How pH and ORP Sensors Work

Principles and Practice in Water Quality Monitoring

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Demonstration Coordinator

June 9th, 2020

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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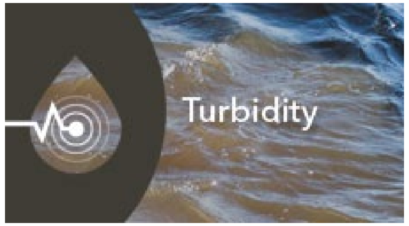
Recording available

Recording available



Recording available

June 9th

June 16th

June 23rd

Recordings Available

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- How Anti-Fouling Works
- How Algae Sensors Work
- How Turbidity Sensors Work

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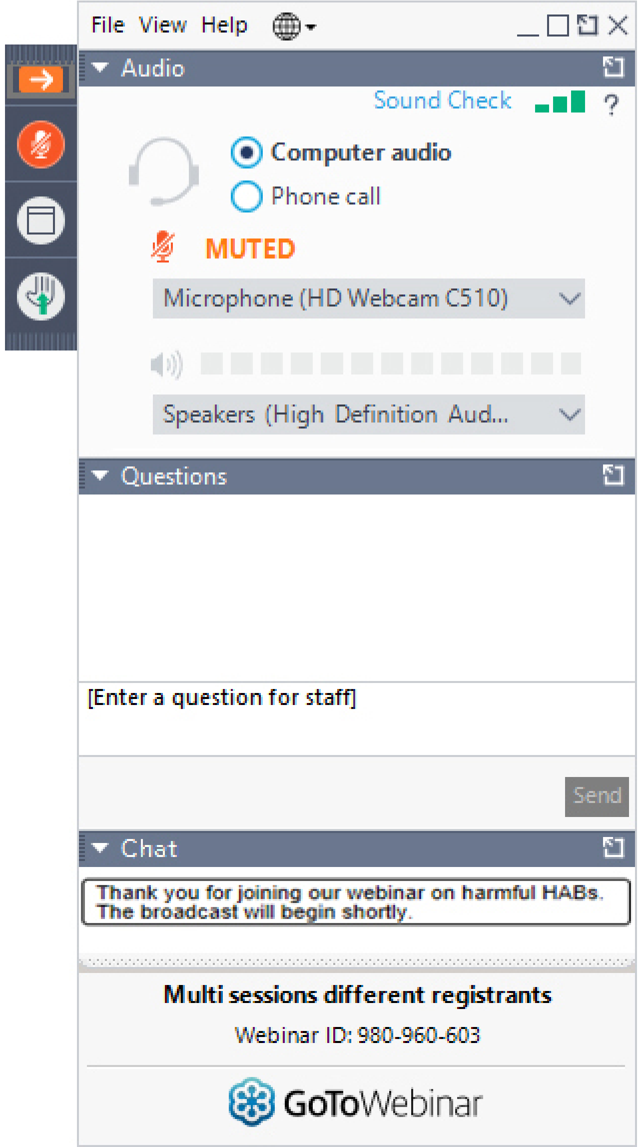
Ask Questions
We'll try to answer as many as we can during the presentation

Chat
You can also use the Chat panel to ask questions or contact us if you're having technical difficulties



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Please Ask Questions!

Ben Sutter

BACKGROUND

BS in Chemistry from
Wright State University

- Technical Applications and Support Specialist
- Demonstration Coordinator
- 5 years working as a specialist on lab and field analytical equipment,
- Specializes in photometers, pH and ORP sensors, ISEs, and other electrochemical parameters

Overview

I. pH/ORP: What and Why?
II. The pH Sensor: History, Types, Construction
III. Calibration, Care, and Practical Use of pH/ORP Sensors
IV. Real-world Applications for pH and ORP

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pH/ORP: What and Why?

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What is your highest priority when selecting a pH or pH/ORP sensor for environmental monitoring?

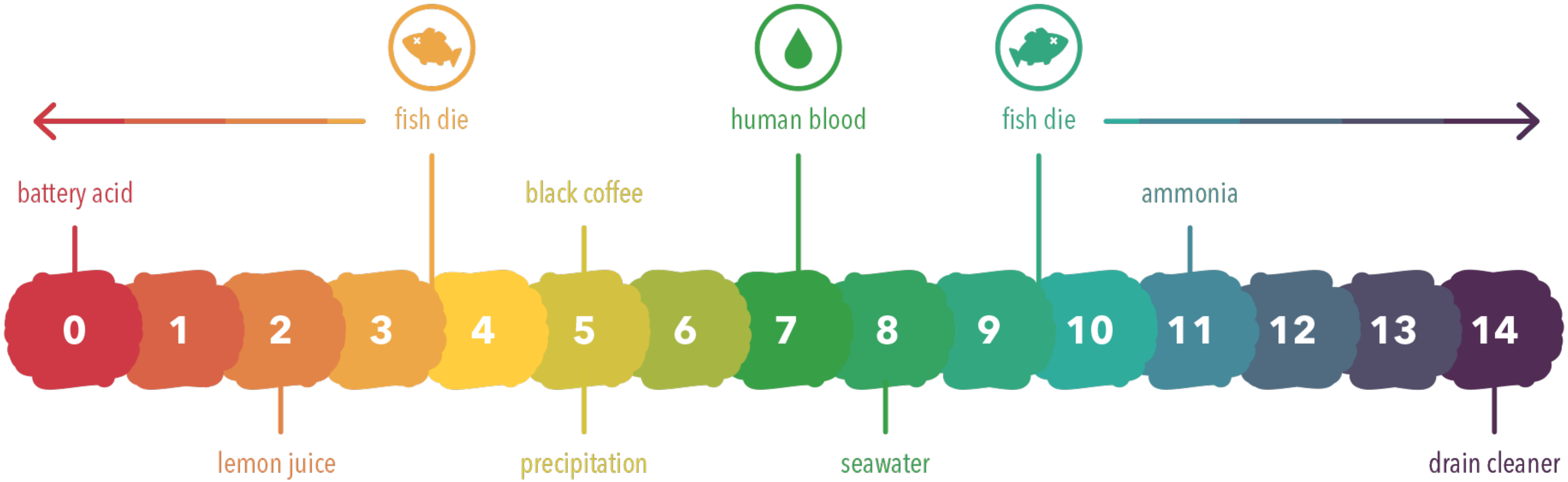
Reasons to Monitor pH and ORP

Major contributors to pH and ORP change:

- Soil/bedrock composition
- Biological activity (*e.g.* algae blooms)
- Dumping/discharge (acid mine drainage)
- Acid rain

Why is pH Important?

- Acts as a hard limit for aquatic life
- Human blood pH must be between 7.25 and 7.35
- Sudden changes in pH or ORP may have to be correlated with events



pH and ORP: Explaining Them Together

There are *many* similarities between pH and ORP sensors

- Same reference
- Same hardware (basically)
- Similar sensing bulb element
- They are both ISEs (Ion Selective Electrodes)

They measure in the same basic way

pH is more absolute, ORP is more relative

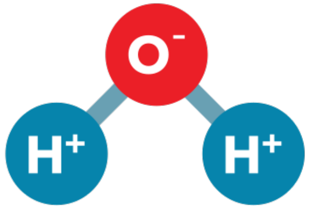
pH measures acid/base reactions;
ORP measures redox (reduction/oxidation) reactions

H^+ Ions and pH

pH is the measurement of H+ ions in water; sometimes called potential hydrogen. Aqueous solutions all contain some measure of H+ ions since H_2O is constantly dissociating with itself.

Water's chemical formula **H_2O**

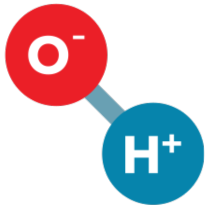
Model of water



Resulting Ions when water dissociates

H^+

OH^-



More of these = more acidic

More of these = more basic

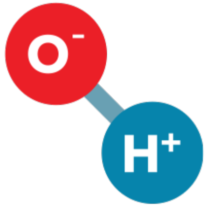
pH Units

The units of pH are simply **pH units**.

