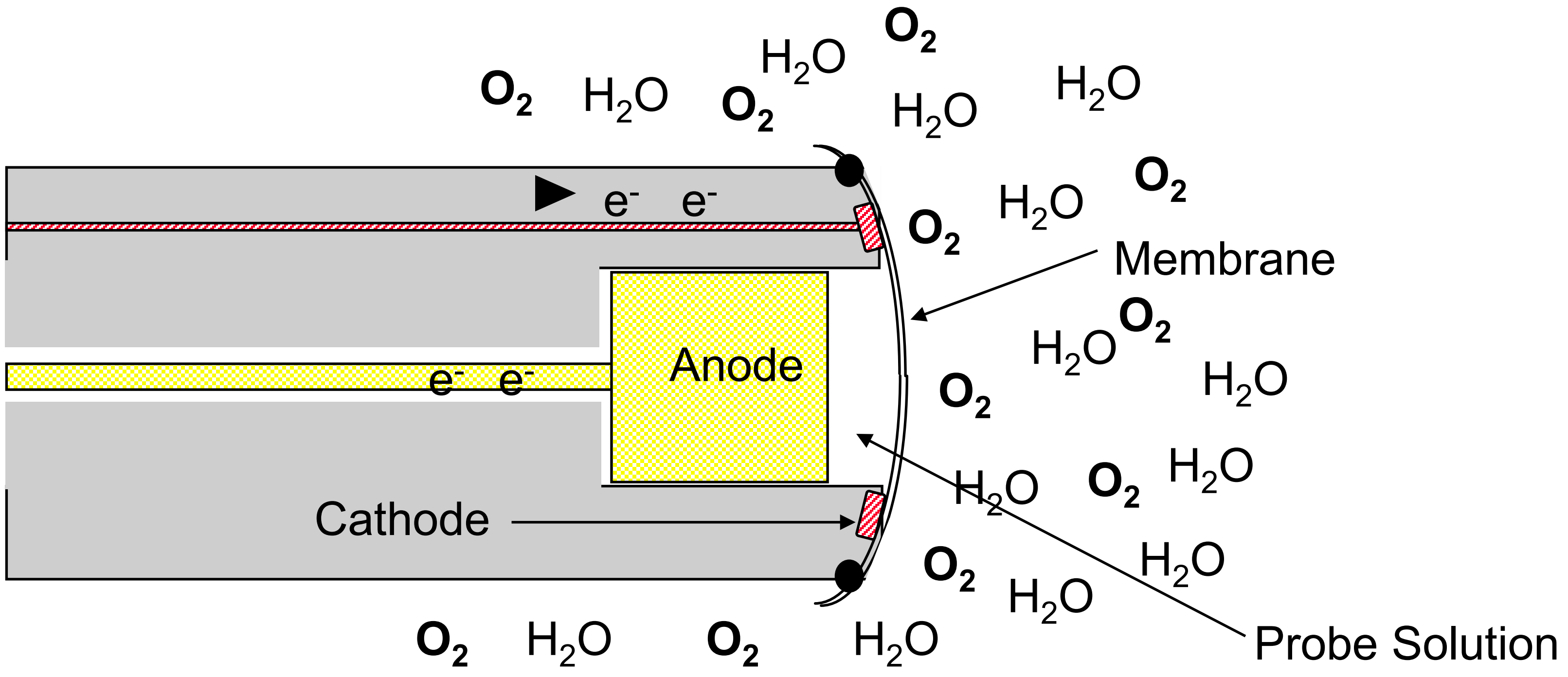
Oxygen is constantly moving through the Diffusion Layer, affecting the luminescence of the sensing layer.



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.

