Essentials of Practical pH Measurement

Johnny Spigner, Technical Sales Manager
Don Ivy, Western Area Sales Manager
Thermo Scientific Electrochemistry Products
October 2010

The world leader in serving science

Measuring pH

What is pH?

- pH by definition is the hydrogen ion activity of a sample
- activity is the "free" ion rather than total

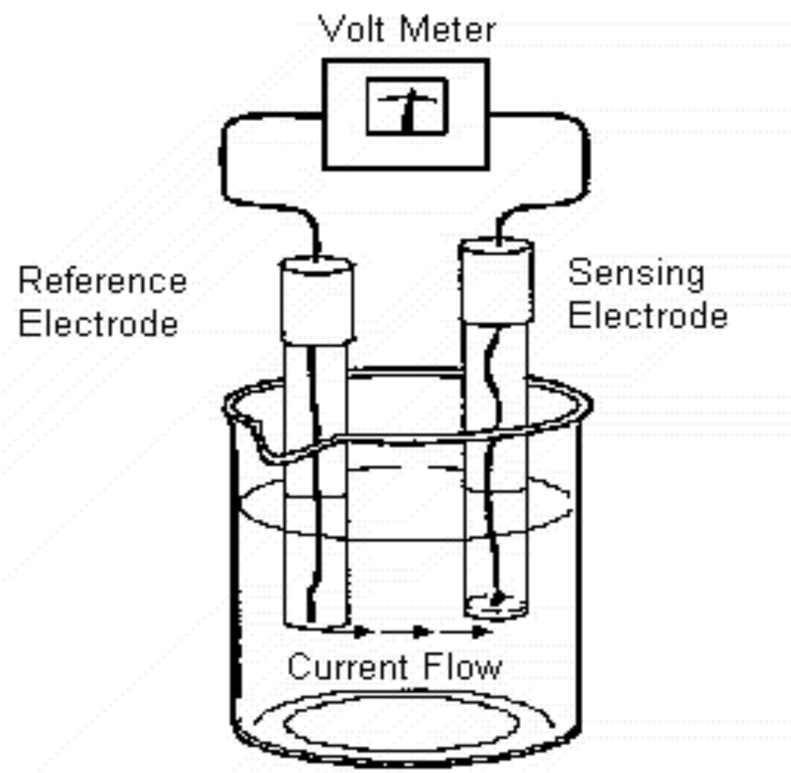
pH electrodes are a type of ion selective electrode (ISE) measuring free hydrogen ion concentration

- anything that gives more H^+ than HOH is acid
- anything that gives less H^+ than HOH is alkaline (basic)

pH Measuring System

The pH meter measures a voltage signal coming from the electrode.

…or more specifically, it measures, in mV, the voltage potential difference between the inside of the pH electrode and the outside sample (reference).



- *Acts as a volt meter*
- *Translates electrode potential (mV) to pH scale*

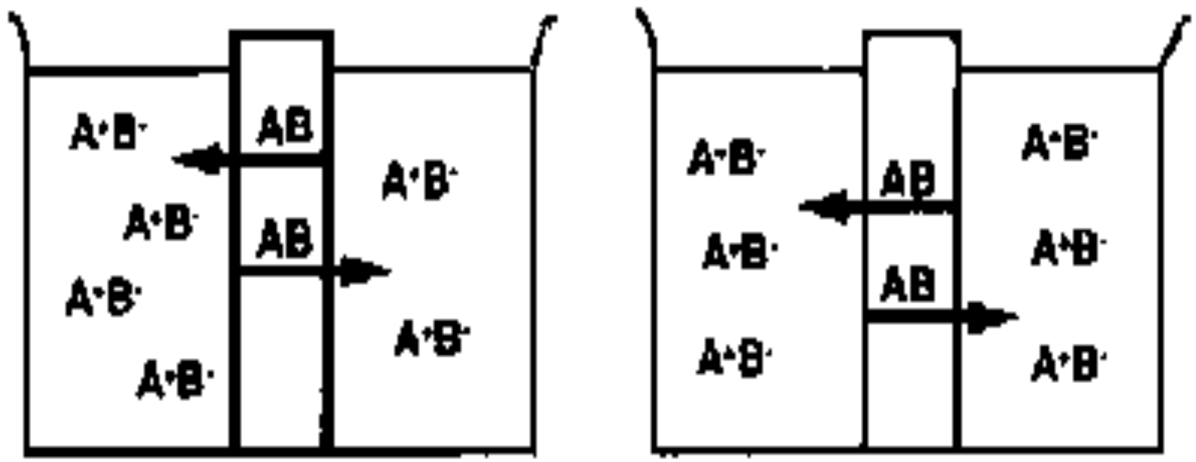
pH Meters

- pH Meter function:
  - *Stores calibration curve*
  - *Adjusts electrode slope*
  - *Adjusts for temperature changes*
  - *Signals when voltage potential (mv) reading is stable*

Measuring pH

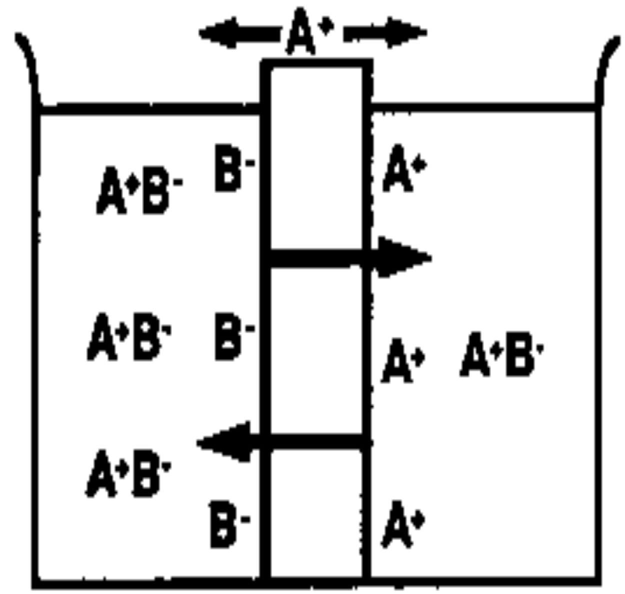
How Do Electrodes Work?

- If two solutions are separated by an ion-permeable membrane, they will equilibrate:



How Do Electrodes Work?

- If the electrode membrane is permeable to only one ion species, a charge will quickly develop that opposes further ion movement.
- The charge that develops across the membrane is proportional to the difference in the ion concentration on either side.



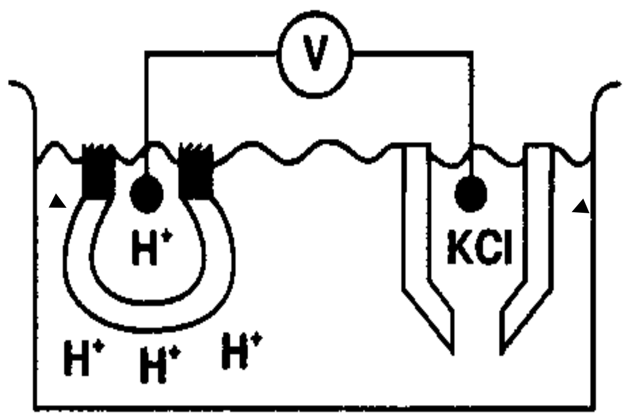
Measuring pH

How is pH Measured?

- A voltage signal develops across the permeable glass membrane.

sensing membrane

Half-cell electrode??



reference membrane

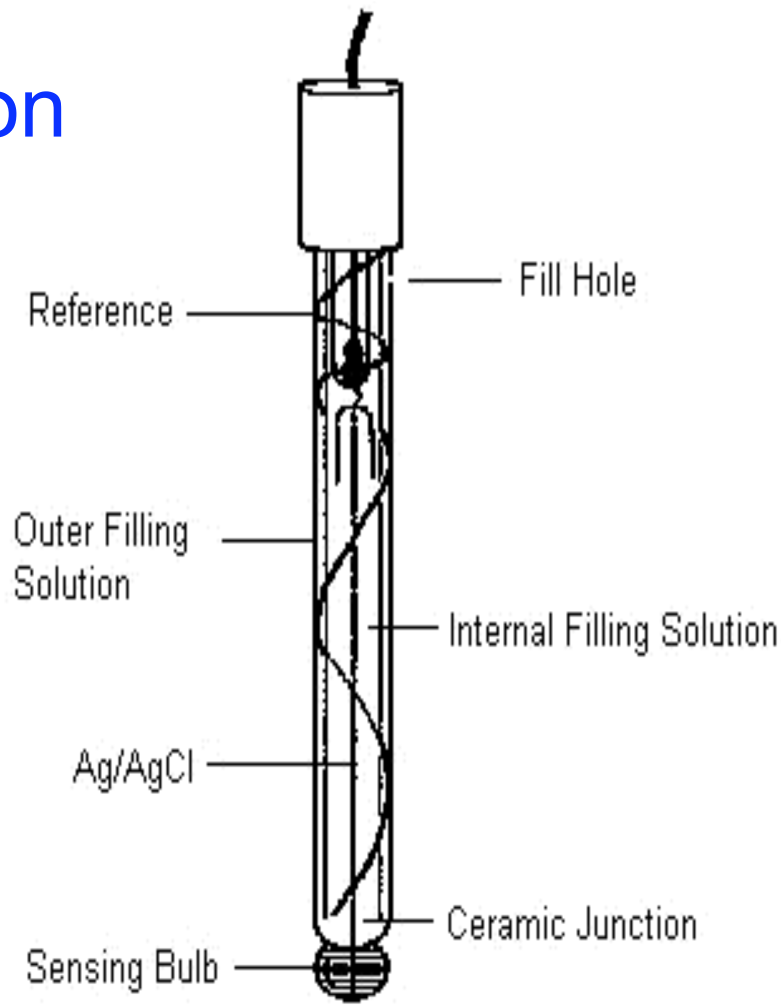
Combination electrode??