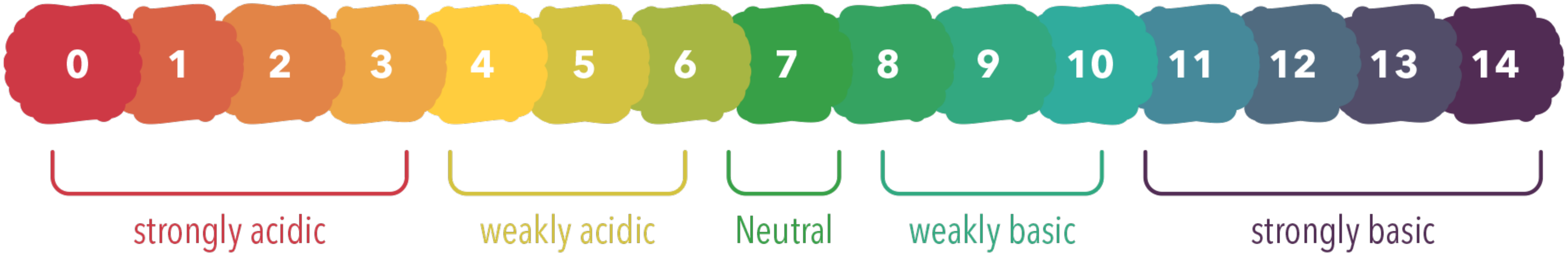
H^+

More of these = more acidic

OH^-



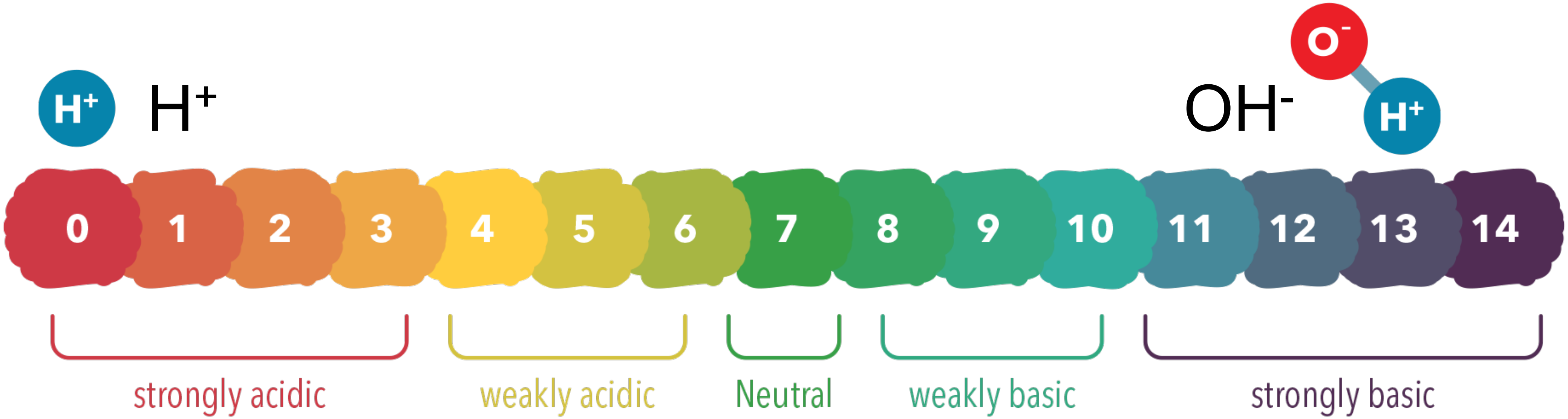
More of these = more basic



Definition of pH

$$pH = -\log_{10} a_{H+}$$

a_{H+} = the hydrogen ion activity (concentration)



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pH is an Exponential Scale

pH		H+ Activity	OH- Activity
0	10^{0}	1	0.00000000000001
1	10^{-1}	0.1	0.0000000000001
2	10^{-2}	0.01	0.000000000001
3	10^{-3}	0.001	0.00000000001
4	10^{-4}	0.0001	0.0000000001
5	10^{-5}	0.00001	0.000000001
6	10^{-6}	0.000001	0.00000001
7	10^{-7}	0.0000001	0.0000001
8	10^{-8}	0.00000001	0.000001
9	10^{-9}	0.000000001	0.00001
10	10^{-10}	0.0000000001	0.0001
11	10^{-11}	0.00000000001	0.001
12	10^{-12}	0.000000000001	0.01
13	10^{-13}	0.0000000000001	0.1
14	10^{-14}	0.00000000000001	1

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Nernst Equation

Establishes the relationship between the measured voltage and the ionic activity of the solution

- $y = mx + b$

- E = Voltage
- T = Temperature (in K)
- a_{H+} = H+ concentration (pH!)

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

$$y = (m)\ x + b$$

Where:

E = Measured voltage between the hydrogen ISE and the reference
E_0 = Standard potential of the electrode at a reference point
R = Universal gas constant (R = 8.314 J mol^{-1} K^{-1}; J for Joule, K for Kelvin)
T = Temperature in Kelvin
n = Electrical ionic charge (n = 1 since H^+ has a single positive charge)
F = Faraday constant (F = 96485 C mol^{-1}; C stands for Coulombs, not °C)
a_{H^+} = Hydrogen ion activity