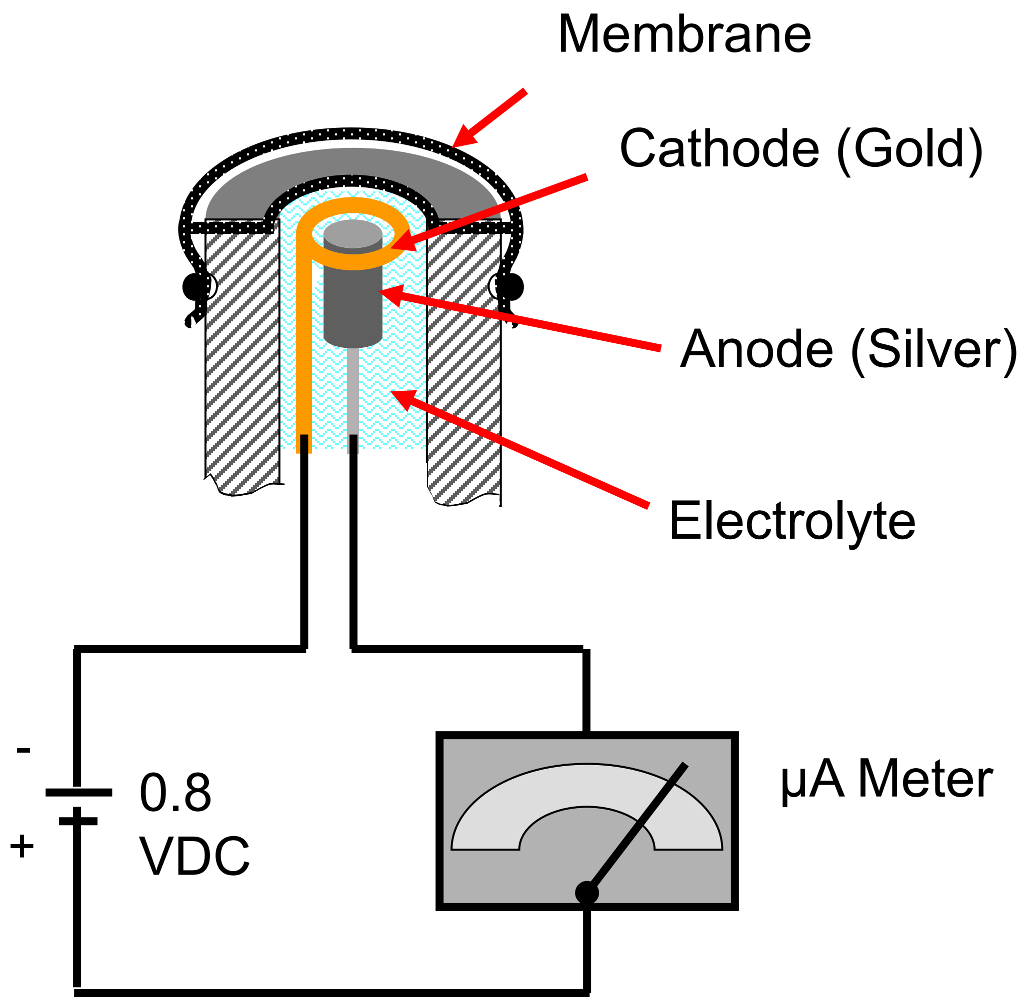
DO: Electrochemical (Clark) Technology



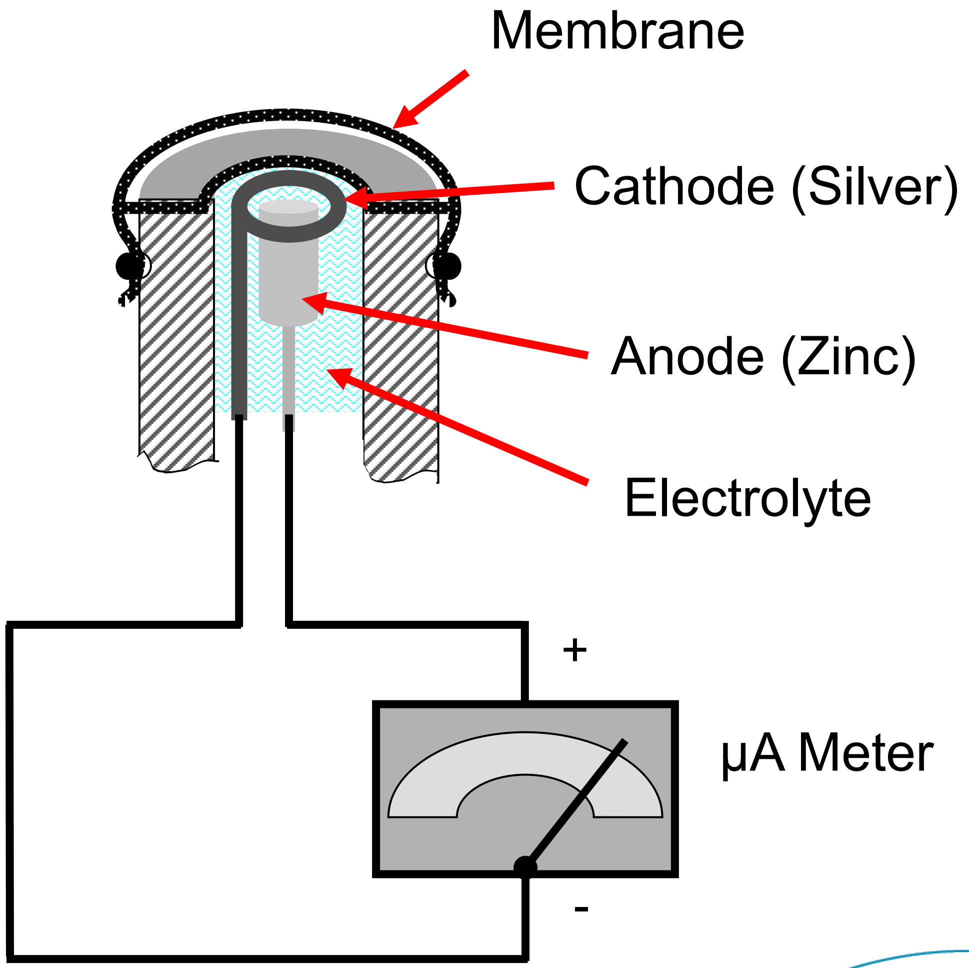
- Oxygen diffuses through membrane
- Oxygen reduced (consumed) at cathode
- Electrons flow = electrical signal
- Oxygen concentration proportional to signal level

DO: Electrochemical (Clark) Sensor Types

Polarographic Sensor



Galvanic Sensor



Functions like a battery (self polarizing)

DO: Polarographic vs. Galvanic

Similarities:

- Both are “Steady State”
- Both reduce oxygen, thus require stirring
- Both use a membrane and electrolyte solution

Differences:

- Galvanic “Fast On” but is always on when oxygen is present
- Polarographic requires warm up but is off when turned off.
- Galvanic sacrifices anode in reaction, thus has a shorter theoretical sensor life.
- Polarographic sacrifices solution in reaction. Thus offers a longer theoretical sensor life.

Good Laboratory Practice

TIPS FOR IMPROVED ACCURACY

Calibration

1

ISE: Calibration

- ✓ Prepare fresh standards using serial dilution
- ✓ Use pipette and volumetric flasks