- An algorithim in the meter firmware translates the received mV signal into a pH scale.

Measuring pH

pH Electrode Composition

- Sensing Bulb
- Reference
- Reference Solution
- Internal Fill Solution
- Junction



Measuring pH

pH Electrode Reference Types

- Calomel reference
  - *Fixed Hg_2^{++} activity in contact with solid mercury*
- Silver reference
  - *Fixed Ag+ activity in contact with silver wire*
  - *Single and double junction design*
- ROSS reference
  - *Redox couple (Iodide/Iodine)*
  - *Double junction design*

Measuring pH

pH Electrode Junction Types

- Wick junction
  - *Glass fiber, fiber optical bundles, Dacron, etc.*
  - *Common in epoxy body electrodes*
- Ceramic junction
  - *Porous ceramic, wooden plug, porous Teflon, etc.*
  - *Common in glass body electrodes*

ceramic junction

Measuring pH

pH Electrode Junction Types

- Liquid junctions
  - *Sure-Flow*
  - *Ground glass sleeve*
  - *Laser drilled hole*

“Sure-Flow” liquid junction

Measuring pH

Calibration

- The Nernst Equation

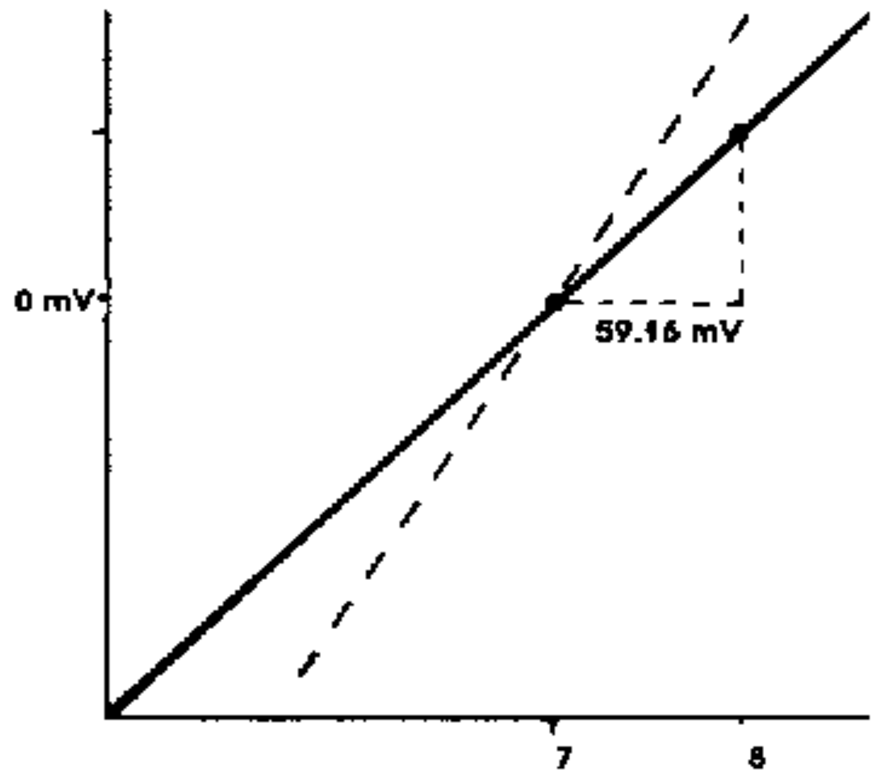
  $$E = E_0 + s \log a_H$$

  - E = measured potential
  - E_0 = reference potential
  - s = slope = RT/nF = 59.2 mV at 25 ^{o}C
  - a_H = activity

ThermoFisher SCIENTIFIC

Calibration

- % slope is the change in mV value divided by the Nernstian theoretical value of 59.2 mV, the expected change in mV per pH unit at 25°C



ThermoFisher SCIENTIFIC

Calibration

- Newer meters automatically calculate slope
- If the meter does not provide a calibration slope, you can check the slope manually by using your buffers' mV value to compare to the Nernstian response (59.2 mV/pH unit)
  - *Example:*
    - pH 7 = -10 mV
    - pH 4 = +150 mV
    - Slope = 160 mV/177.6 mV = 90.1%

Measuring pH

Calibration

- Always calibrate with at least 2 buffers
- Always calibrate with buffers that bracket the expected measurement range
- *Calibrate with buffers that are no more than 3 pH units apart*
- Check calibration drift with 1 buffer
- Track calibration slope on a daily basis

Measuring pH

Calibration

- Electrode slope guidelines
  - *Ideal range: 95% - 102%*
  - *Cleaning range: 92% - 95%*
  - *Replacement range: below 92%*

Measuring pH

Making Accurate Measurements

- Common measurement problems

  Readings not reproducible

  Slow response

  Drifty response

  Inaccurate

Measuring pH

Making Accurate Measurements

- Common error contributors

    Temperature effects

    Buffers

    Electrode selection vs. sample type

    Electrode maintenance

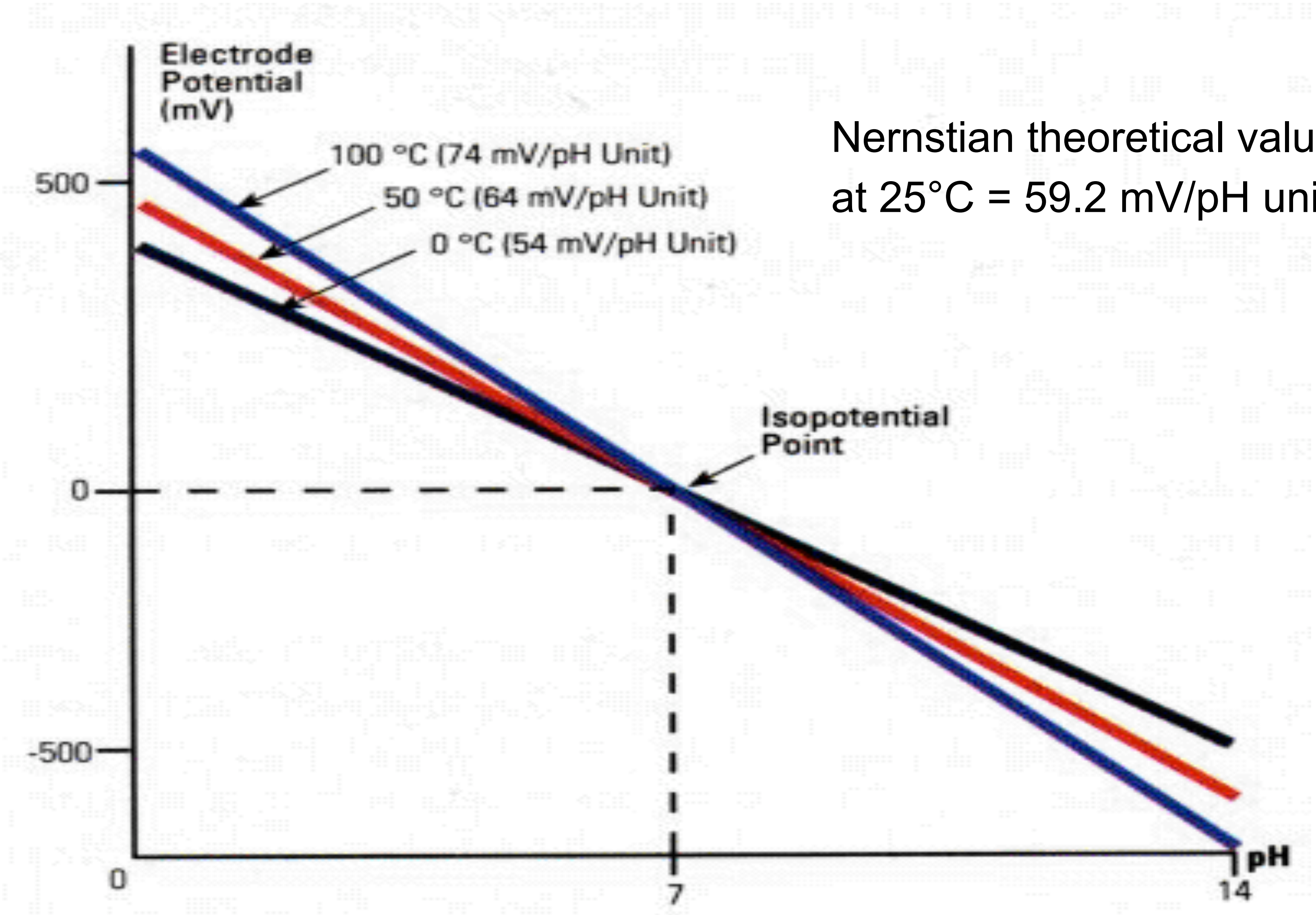
    Electrode wear

    Technique

Making Accurate Measurements

- Temperature effects
  - The expected mV value per pH unit changes as the temperature changes
  - The calibration slope should change as temperature changes
  - Temperature compensation adjusts the calibration slope for improved measurement accuracy...