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Definition of ORP

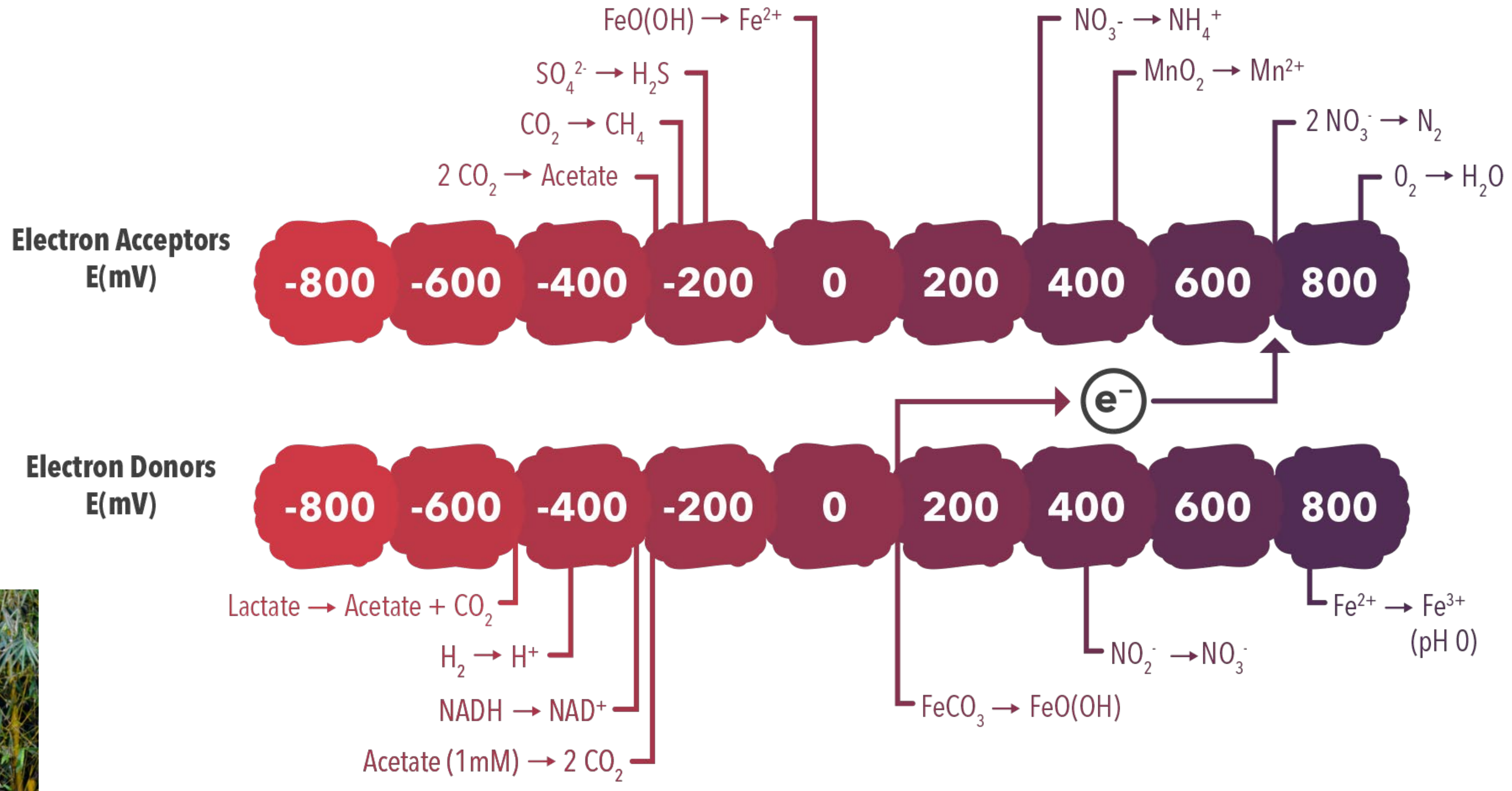
Oxidation-Reduction Potential

pH measures acid-base reactions; ORP measures oxidation-reduction reactions!

Oxidation-Reduction = Redox

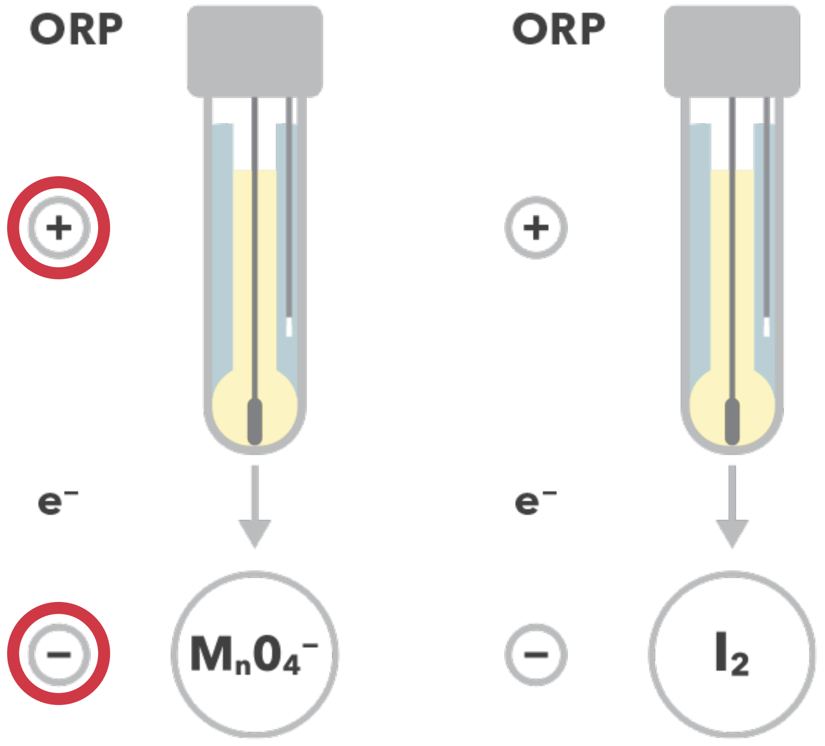
As more electrons become available, the ORP becomes more negative

LEO GER



ORP Measurement

- **ORP**
  - The redox potential can be considered a measure of the ease with which a substance either absorbs or releases electrons
  - *“electron pressure”*
  - Also bound by the Nerst Equation



Permanganate ion strongly oxidizing in solution

Iodine diatom weakly oxidizing in solution

The pH Sensor: History, Theory, Construction

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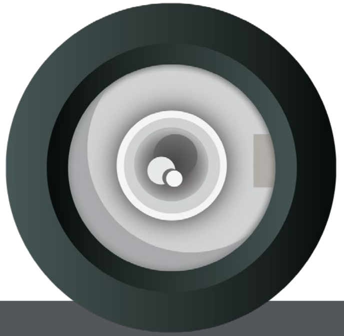
Which of the following best describes your experience with environmental monitoring of pH?

pH Measurement Types

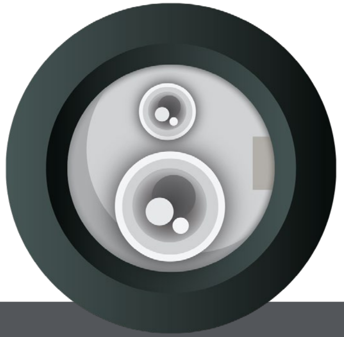
- Litmus Paper
- Indicators
- Titration
- Combination pH probes

YSI pH/ORP Sensors - Field

exo™
Continuous Monitoring



pH
Sensor



pH + ORP
Sensor

The pH Sensor

A pH sensor measures a voltage between two points:

The glass electrode

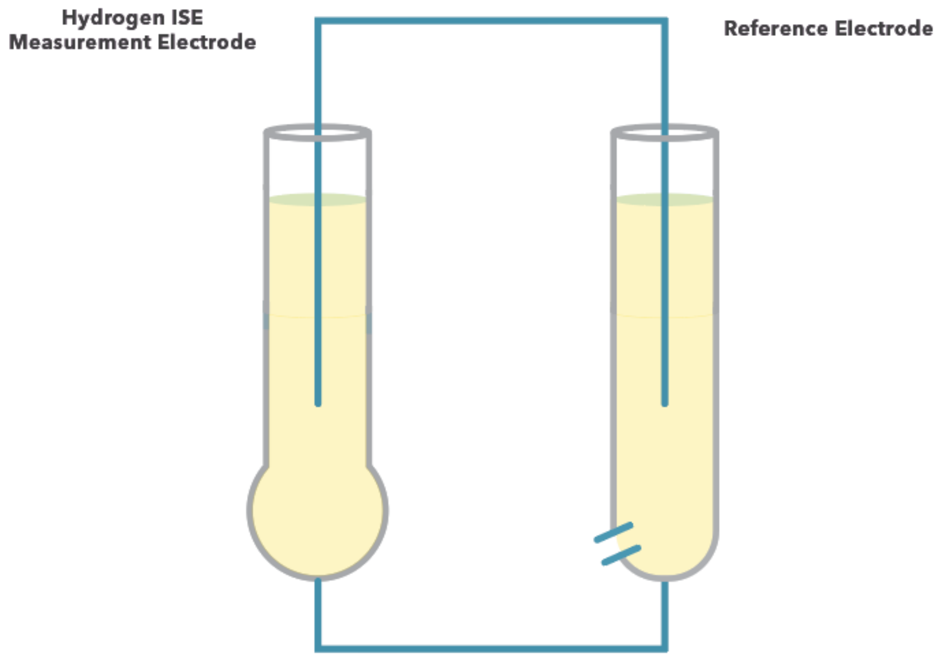
The reference electrode

- Has a potential that is designed to be unchanging

Glass Electrode + Reference Electrode =

Combination Electrode

Historically, they used to be completely separate probes

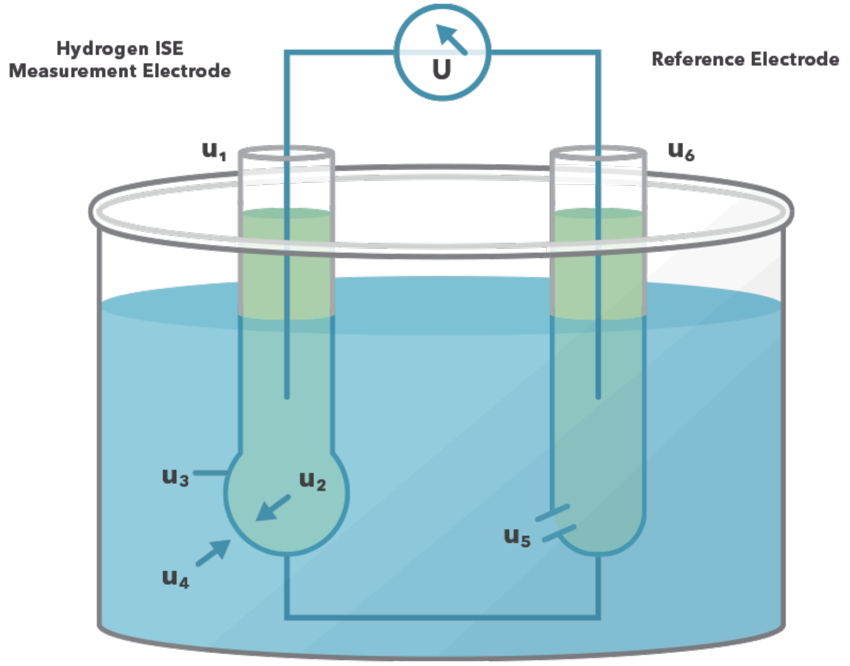


Potentials - Definition

$$U = u_1 + u_2 + u_3 + u_4 + u_5 + u_6$$

A voltage is a potential difference between two points!

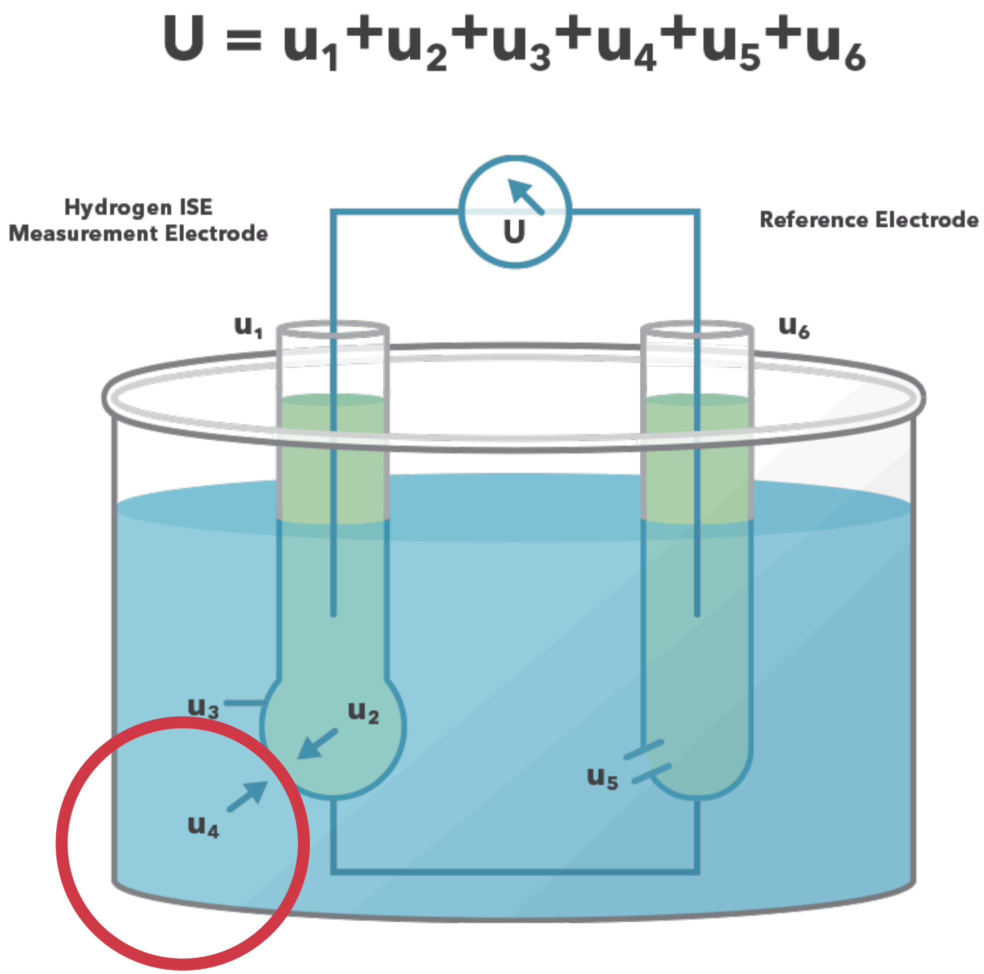
- These potentials are accounted for in the construction of the probe
- At pH 7, U = 0 mV



- u_1: the potential in the measurement system of the glass electrode
- u_2: the potential on the inside of the membrane
- u_3: the asymmetry potential of the glass membrane
- u_4: the potential on the outside of the membrane
- u_5: the diffusion potential of the reference junction
- u_6: the potential of the reference element of the reference electrode

Potentials – u_4

- u_4 is the only potential that is changing
- u_4 = potential of the liquid that is in contact with the outside of the bulb



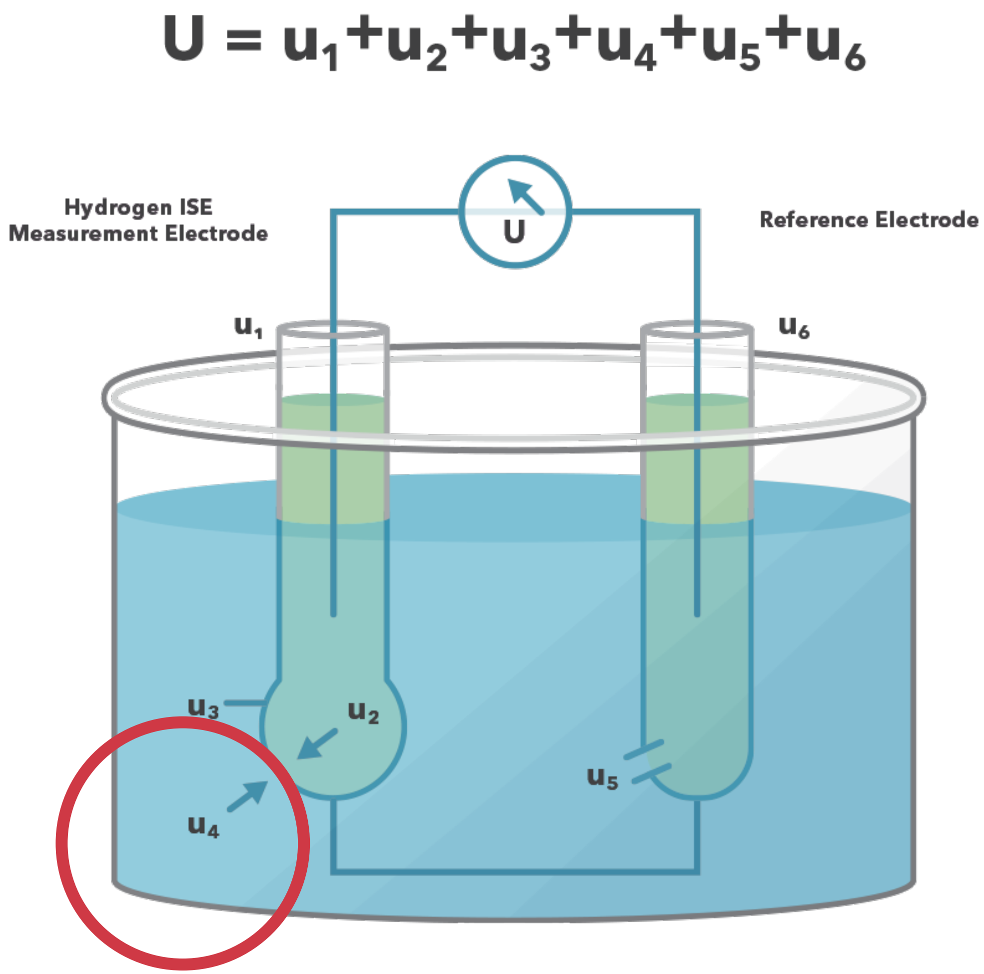
Potentials – Relationship to Nernst

- Nernst Equation Establishes the relationship between the measured voltage and the ionic activity of the solution