- ✓ Ensure temperature consistency (25^{o} C)
- ✓ Evaluate the slope and compare to appropriate ranges (monovalent vs divalent)

Read our Full Step by Step Guide on YSI.com
(QR Code)

YSI ISE Startup and Calibration Guide

pH: Calibration

- ✓ Use fresh, unused, unexpired buffers
- ✓ Perform at least a 2 – point calibration
- ✓ Ensure temperature consistency (25^{o} C)
- ✓ Check the millivolts in each buffer

Read our Full Step by Step Guide on YSI.com

(QR Code)

YSI pH Startup and Calibration Guide

DO: Calibration

Three primary methods are accepted:

- ✓ Winkler Titration
- ✓ Air Saturated Water
- ✓ Water Saturated Air

Read our Full Step by Step Guide on YSI.com

(QR Code)

YSI Dissolved Oxygen Handbook

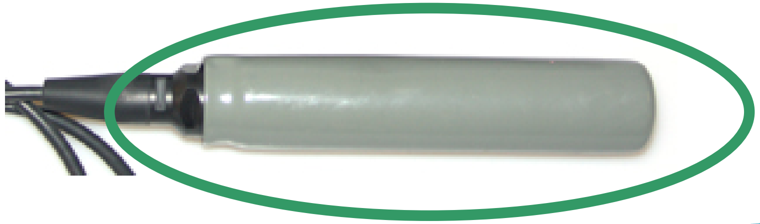
DO: Water-Saturated Air Calibration

Easy process

- Place probe in moist air
- Wait for the air in chamber to become completely water-saturated
- Allow temperature and DO readings to stabilize
- Enter % Calibration Mode
- Enter True barometric pressure or altitude - if no internal barometer
- Enter Salinity Correction Value