Making Accurate Measurements



Nernstian theoretical value at 25°C = 59.2 mV/pH unit

Making Accurate Measurements

- Temperature effects
  - Samples / buffers have different pH values at different temperatures
  - Record temperature with pH readings
  - It is not possible to normalize pH readings to a specific temperature, but you can improve accuracy by enabling the meter to adjust the slope

Making Accurate Measurements

- Temperature effects
  - Calibrate and measure at the same temperature
  - Use automatic temperature compensator (ATC) or 3-in-1 Triode electrode
  - Manually temperature compensate using temperature control on meter
  - Use LogR temperature compensation

Making Accurate Measurements

- Always use fresh buffers for calibrations

Check bottle expiration and date opened

- Use pH 4 and pH 7 buffers within 12 months after opening.
- Use pH 10 buffer within 3-6 months after opening.

Use fresh buffer for each calibration

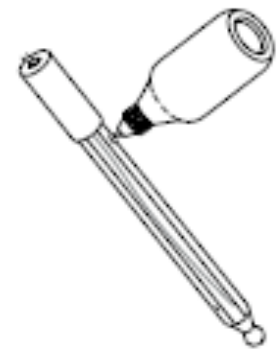
- Calibrate only once in buffer… don't re-use buffer.

Individual Buffer Packets

- Only opened once, so the 2-year shelf-life is also the use life.

Making Accurate Measurements

Use good measurement technique



- Uncover fill hole during measurement
- Make sure level of fill solution is high
- Make sure electrode bulb has been hydrated

ThermoFisher SCIENTIFIC

Making Accurate Measurements

Use good measurement technique

- Shake any air bubbles out of the electrode
- Gently stir buffers and samples
- Rinse and blot electrodes between samples
- Use insulation between stir plate and sample container to minimize heat transfer

Thermo Fisher SCIENTIFIC

Making Accurate Measurements

- Check for scratches on electrode bulb
- Replace the fill solution in the electrode periodically
  - *Weekly or monthly, depending on use frequency*
  - *Fill solution concentration is maintained*
  - *KCl crystallization is prevented*
- Make sure to use the correct fill solution
  - *Ross electrodes cannot use Ag/AgCl fill solutions*
  - *Single Junction Ag/AgCl electrodes cannot use double junction Ag/AgCl fill solutions*
  - *Calomel electrodes cannot use Ag/AgCl fill solutions*

Electrodeorage

- Short-term storage
  - *Use electrode 'Storage Solution'*
  - *Alternatively, soak in 100 ml pH 4 or 7 buffer (manufacturer recommendation dependent) mixed with 0.5 g KCl*
- Long-term storage
  - *Fill electrode, close fill hole, store with storage solution in protective cap*

Troubleshooting Sequence

1. Meter
2. Buffers
3. Sample
4. Combination Electrode

   (or reference followed by pH electrode)
5. Technique

Troubleshooting pH Meters

Meter Check

- Use meter shorting strap
- Reading should be 0 mV +/- 0.2 mV

Troubleshooting pH Meters

Buffer Check

- Ensure buffer solutions are within factory expiration date and maximum recommended open date

Troubleshooting

Sample Check

- Verify sample analysis
  - Junction is submersed in sample
  - Electrode body and inner fill solution are compatible with sample components
  - Sensor is not being “coated” with sample
- Confirm temperature compensation

Troubleshooting

Electrode Check

- Check slope range (95% - 102%)
- Check response times in buffers

  … stable reading within 30 seconds
- Verify mV readings are in the correct range for buffers using meter mV mode
  - pH 7.00 is 0 ± 30 mV
  - @ 25°C pH 4.01 is +178 ± 30 mV
  - @ 25°C pH 10.01 is -178 ± 30 mV

ThermoFisher SCIENTIFIC

If Electrode Failed Test

- Check for air bubbles near bulb
- Verify correct filling solution is being used
- Check for salt crystal formation inside electrode
- Check that junction is open by suspending in air for ten minutes…

KCl crystal formation will occur
if the junction is open

…then re-hydrate the bulb

If Electrode Failed Test

- Perform junction / bulb cleaning procedures consistent with possible contaminate type

  - *Example: 0.1 M HCl for general cleaning*
  - *Example: 1% pepsin in HCl for proteins*
  - *Example: Bleach for disinfecting*
  - *Example: detergent for grease & oil*

- Re-test electrode for mV readings

ThermoFisher SCIENTIFIC

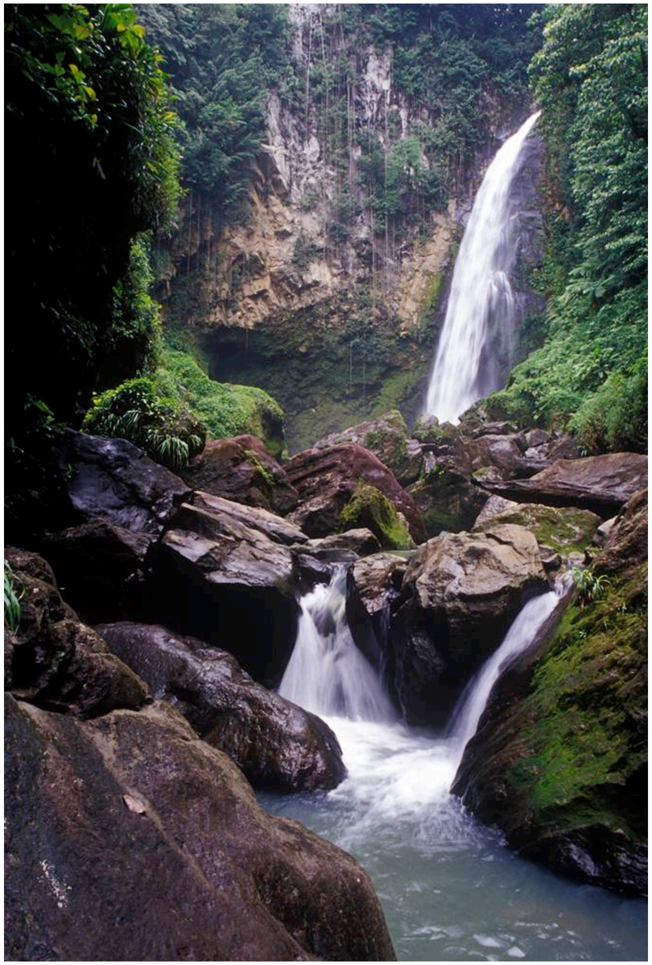
pH Clinic Program

FREE pH Meter / Electrode Diagnostic Service

- Meter and Electrode evaluated individually
  - Troubleshooting advice
  - Care and maintenance planning
  - Electrode selection recommendations
  - Leave-behind report
  - Method evaluation and applications support

Thermo Fisher SCIENTIFIC

Hands On!



Ammonia ISE: Calibration, Measurement, Maintenance and Troubleshooting

The world leader in serving science

Introduction

- Ammonia
  - •Gaseous compound
  - •Basic (high pH)
  - •Found naturally in salt form (NH_4Cl)
- Ammonia in effluent
  - •Environmental impact
  - •EPA Regulated
  - •Typical levels less than 1mg/L
  - •Excess causes algal blooms
  - •Toxic to aquatic organisms at very low level

Why Use Ion Selective Electrodes?

- EPA approved methods: *Ammonia in wastewater*
- Ammonia ISEs detect the species in solutions
- ISE meters report concentrations
  - *No manual calibration curves are required*
- ISE meters generate sophisticated curves which are held in the meter’s memory
  - *Run standards*
  - *Run unknowns*
  - *Read results*

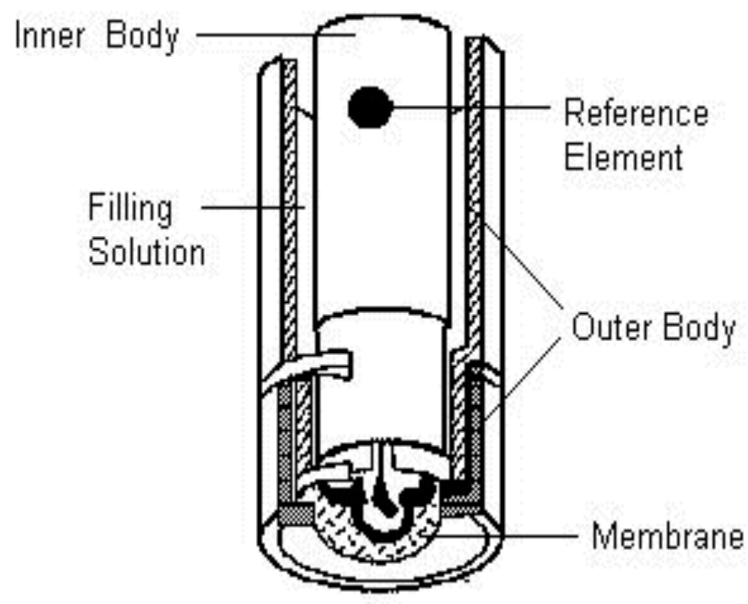
- Ammonia: Gas Sensing Electrodes

Measuring Ammonia with ISEs

- Electrode advantages
  - •No harmful reagents
  - •Quick analysis
  - •No color or turbidity interferences
  - •No distillation required
  - •Low level detection
  - •Direct or Known Addition Methods
  - •Automation capabilities
  - •Affordable instrumentation
  - •Lab or field applications