- $u_4 = E$

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

$$u_4 = (2.303RT/nF)\ \log a_{H+} + E_0$$



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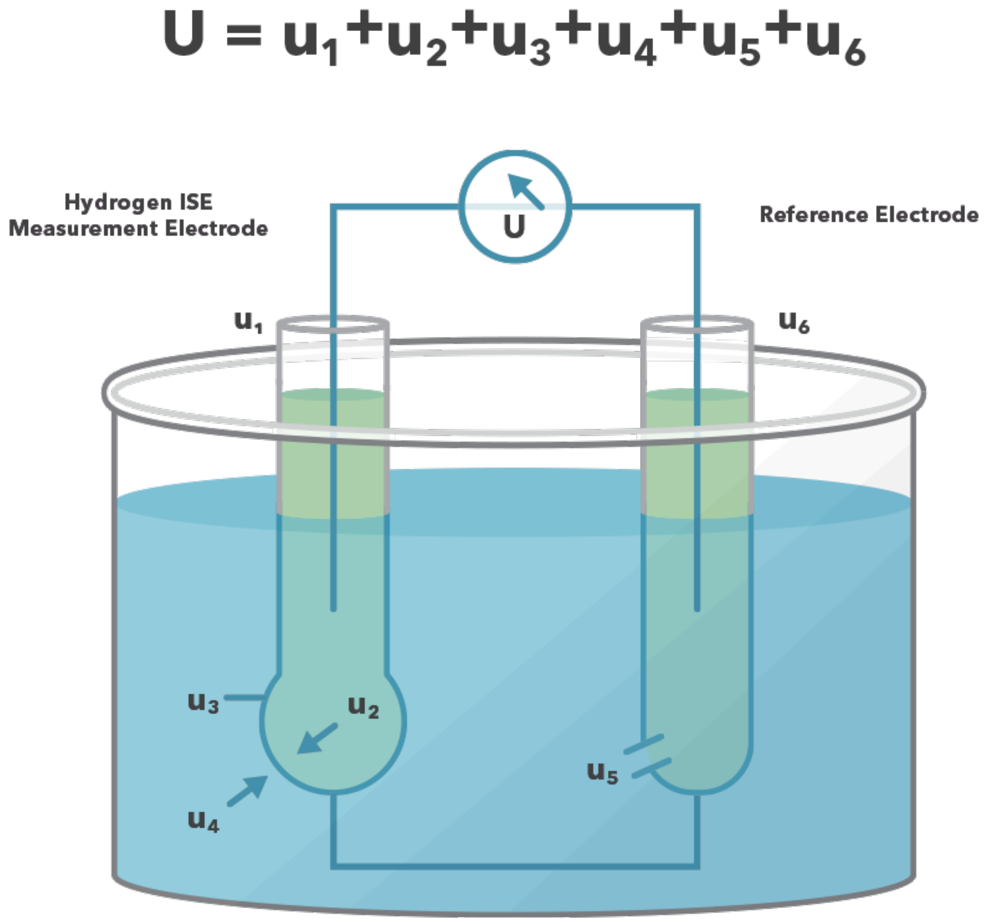
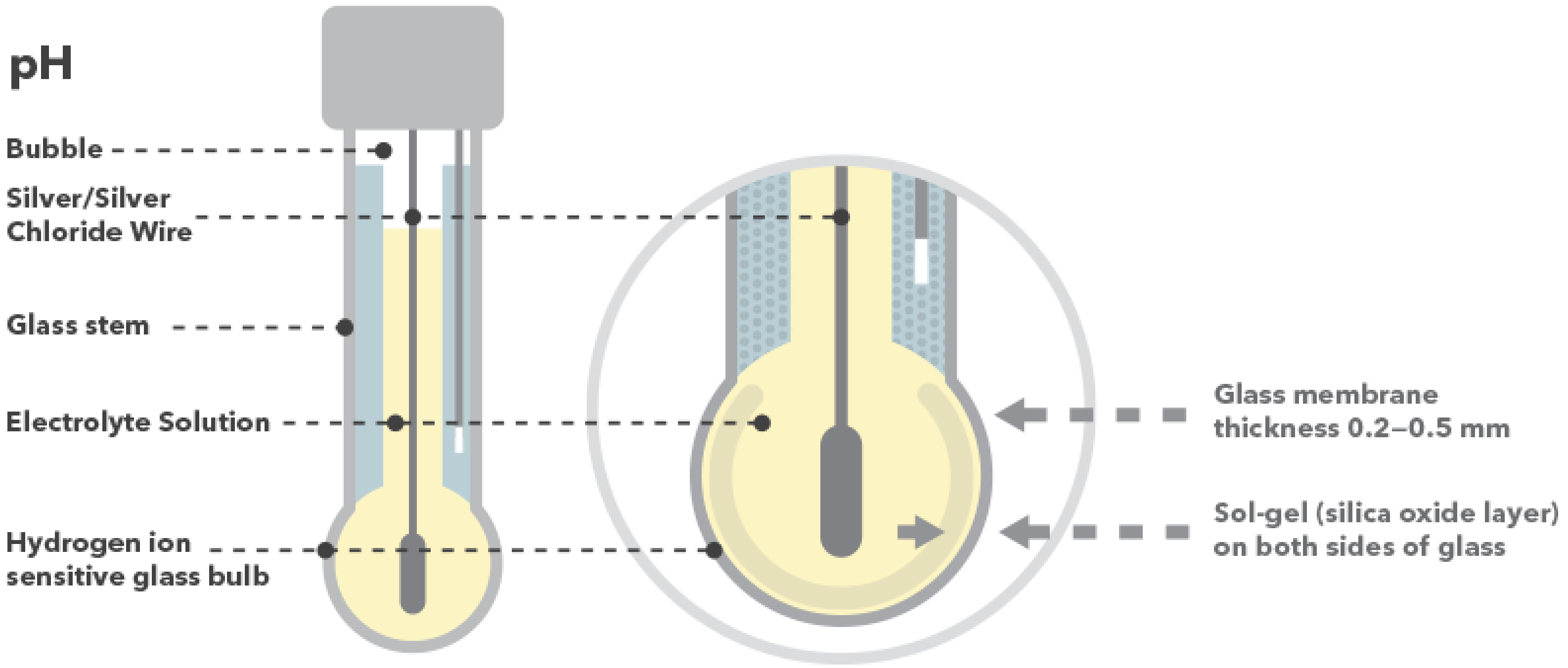
pH and ORP Probes are ISEs

- **pH and ORP Sensors are Ion Selective Electrodes (ISEs)**
  - ISEs are designed to measure a single type of ion
  - pH sensor is an ISE for the hydrogen ion H^+
  - ORP sensor is an “ISE” for electrons