DO: Two Point Calibration

- One point at Zero and the other at full saturation
- Make a solution of zero oxygen
  - Sodium sulfite solution
  - Active Dry Yeast
  - Nitrogen gas
- Follow with water-saturated air calibration

DO: Calibration Musts

- Remove water droplets from the membrane/sensor surface if performing an air calibration
- Ensure the calibration chamber and cal water are clean
- Allow sensor to stabilize (polarographic type needs at least 5-10 minutes)
- Allow temperature to stabilize

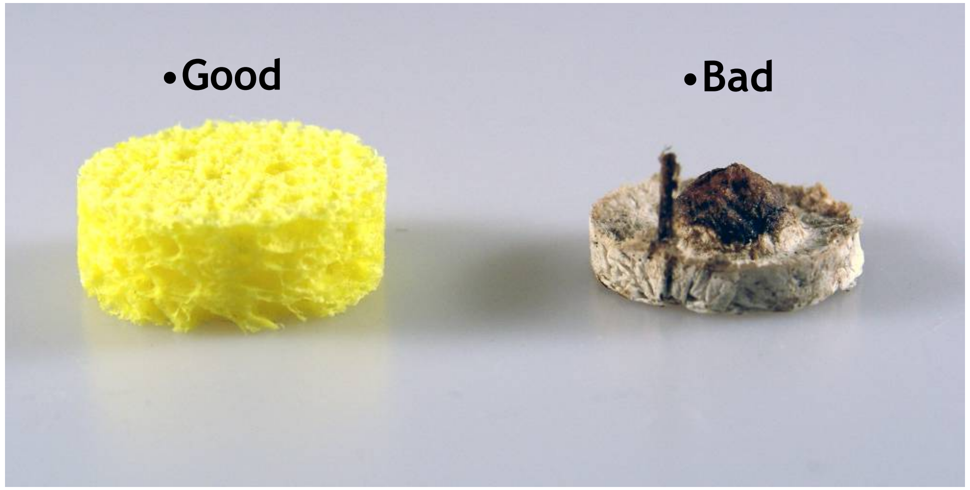
<u>For membrane-covered sensors:</u>

- Visually inspect the membrane or sensor surface and probe solution - electrochemical
- Stir if calibrating in solution – electrochemical only (not recommended)

- Bad
- Good

DO: Calibration Musts

- Enter your altitude or True Barometric Pressure, depending on instrument
- Enter or verify your salinity correction value
- Calibrate close to sample temperature (+/- 10ºC) for highest accuracy if using an older, analog instrument
- Verify or physically calibrate daily, not between samples



For Optical Sensors:

Visually inspect sensor cap for cleanliness or large scratch in the paint surface

Ensure Sensor Cap is hydrated

Verify calibration regularly

DO: Video of Calibration

2

Maintenance

ISE: Maintenance

- Prepare fresh standards using serial dilution
- Use pipette and volumetric flasks
- Replace membrane when damaged or when response is slow
- Check membrane integrity in pH 4 buffer
- DO NOT: Use calibration with a slope outside the range -52 to -62 mV per decade