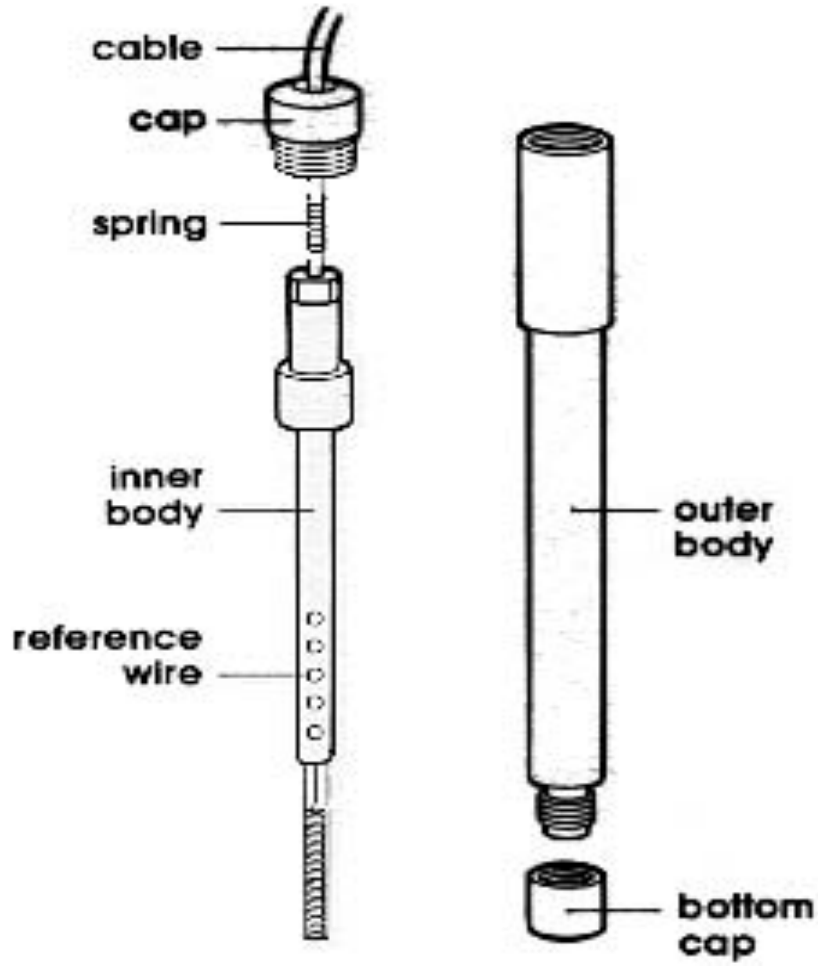
Gas Sensing Electrodes

- Gas sensing electrodes work by measuring the pH change caused by diffusion of the gas through a hydrophobic but porous membrane
- Short term storage: in dilute standard
- Long term storage: store dry



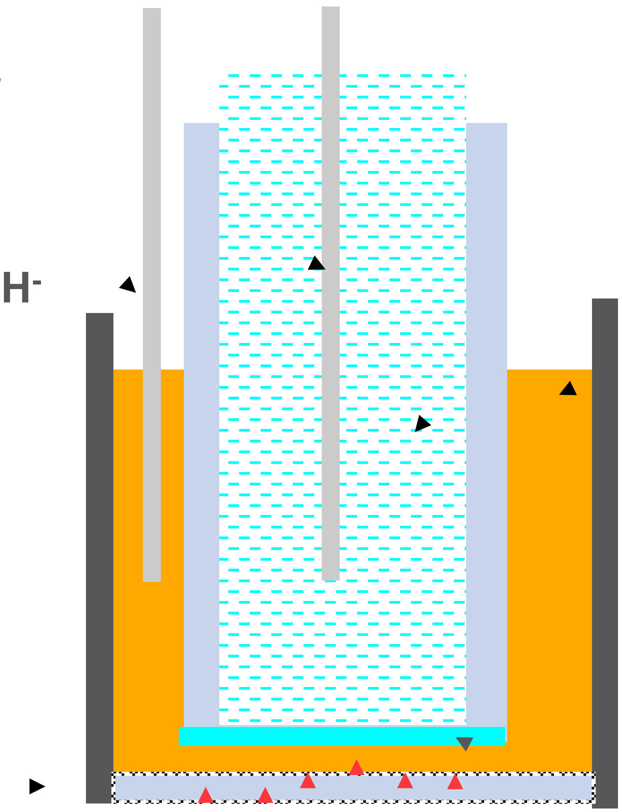
Gas Sensing Electrodes

- Ammonia
  - EPA approved for wastewater
  - 0.01 ppm detection limit
  - Combination electrode
  - Replaceable membranes



Electrode Structure

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$



Electrode Structure

- Theory of Operation
  - Membrane permeable only to gas
    - Ammonia diffuses through until the partial pressure is equal on both sides
  - Inner stem: pH electrode
  - IFS: fixed amount of NH_4+ (excess)
  - NH_3 is directly proportional to OH-
  - pH electrode can indirectly detect change in NH_3

$$\frac{[NH_4]\,[OH^-]}{[NH_3]} = \text{constant} \quad \blacktriangleright \quad [OH^-] = [NH_3] \bullet \text{constant}$$

Ammonia ISE Assembly

- Soak inner body in fill solution for 2 hrs.
- Replace the membrane every 2-4 weeks
- Use tweezers to handle membrane
- Stretch membrane until taut
- Use 2.0 - 2.5 mls of fill solution (approx. 50 drops)
- Shake electrode down after assembly

Ammonia ISE Storage

- Store in 10-100 ppm ammonia standard
- Between measurements store In 10 ppm standard with NaOH (ISA)
- Condition electrode in pH 4 buffer for several minutes before starting low level calibration

Ammonia ISE Inner Body Check

- Place electrode in pH 7 buffer: read mV
- Rinse electrode
- Place electrode in pH 4 buffer
- mV’s should change by at least 100 after 30 seconds
- mV’s should change by at least 150 after 3 minutes

Ammonia Slope Check

- Prepare 100 mls DI water
- Add 2 mls ISA
- Add 1 ml 1000 ppm ammonia standard
- Record mV reading
- Add 10 mls 1000 ppm ammonia standard
- Record mV reading
- Slope range: 54-60 mV

Ammonia ISE Hints

- Use electrode at a 20 degree angle: check for bubbles at membrane
- Calibrate with standards that bracket sample concentration
- Samples should be acidified if stored
- Replace membrane / clean inner body in 0.1M HCl when response is sluggish or slope is low

Direct Measurement

- Preferred method in most cases:
  - *Many samples with similar backgrounds*
  - *High volume of samples*
  - *Wide range of concentrations*
  - *Easy*
- Calibrate by comparison with known standards
- Read by preparing calibration curve or using ISE meter
- Precision is +/- 2%

Direct Measurement

- Calibrate every 2 hours
- Always calibrate with standards that bracket expected concentration range
- Always use at least two standards that are ten fold apart in concentration
- Slope range for monovalent ions: 54-60 mV (ammonia)

Practical Considerations

- Method interferences

  Many method interferences can be overcome by using Ionic Strength Adjuster (ISA)

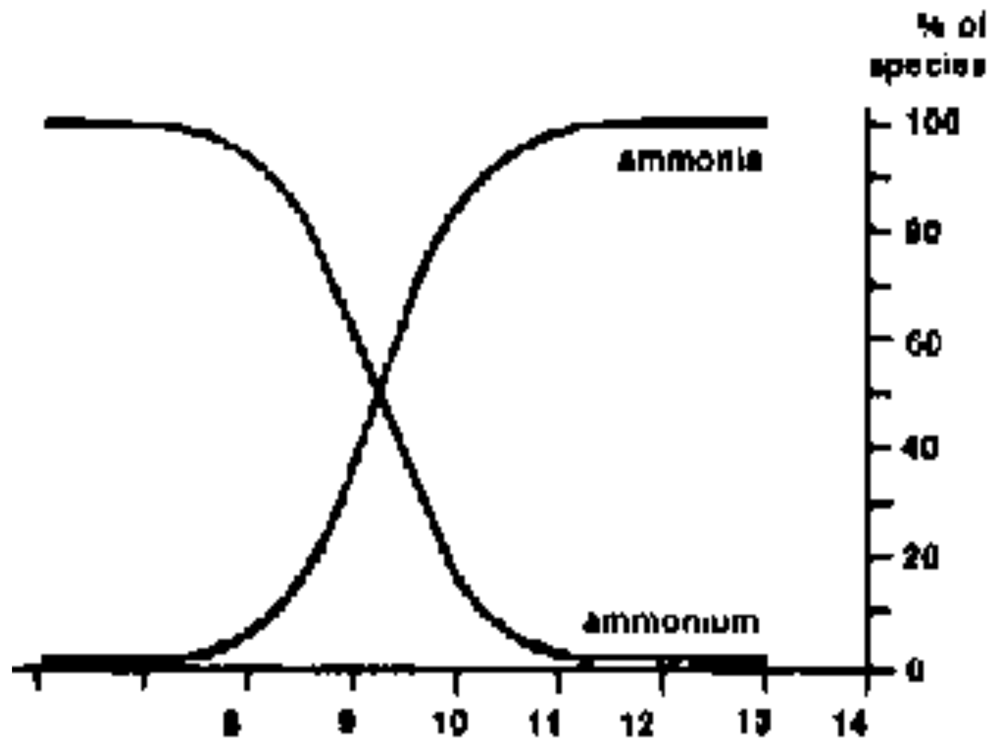
  - added to samples and standards to maintain constant background
  - minimize ionic strength differences
  - can complex interferences
  - can adjust pH to proper range