The pH Bulb

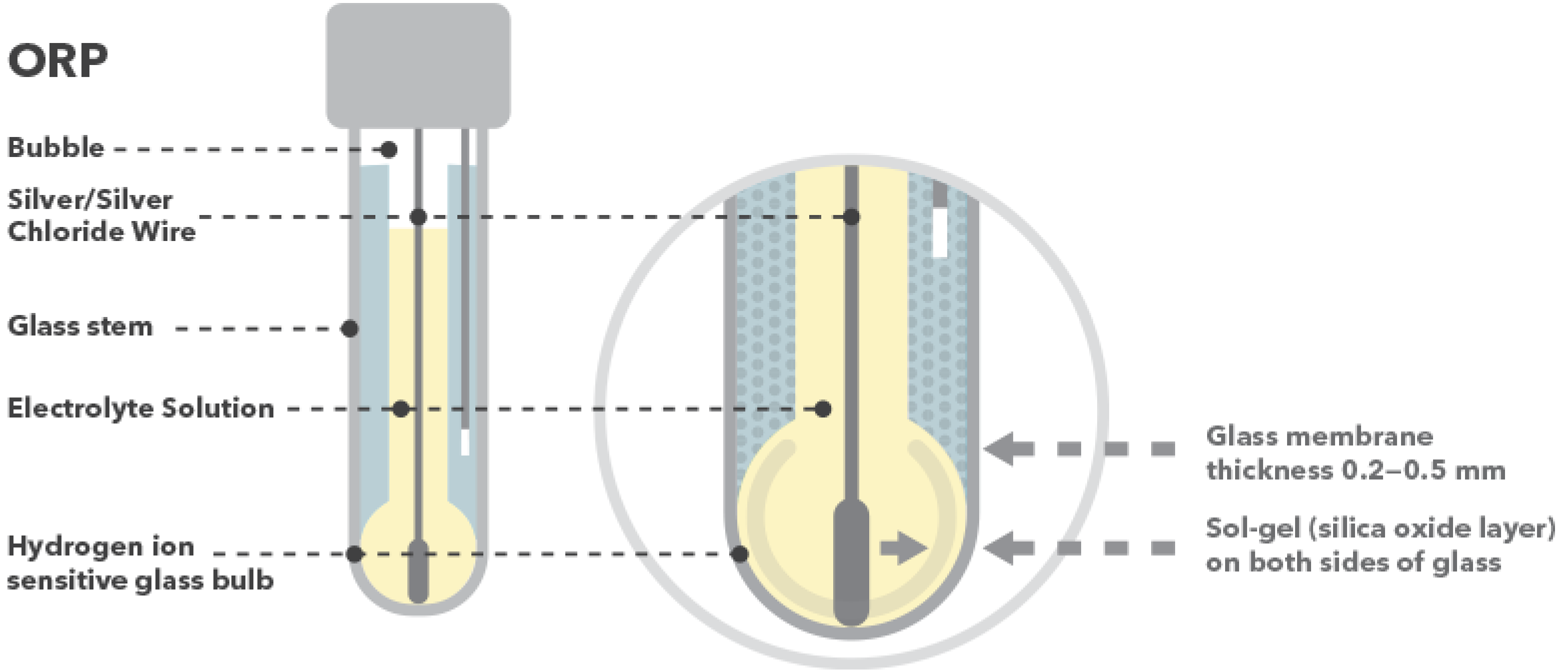
The bulb of the pH sensor is where the H+ detecting ions are, and is the most delicate and arguably the most vital portion of the pH sensor.



The ORP Bulb

ORP bulbs are similar to pH bulbs

Ag/AgCl wire makes direct contact with the bulb



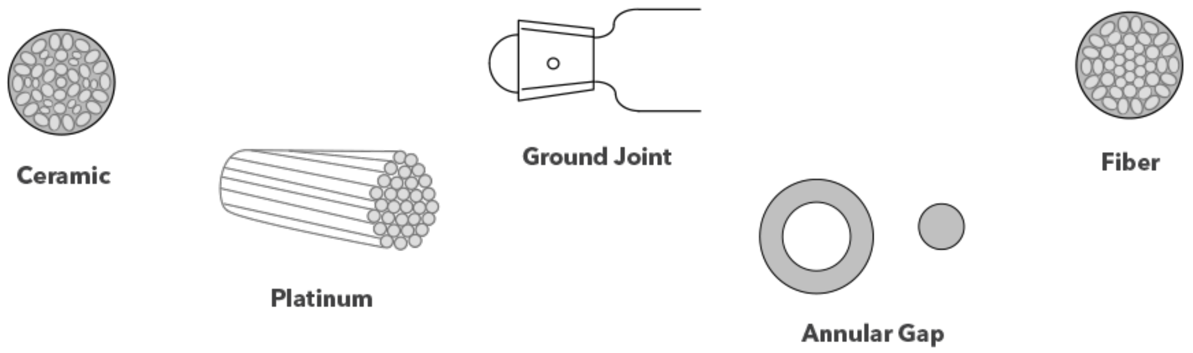
Reference Junctions – Lab

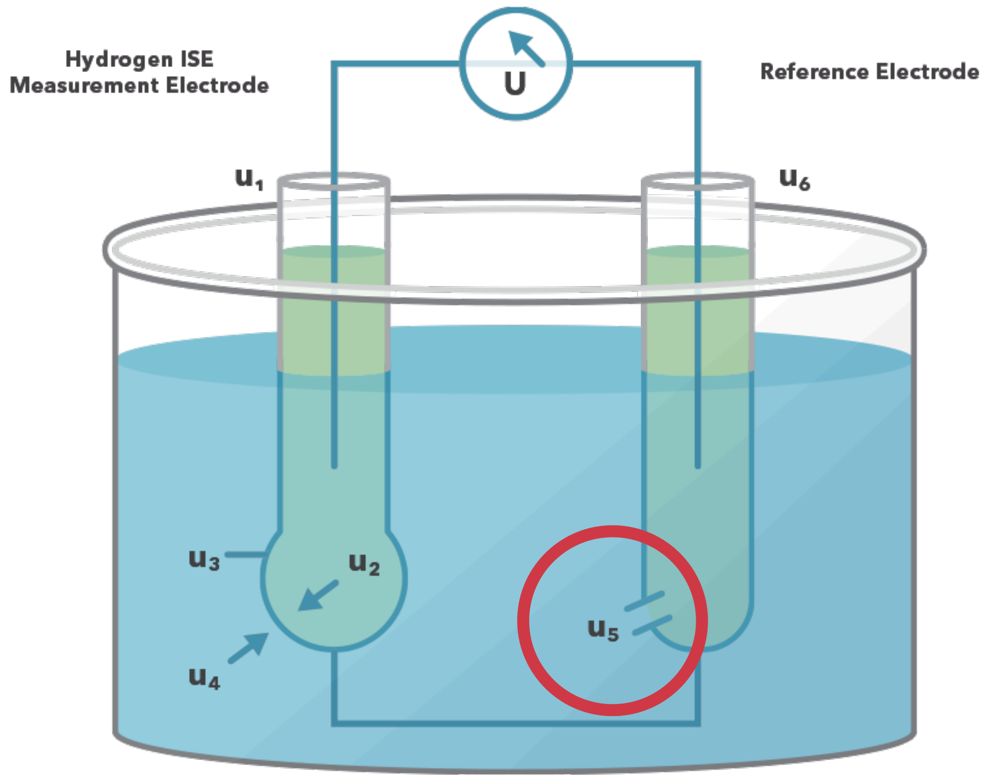
The junction is there to allow the filling solution of the probe to leak into the sample.