Ammonia ISE is spring loaded to refresh fill solution around the pH electrode

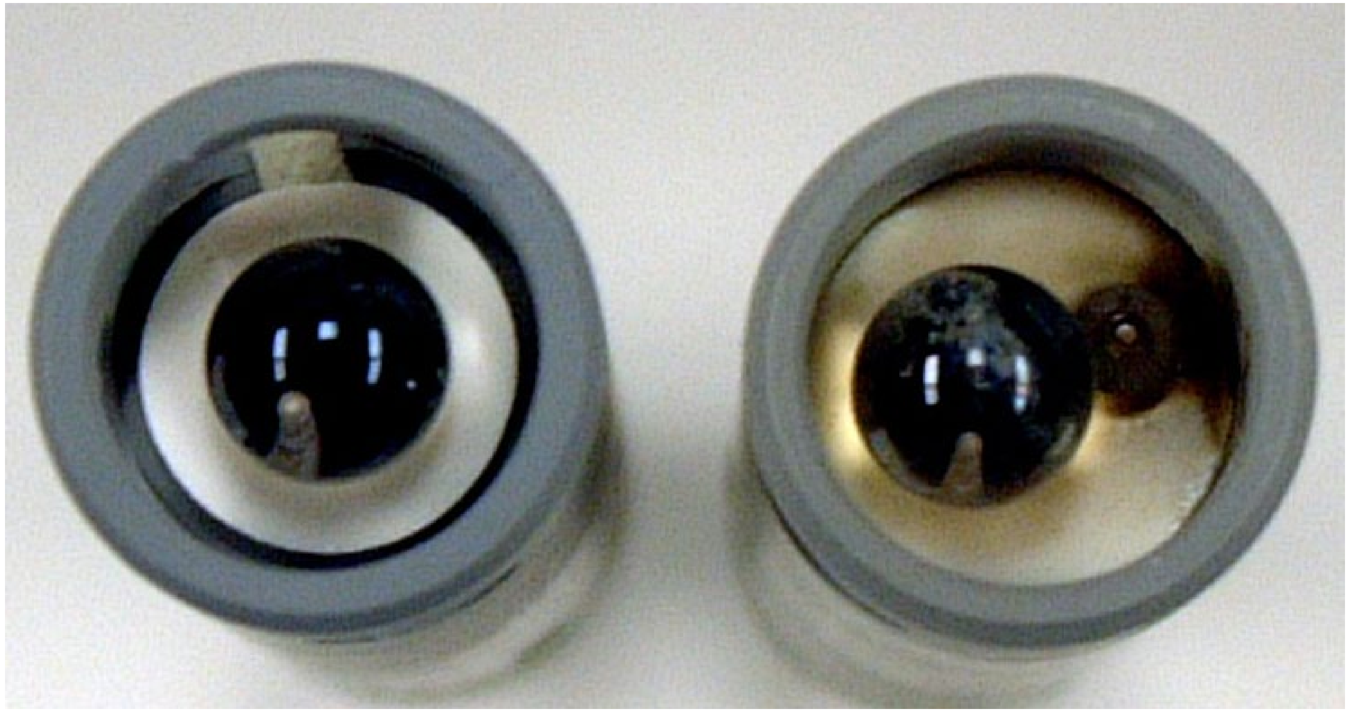
pH: Maintenance

- Clean electrode
  - Dirty electrode results in
    - slow response of in buffers
    - slow sensitivity
- Don’t let the reference dry out!
- Never store your sensor in distilled or deionized water
- Stir for lab samples
- For low ionic strength water, or long cable lengths, consider amp’d probe

pH: Maintenance

Clean pH Probe

Dirty pH/ORP Probe



pH: Maintenance – Field Electrodes

1. Soak in mild soap solution for 15 minutes.
   - Rinse with DI water, then soak in tap water for 5 minutes.
2. Soak in a 1:1 solution of bleach and tap water for 30 minutes.
   - Rinse, then soak in deionized water for 30 minutes.
3. Soak in buffer 4 for 1 – 2 days

NEVER soak or store a pH/ORP probe in DI or distilled water. This will effectively neutralize the probe and render it useless in a very short period of time

pH: Maintenance – Lab Electrodes

Inorganic Adhesions

- Soak in 0.1 M HCl or NaOH
  - If buildup remains, cautiously heat to $50^{o}C$ before increasing concentration.

Organic Adhesions

- Rinse with organic solvents if possible.
  - Wipe with a lint free soft cloth.