Practical Considerations

- Method interferences

ISA example

- Ammonia ISA adjusts pH to proper range for conversion to ammonia



Practical Considerations

- Temperature effects

  A change in temperature will cause electrode response to shift and change slope

  - On average, a 1°C change in temperature gives rise to a 2% error for monovalent ISE's (ammonia)
  - Temperature compensation is possible only if the isopotential point of the ISE electrode is used to adjust the calibration curve
  - For ammonia measurements make sure standards and samples are the same temperature

Troubleshooting Sequence

1. Meter
2. Standards
3. Ammonia Electrode
4. Sample
5. Technique

Measurement Variables

- Concentration range
- Ionic strength
- Temperature
- pH
- Stirring
- Interferences
- Complexation

Making Accurate Measurements

- Bracket sample values with standards
- Use serial dilution to prepare calibration standards
- Adjust ionic strength
- Remove method interferences
- Remove electrode interferences
- Operate at a constant temperature
- Stir standards and samples gently

What's New? High Performance Probe

- Features
  - Transparent outer body
  - Fill line
  - New fill solution / membrane
  - ISA for low level samples
  - Pre-assembled outer bodies
- Performance
  - Better detection at low levels
    - 0.01mg/L detection limit
  - Faster response time

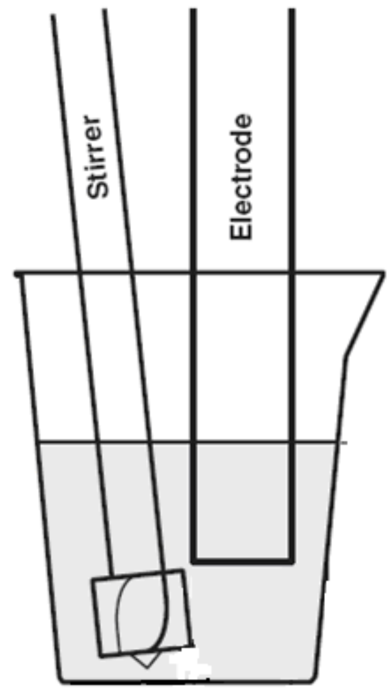
Optimization Techniques

- Prepare standards by serial dilution: *improves accuracy*
- Rinse probe by immersion
  - •More effective than squirting with rinse bottle
  - •Doesn't disturb layer of IFS between membrane and inner stem
  - •Use 0.1M KCl in pH 4 buffer as rinse to speed up rinse process and ensure electrode is completely clean
- Condition electrode
  - •Exposure to ammonia prior to calibration / use greatly improves performance
  - •15 minutes in 1mg/L standard (with ISA) greatly improves performance

Optimization Techniques

- High Performance Ammonia Electrodes:
  - •Improved membranes, including pre-assembled outer bodies
  - •New fill solution
  - •Specific ISA for low level measurements

- Sample Stirring
  - Set stirrer to sit just below electrode surface
    - Reduces carryover and bubbles on probe surface



Troubleshooting

While we would all like testing to go according to plan everyday, that is sometimes not the case.

Troubleshooting

Steps to Follow if Electrode is Not Working Properly

1. Solutions
   - Check solutions being used are all correct
   - For overnight and long term storage (up to 1 week), electrode should be in internal fill solution (IFS).
   - Re-check standards preparation
   - Prepare fresh standards
   - Make sure the correct amount of ISA has been used in all standards and samples

3. Conditioning
   - Has the electrode been conditioned?
   - Has anything been done to the electrode that would require it to be reconditioned?

Troubleshooting

Steps to Follow if Electrode is Not Working Properly

3. Slope/Drift check
   - Perform low level slope check according to manual
   - In first solution used to check slope, record both the two and three minute readings to get a drift value
   - If slope fails, repeat slope check. A second failure indicates membrane should be changed. Failure with a second membrane indicates inner stem should be checked.
   - If drift fails, pull up on electrode cable to refresh IFS. Electrode must be reconditioned after this is done.

Troubleshooting

Steps to Follow if Electrode is Not Working Properly

4. Membrane Change
   - If drift and/or slope do not read as desired, change the membrane and internal fill solution
   - Take care to not stretch or touch the middle of the membrane during installation.
   - Repeat slope/drift check.

Troubleshooting

Steps to Follow if Electrode is Not Working Properly

5. Inner Body Check

- If all above steps fail, check the performance of the inner body according to manual
- Inner Body Check failure indicates electrode replacement is required
- If electrode passes check, re-assemble with fresh IFS and new membrane. Check slope and drift again.

If electrode passes the Inner Body Check, it has capability to perform to specification.

Thermo Fisher SCIENTIFIC

The world leader in serving science

Measuring Dissolved Oxygen:

Polarographic and Luminescence Technologies

The world leader in serving science

Dissolved Oxygen Measurement

Common Applications

- *Wastewater:* treatment effectiveness
- *Surface and Drinking Water:* overall quality
- *Environmental Monitoring:* pollution levels
- *Aquaculture:* production levels
- *Research Sites:* biological systems support and bio-reactions
- *Industrial Sites:* system corrosion control
- *Food & Beverage Processing:* taste and color
- *Pharmaceutical and Biotech:* quality control
- *Seawater:* quality, pollution, salinity levels

Dissolved Oxygen Measurement

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.

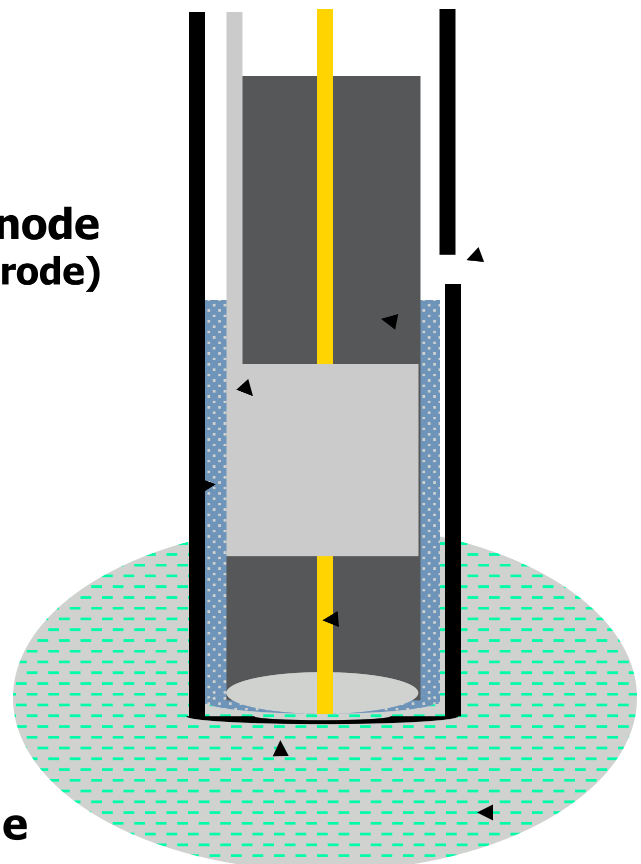
The DO value is determined from the reduction reaction that produces a current flow directly proportional to the dissolved oxygen concentration.

Dissolved Oxygen Measurement

Electrochemical or “Clark” Method

- Saves time, money, and labor
  - No reagents or wet chemistry titration preparation
- Greater measurement accuracy
- No reagents’ 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.

Dissolved Oxygen Measurement

- 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.

Common Difficulties Using the “Clark” Method DO Probe

- Barometric pressure
  - Dissolved oxygen concentration and therefore measurement affected by barometric pressure change
  - Potential error with weather fluctuation and elevation change
  - Potential error is reduced to <0.5% when automatic correction sensor is built into meter
- Sample Stirring
  - Oxygen is consumed at the cathode
  - Oxygen must arrive at the sensor faster than it can be consumed
  - Stirring is necessary to avoid oxygen depletion at the membrane

Common Difficulties Using the “Clark” Method DO Probe

- Temperature
  - DO levels (oxygen solubility) change with temperature
  - The DO diffusion rate across the gas permeable membrane changes 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 with meters designed to incorporate a pre-determined salinity correction factor

Common Difficulties Using the "Clark" Method DO Probe

- Interfering gases
  - Chlorine, Nitrous Oxide, H2S
  - Hydrogen, Carbon Monoxide, Carbon Dioxide
- Probe maintenance
  - Membranes and Electrolyte
    - Replenishment, replacement and proper assembly
  - Cathode and Anode Cleaning

Dissolved Oxygen Measurement: Polarographic

- Membrane maintenance should be performed when readings become unstable or slow or alternately, every one to three months, depending on usage and sample type.