No junction = No function

Application specific

Different flow rates, materials





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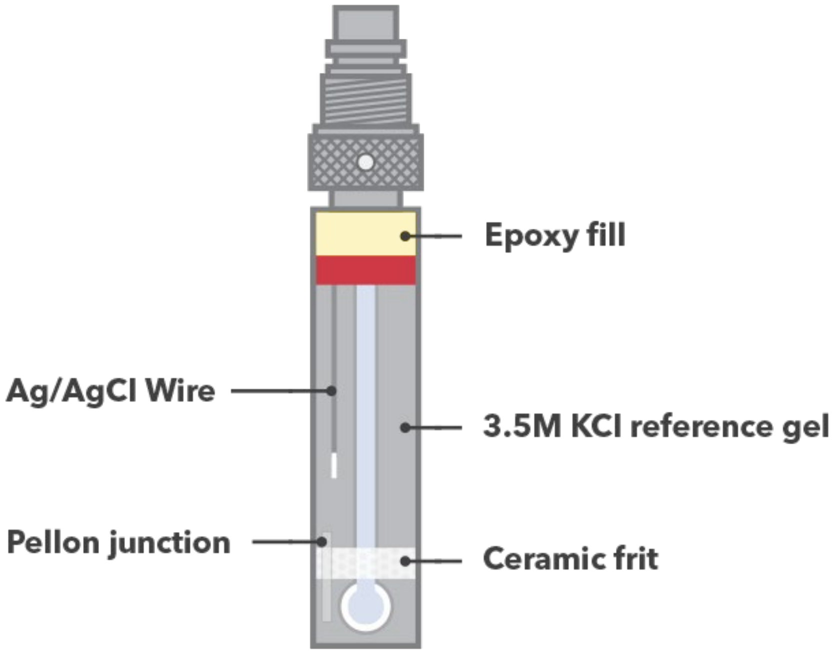
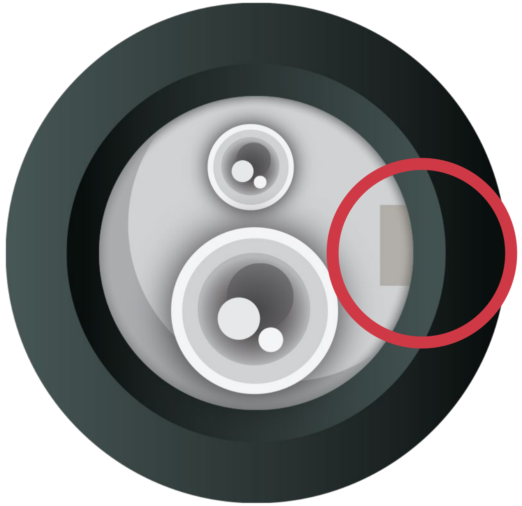
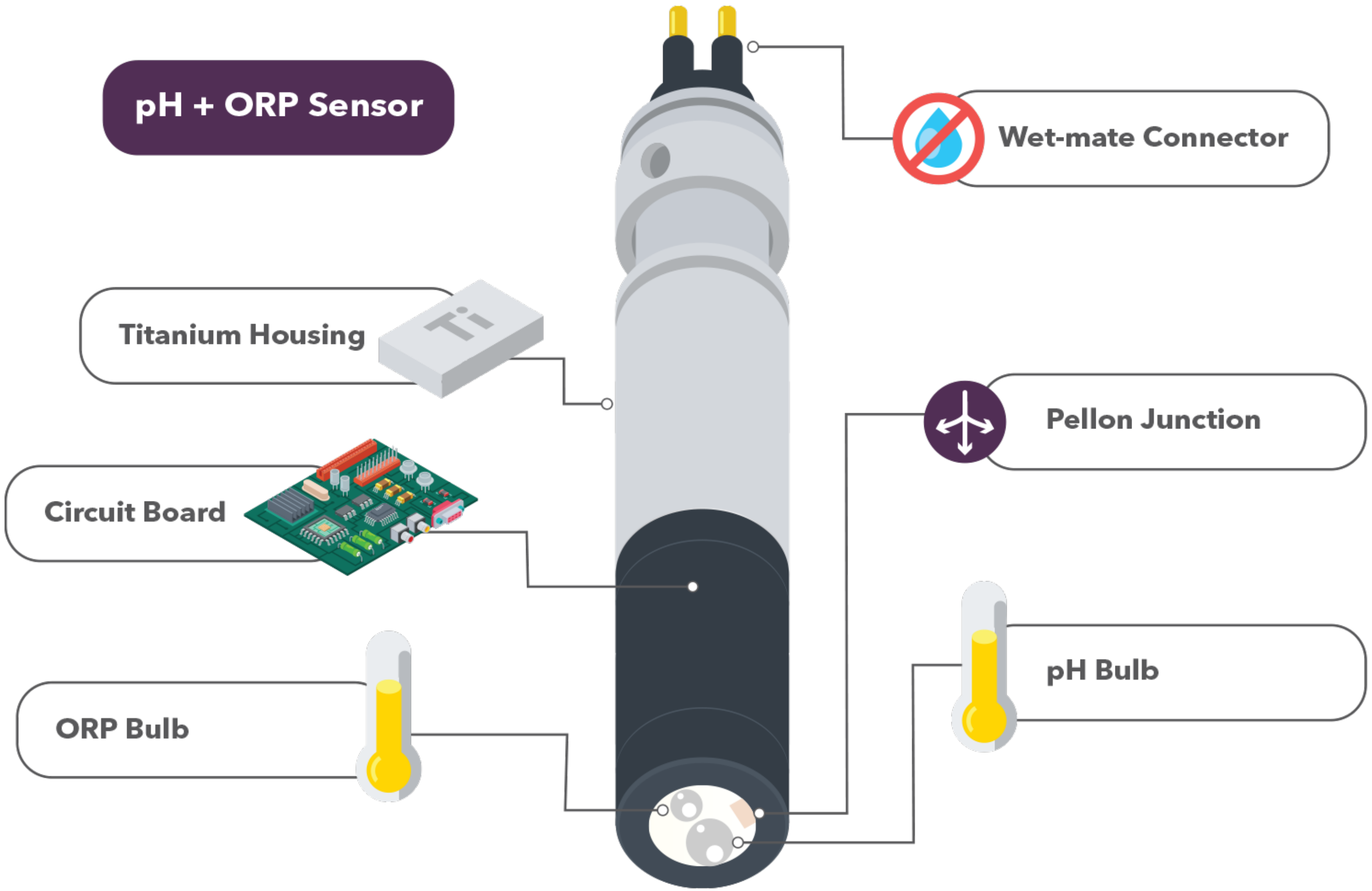
Reference Junctions - Field

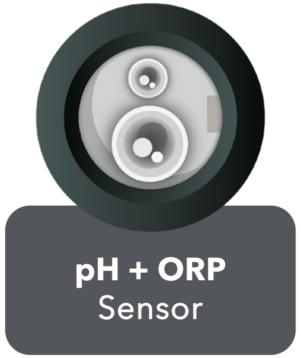
- Pellon Junction
- Resembles a wick for an oil lamp
- Using a gel allows the probe to be water-tight and very slowly release its fill solution
- Both pH and ORP use the same reference gel!





Anatomy of YSI's pH + ORP Sensor





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The pH Sensor: Calibration, Care, Practical Use

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When calibrating your pH sensor, how many calibration points do you use?

Calibration Basics – Why We Calibrate

- Calibration establishes a slope
- Instrument saves that slope
- **The accuracy of the pH sensor depends on the quality of the calibration**

Calibration Basics – Buffers

- What is a buffer?
- Commonly in values of pH4, 7, 10
- For a majority of applications, we want to use a 2 or 3-point calibration
  - Don't use a 1-point calibration for pH

- Other buffer sets – classic chemistry
- Other buffer types – TRIS for nucleotides

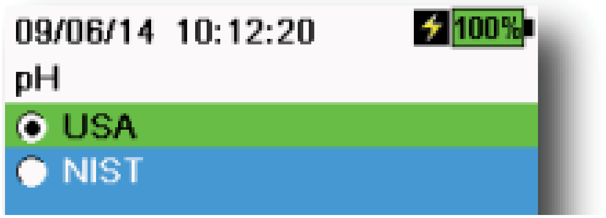

Figure 27 Setup pH

Setup pH

→ **Setup** → **pH**

Select USA auto-buffer recognition (4.01, 7.00, and 10.00) or NIST auto-buffer recognition (4.01, 6.86, and 9.18) (Figure 27).