Protiens

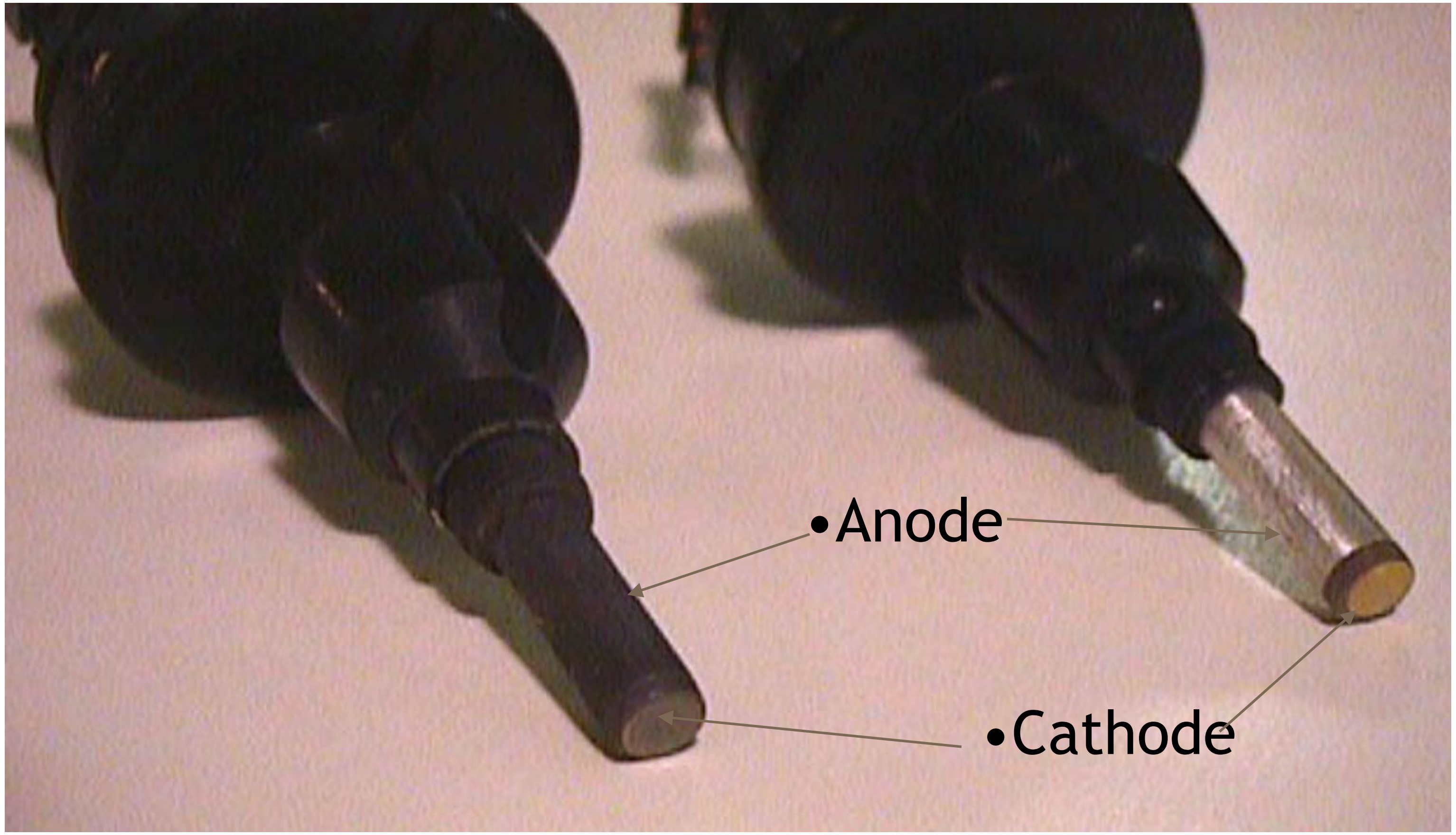
- Placed in a pepsin/HCl solution for 1 hour.

YSI pH Handbook!

After any cleaning method the electrode should be rinsed, then soak in tap water for 1 hour.

Then a calibration should be performed.