1. Disconnect the probe from the meter.
2. Remove the stir paddle by firmly grasping it and pulling it straight out.
3. Unscrew the membrane cap from the probe, dispose of the electrolyte solution and membrane cap, and then rinse the probe with distilled water for a few seconds to remove any contaminants.

Dissolved Oxygen Measurement: Polarographic

4. If the cathode appears to have a dull finish, clean it with a polishing disk.

   Place a few drops of distilled water on a polishing disk. Polish the probe by gently rubbing the surface of the cathode on the wet polishing disk in a circular motion for 10 seconds. Once the probe is polished, rinse it with distilled water and blot dry with a lint-free tissue.

   If the cathode has a bright finish, rinse it with distilled water, blot dry with a lint-free tissue.

Dissolved Oxygen Measurement: Polarographic

5. Fill a new membrane cap about ¾ full with the electrolyte solution. Ensure that the inner surface of the membrane does not have bubbles on it. To remove bubbles, hold the membrane cap and tap the side of the cap with your finger. This should cause any bubbles to rise to the surface and away from the membrane.
6. Screw the new membrane cap onto the probe until the membrane cap is finger tight. Wipe off any displaced electrolyte solution on the probe.
7. Replace the stir paddle by aligning it in the hole and firmly pushing it into place.

Dissolved Oxygen Measurement: Polarographic

8. Polarize the probe

The probe must be polarized before use.

To polarize a new probe, attach the probe to the meter, connect the meter to a power supply, and wait 30 to 60 minutes.

The probe is continuously polarized when it is connected to the meter, so this process does not need to be repeated unless probe maintenance is performed or the probe is disconnected from the meter for more than an hour.

If the probe is disconnected from the meter for less than an hour, allow the probe to polarize for 5 to 25 minutes before use.

RDO®: Luminescence Based Technology

Optical / Luminescence DO Measurement Features

- Accuracy and Precision equal to or better than Winkler or Clark DO Measurement Methods
- Fast Response
  - Polarization or warm-up time not required… RDO is ready to take readings immediately
  - Highly sensitive lumiphore obtains readings quickly
- Improved Accuracy for Low Level Oxygen Measurements

RDO®: Luminescence Based Technology

Optical / Luminescence DO Measurement Features

- 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
  - Optical / Luminescence Technology works well in electrically busy areas
  - Cable length does not affect performance

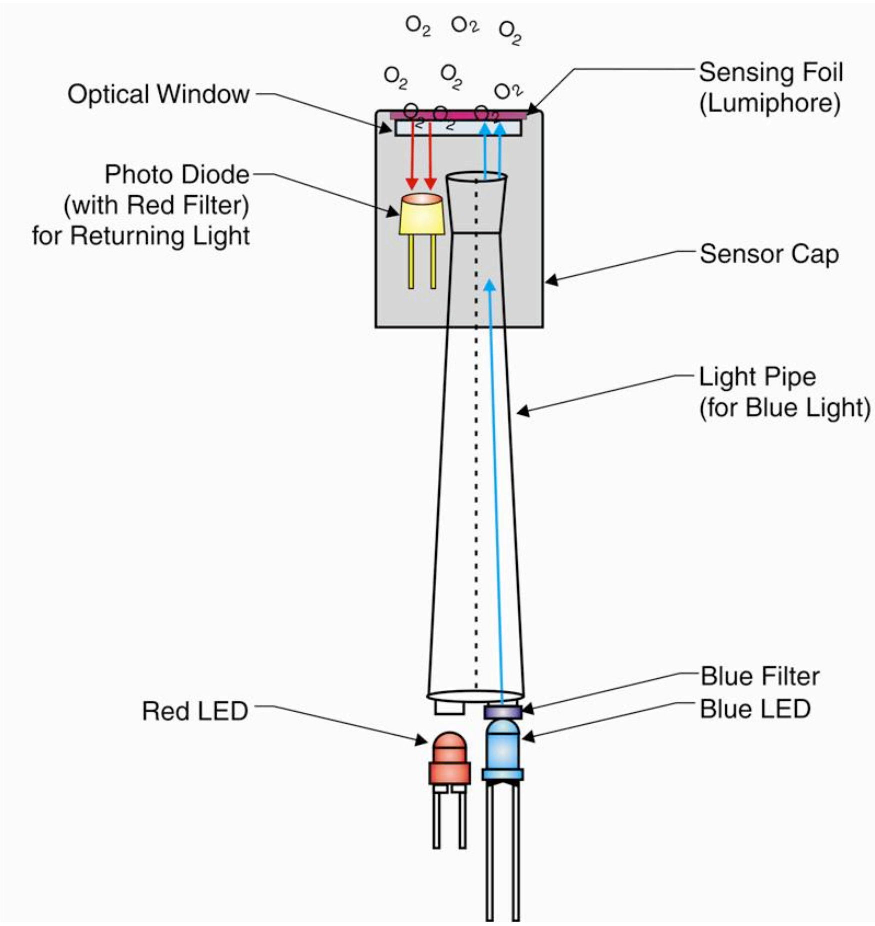
RDO®: Luminescence Based Technology

Optical / Luminescence DO Measurement Features

- *Reduced maintenance costs and time commitment*
  - No membranes to change
  - No solutions
- *Available in Thermo Scientific RDO®*
  (Rugged Dissolved Oxygen) meters and probes

RDO®: New Method for DO Determination

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.

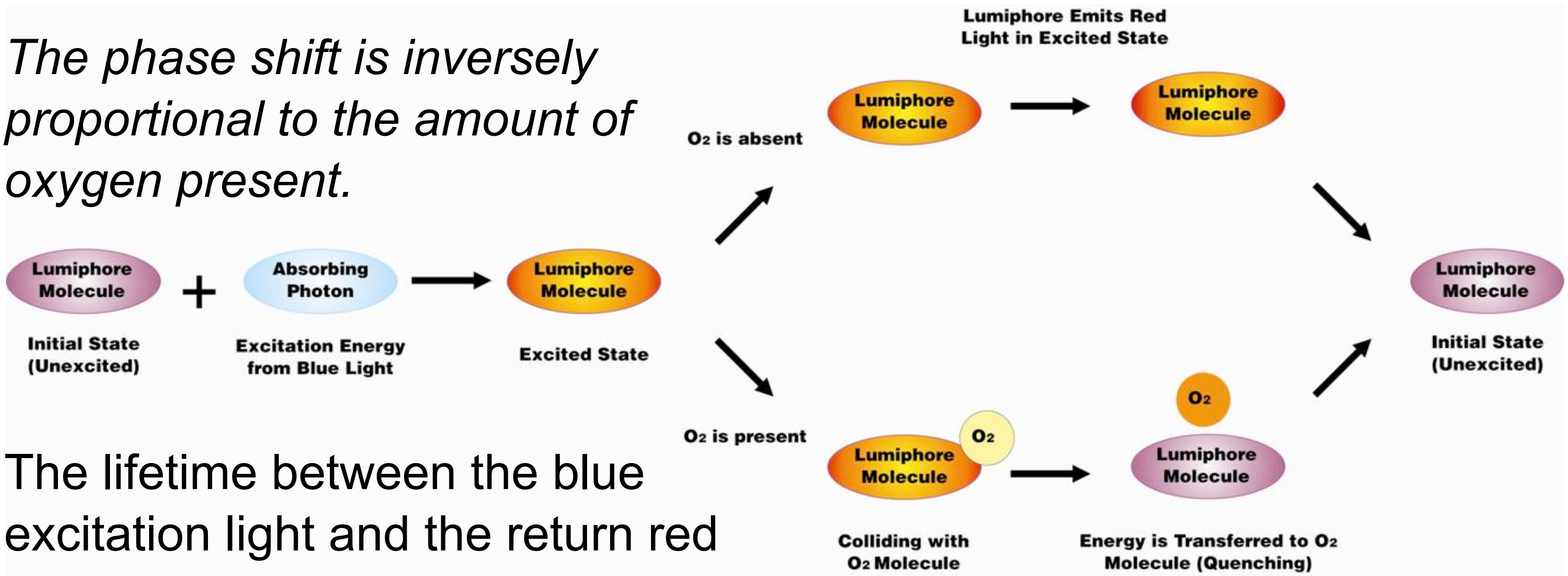
This dissolved oxygen measurement is based on luminescence "lifetime" rather than "intensity".

RDO®: New Method for DO Determination

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.