DO: Electrode Maintenance



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DO: Anode Maintenance – Steady State Polarographic Only

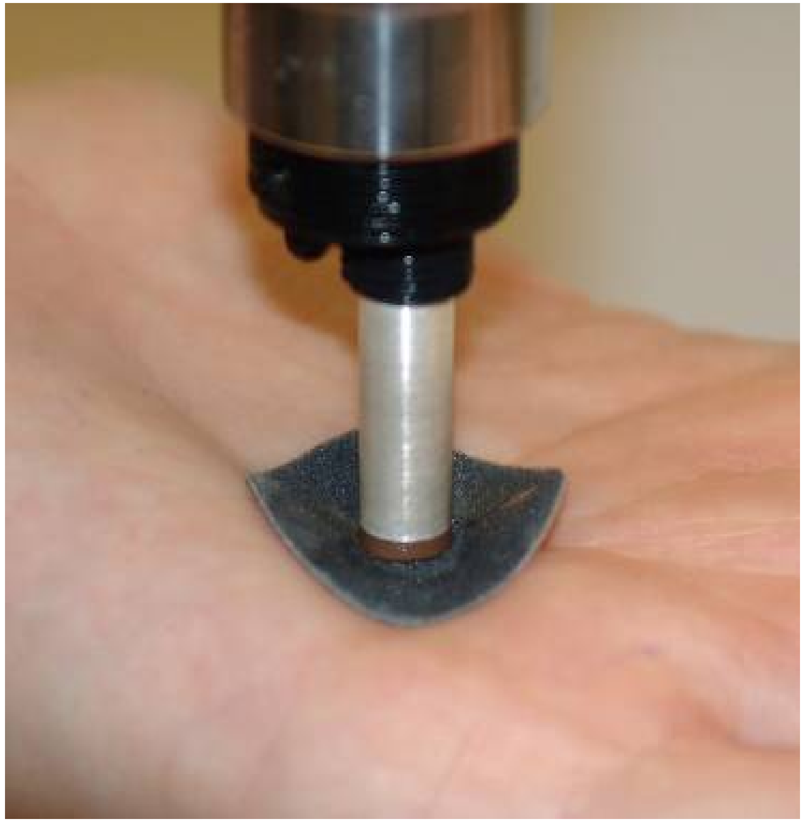
- Anode fouling typically causes low probe current errors
- Depending on sensor type, soak overnight in 3% household ammonia cleaner or sand with 400 grit wet/dry paper
- Rinse thoroughly with DI water
- Only clean if necessary
- Do not perform on Galvanic sensors

DO: Use of Ammonia

- Only if necessary because silver is removed in the process
- Soak overnight in 3% household ammonia or 14% ammonium hydroxide for 3 minutes
- Do not leave in ammonia beyond the recommended time
- Rinse thoroughly with DI water
- Test to make sure ammonia residual is gone
- Rinse again if necessary

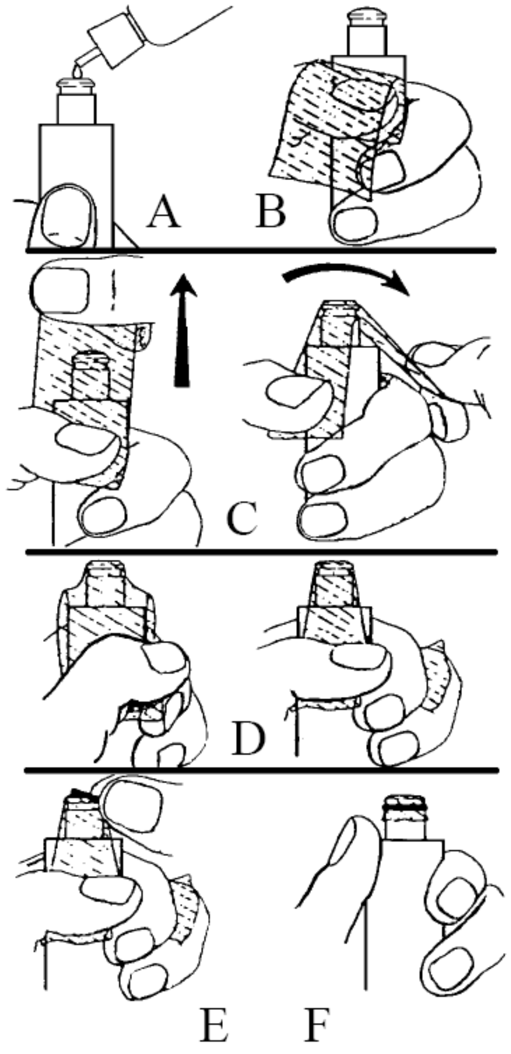
DO: Cathode Maintenance – Polarographic

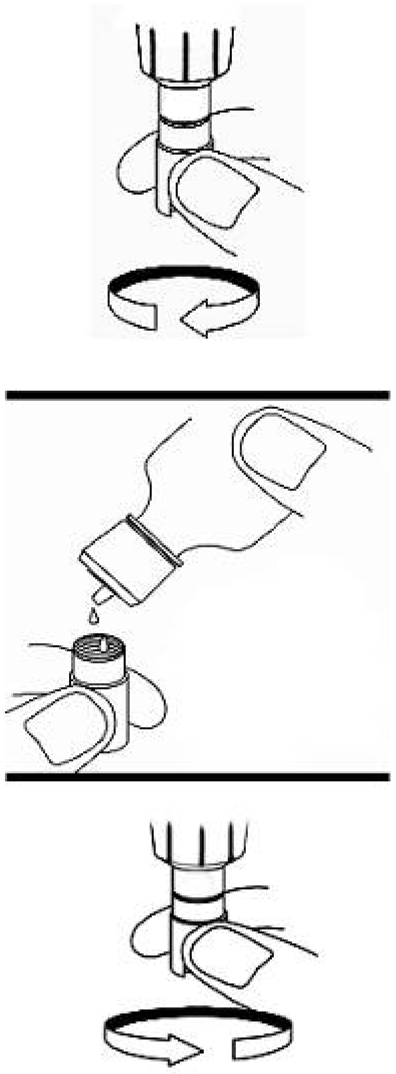
1. Silver deposits and/or tarnishing often cause high probe current errors
2. Remove when necessary
3. Sand cathode using 400 grit wet/dry paper (membrane kit)
4. Use 5680 special tool when sanding sensors w/stretch membrane
5. Rinse with DI water
6. Allow probe plenty of stabilization time before calibration



DO: Changing Stretch/Cap Membranes

- Every 2-8 weeks depending on application
- Flush old electrolyte with DI water
- Fill with new electrolyte
- Install membrane
- Inspect for smoothness and bubbles
- Trim excess membrane -stretch only
- Re-calibrate instrument
- Do not overstretch-can cause high current errors





DO: Optical Sensor Maintenance

- Inspect for damaged and/or dirty paint layer
- Replace cap if significant damage to paint layer
- Small scratches will not impact the sensors accuracy (confirmed with accepted calibration)
- Clean using clean water and a lint free cloth
- If necessary use a mild detergent
- Do not use abrasives, alcohol or organic solvents

Storage

3

ISE: Storage

- ✓ Store in dilute standard between measurements
- ✓ Store in mid-range standard overnight
- ✓ Disassemble and rinse in DI for long term storage
  - Membrane module can be stored dry
  - Internal pH sensor is stored in pH 4 buffer
- ✓ Do NOT: Disassemble too often

Ammonia ISE pH electrode and membrane module

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pH: Storage

✓ Short Term Storage

- Store in appropriate electrolyte solution (ex: 3M KCL)
- If no electrolyte solution, store in pH 4 or pH 7 buffer (temporarily)

✓ Long Term Storage

- Clean probe of debris
- If refillable, ensure it is filled with appropriate electrolyte solution and is closed.
- Store in watering cap with electrolyte solution.

Standard pH electrode with refillable KCl electrolyte

DO: Storage - Electrochemical Sensors

- Turn instrument off when not in use for extended periods
- Short term storage - store with membrane installed in a moist environment but not directly in water
- Long term - rinse with DI water, dry and install dry membrane

DO: Storage - Optical Sensors

- Do not let a sensor cap dry out
- Short and Long term storage - store with sensor cap installed in a moist environment but not directly water
- If it dries out, perform rehydration

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Xylem Portfolio

YSI Process: Instruments with Optical DO

Pro20i Dissolved Oxygen Meter

ProSolo Digital Water Quality Meter

YSI Wastewater Application Page

Xylem Lab Solutions: pH, ISE, and More

**OI Analytical's :
1080 Total Organic
Carbon Analyzer**

**YSI's: Automated
Titration**

**MulitLab benchtop with
YSI Process IDS ProOBOD
probe**

Xylem Lab Solutions: pH, ISE, and More

OI Analytical's :
4100 Water and Soil
Sample Processor

Gerhardt: VAPODEST

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Questions?