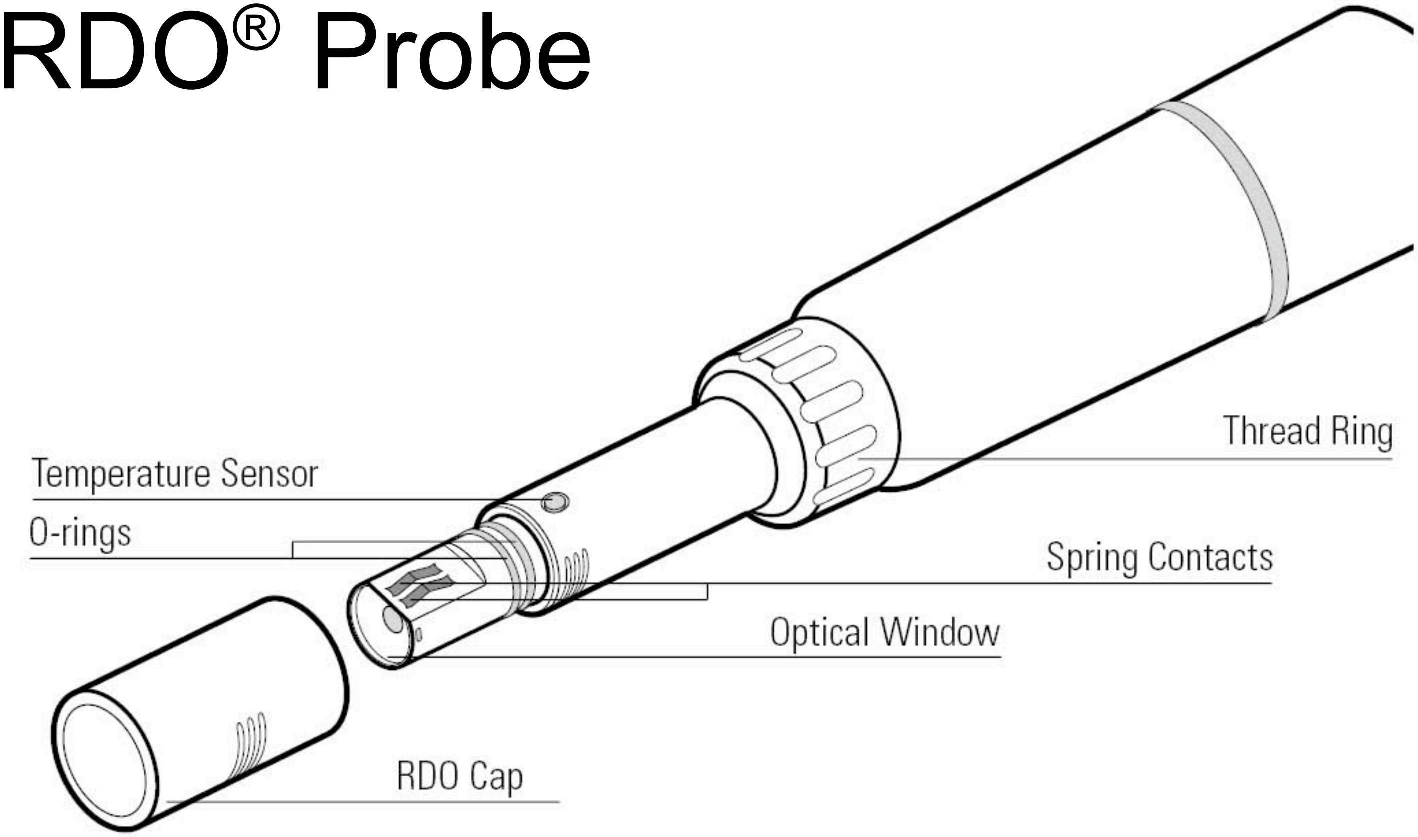


The lifetime between the blue excitation light and the return red light is measured, and the result is used to quantify the dissolved oxygen present.

ThermoFisher SCIENTIFIC

Thermo Scientific RDO®

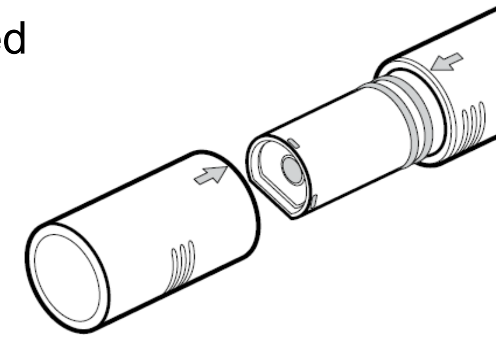
RDO® Probe



Thermo Scientific RDO®

RDO® Probe Features

- “Smart” probe
  - Cap stores calibration data, usage information
  - Readings are sent to the meter and displayed
- Once-a-year maintenance
  - Simple cap replacement: line up arrows
- 3-year probe replacement warranty

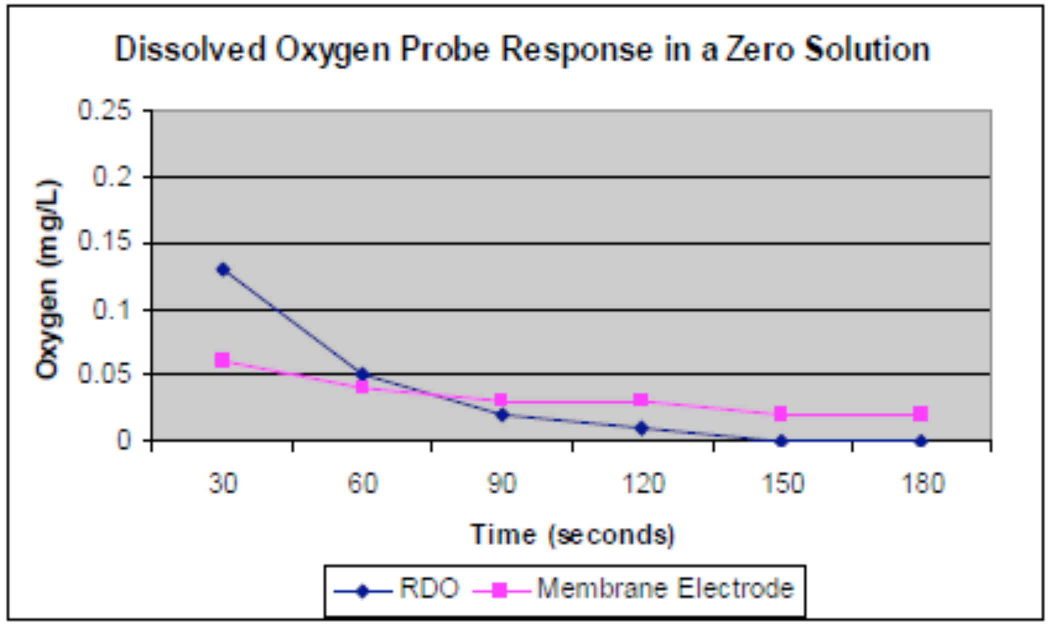


- Includes sensor cap
  - Effectively reads for one year with no performance degradation
  - 1-year sensor cap warranty
- Includes calibration chamber
- Includes stainless steel probe guard
  - Protects sensor cap
  - Provides weight for submersion

Thermo Scientific RDO®: Performance

RDO® shows excellent response in low level oxygen samples.

Response time is comparable to the membrane electrode but RDO® has improved accuracy - it reads the expected zero in the oxygen-free solution.

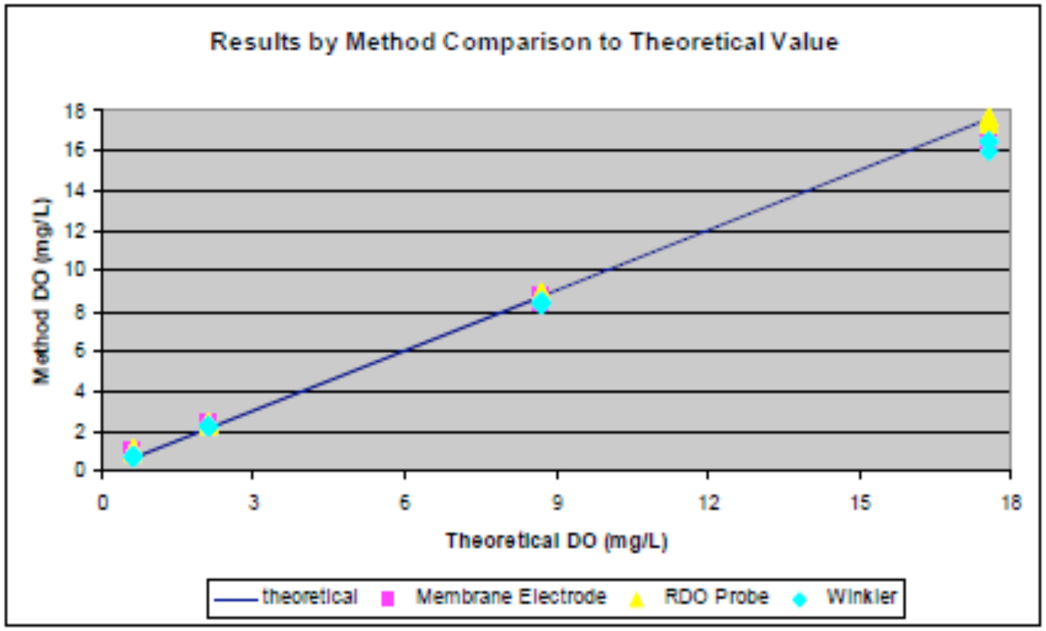


These readings followed a water saturated air calibration, indicating that calibration at a zero point is not necessary for accurate low level measurements with RDO®.

Thermo Scientific RDO®: Performance

Winkler Titration and Membrane Electrode are long-accepted methods for reporting dissolved oxygen results in wastewater.

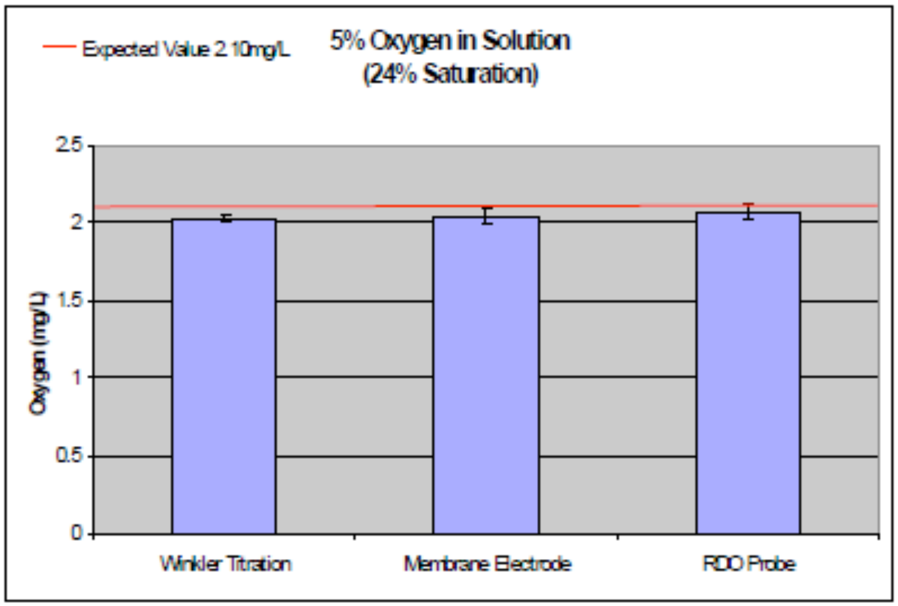
Samples are all deionized water bubbled with gases containing known amounts of oxygen to saturation.

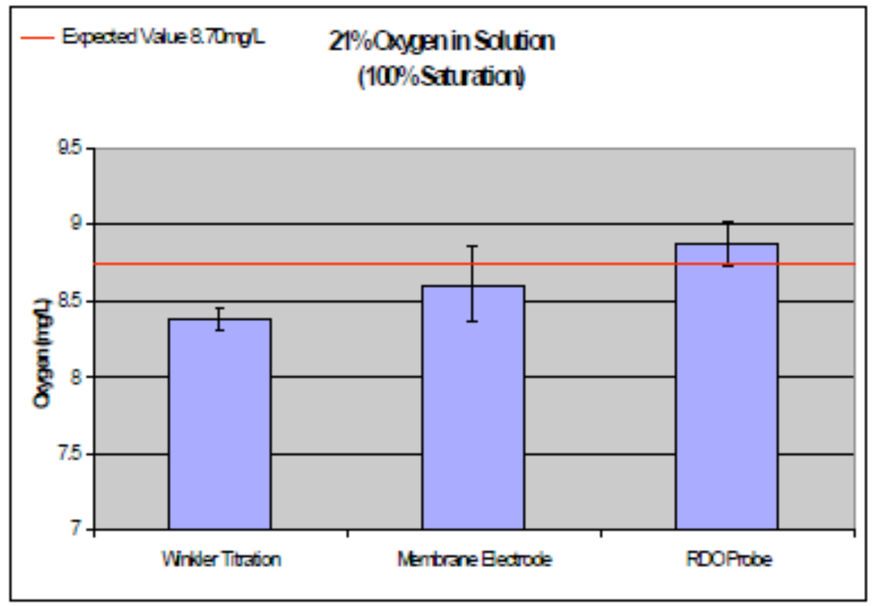


RDO® is well correlated with these methods and has improved accuracy.

Thermo Scientific RDO®: Performance

RDO®: Optical / Luminescence Method Compared to Winkler Titration and Membrane Electrode Methods





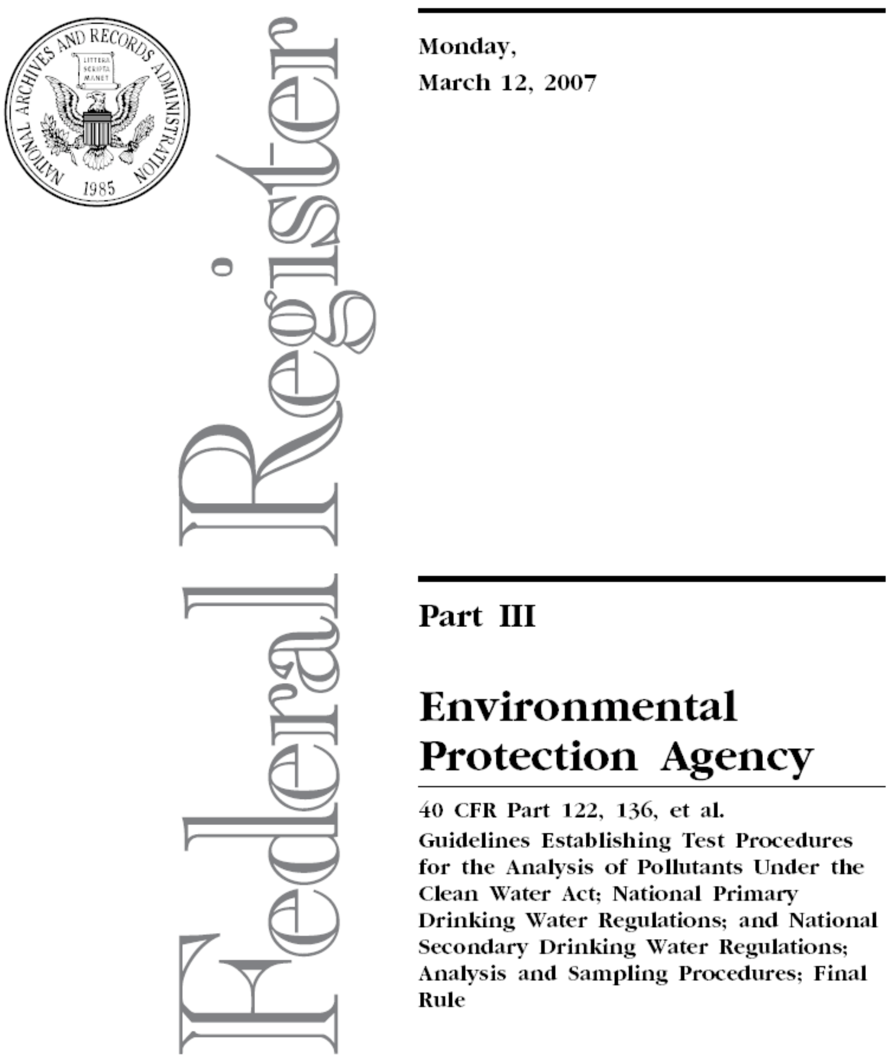
Samples are all deionized water bubbled with gases containing known amounts of oxygen to saturation.

RDO®: New Method for DO Determination

Method Approval: Regulatory Status

- Optical DO technology is written into DO methods by ASTM and USGS, and is currently being tested for incorporation into Standard Methods for the Examination of Water and Wastewater.
- The optical / luminescence technology is accepted by ASTM for wastewater testing in Method D 888-05 Part C Luminescence Based-Sensor Procedure.

Approved DO Methods for Compliance Reporting



Federal Register

Monday,
March 12, 2007

Part III

Environmental Protection Agency

40 CFR Part 122, 136, et al.

Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; National Primary Drinking Water Regulations; and National Secondary Drinking Water Regulations; Analysis and Sampling Procedures; Final Rule

USEPA approved test procedures for Dissolved Oxygen:

- Winkler
- Membrane Electrode - electrochemical

As published in the Method Update Rule (MUR), 40 CFR Part 136.3 on March 12, 2007

RDO®: New Method for DO Determination

Method Approval: Regulatory Status

- The USEPA has recommended that regional EPA offices grant interim approval for the optical DO measurement method for wastewater dissolved oxygen and BOD monitoring. Most regions have accepted the procedure as a wastewater monitoring method.
- RDO® technology meets the requirements of ASTM D888-05 Method C, measuring dissolved oxygen with a luminescence-based sensor.
- The Thermo Scientific Orion RDO® probe was tested as part of the Standard Methods Oxygen Joint Task Group, formed to evaluate the luminescence probe against current methods for inclusion in SM 4500-O for water and wastewater testing.

USEPA Recommends Approval of In-Situ® RDO® Methods

- USEPA released approval letters November 3, 2009 for three new ATP methods for the Thermo Scientific Orion RDO® Optical Probe
  - **DO Measurement** (Method 1002-8-2009)
  - **BOD Measurement** (Method 1003-2-2009)
  - **CBOD Measurement** (Method 1004-2-2009)

- USEPA will recommend inclusion of these methods in the MUR, 40 CFR Part 136.3.

ThermoFisher SCIENTIFIC

RDO®: New Method for DO Determination

Unique features of Orion RDO® ATP Approvals:

- The RDO® was analyzed both as stirred and non-stirred
- First and only ATP applying Luminescence DO Measurement for nine unique matrixes from water and wastewater.
- First and only ATP applying Luminescence DO Measurement for Carbonaceous Biochemical Oxygen Demand (CBOD).

Thermo Fisher
SCIENTIFIC

The world leader in serving science