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Nernst Equation's Relationship to Calibration

- If we solve the Nernst Equation for E when the temperature is 25° C, we get -59.17 mV

- Represents the ideal span of voltage/potential for a single pH unit

-59.17 mV @25° C

7 S = -2.303 RT/nF

The variables R and F are constants and therefore not of further concern. Since the electrode slope (i.e. electrode response) is dependent upon the temperature of the solution, *it is very important that pH measurements be completed with an accurate measurement of temperature*. As an example, let's consider the calculation of slope at 25 °C (298.15 K).

$$S = -2.303 * \frac{8.314\ J}{mol\ K} * 298.15\ K * \frac{1}{1} * \frac{mol}{96485\ C} = \frac{-0.05916\ J}{C}$$

Since V = J/C, the slope at 25 °C is equal to -0.05916 V (-59.16 mV).

Using the same equation, the electrode slope (S) would be equal to -58.16 mV at 20 °C (293.15 K).

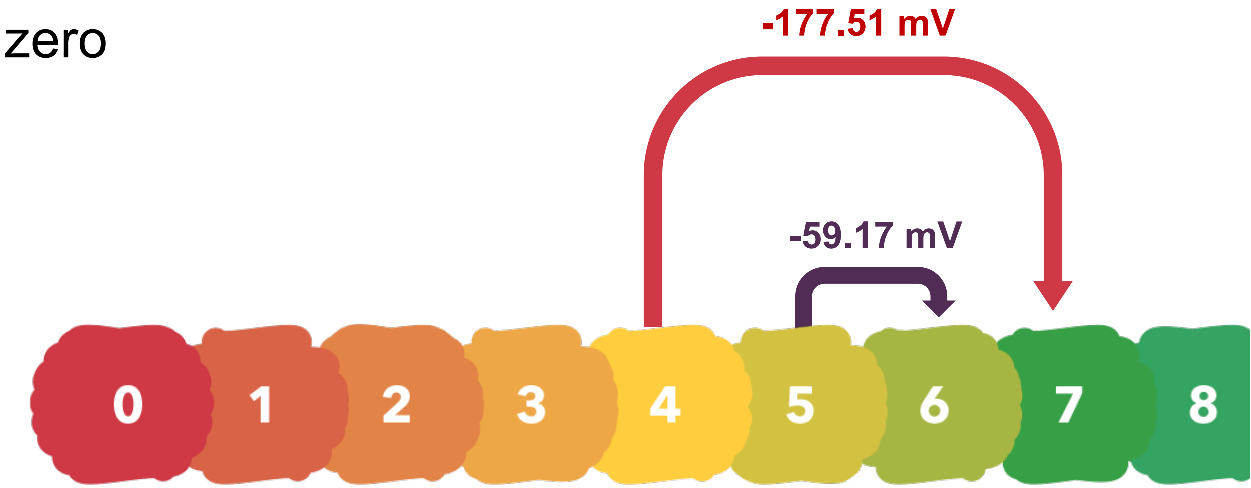
Calibration Basics

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

- **pH 7** 0 ± 50 mV
- **pH 4** 165 to 180 mV added to zero point
- **pH 10** 165 to 180 mV subtracted from zero point

- 1 pH unit = -59.17 mV @25° C
- 3 pH units = -177.51 mV @25° C

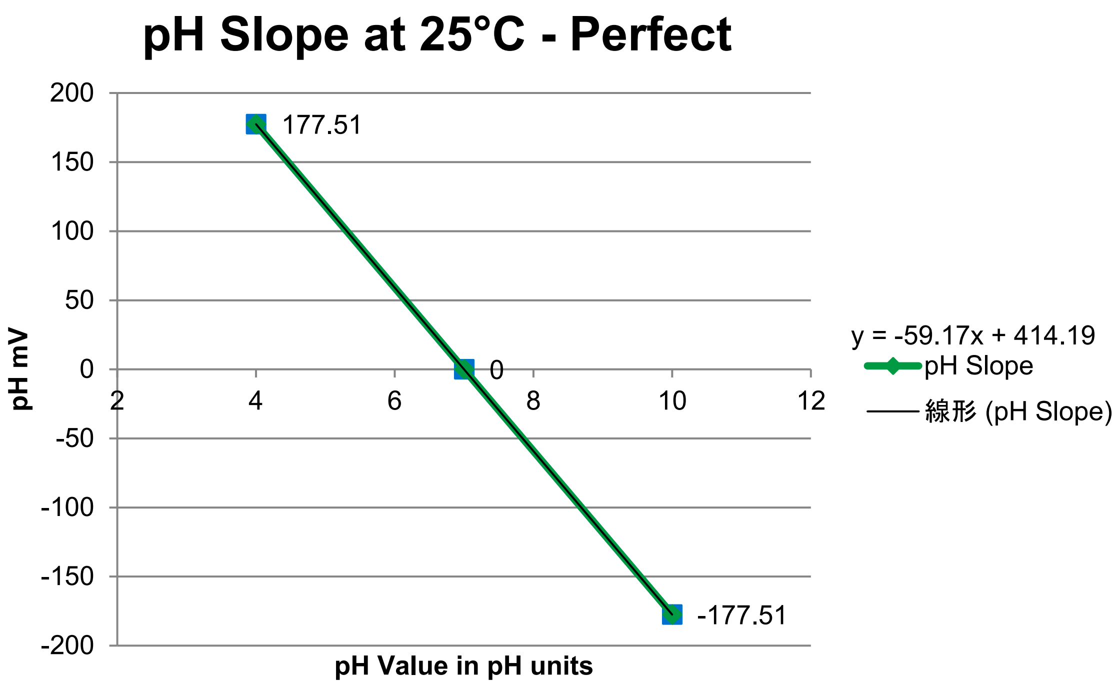
- Note the negative mV per unit



Calibration Basics

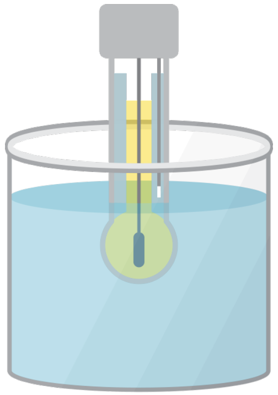
Assuming that we are using buffers 4, 7, and 10:

- pH 7 buffer should read 0 ± 50 mV
  - Ex. -25 mV, 0 mV, 40 mV all acceptable
  - This is called the **zero point**
- pH 4 buffer should read 165 to 180 mV MORE than the zero point
- pH 10 buffer should read 165 to 180 mV LESS than the zero point

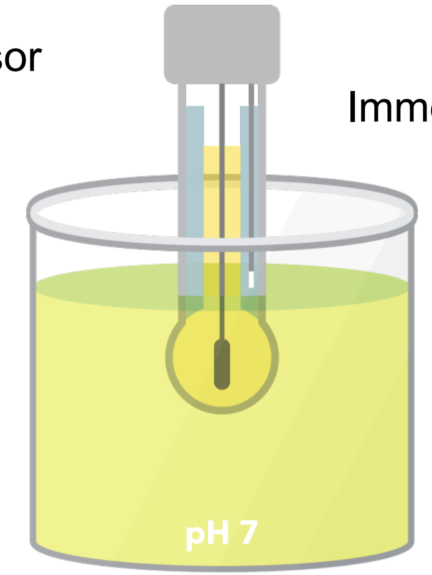


pH – 3 point Calibration   Point 1

Begin cal procedure on hardware

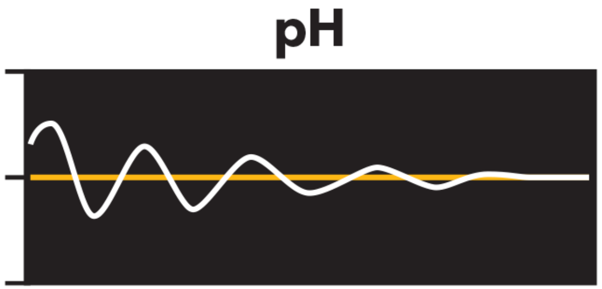


Rinse sensor

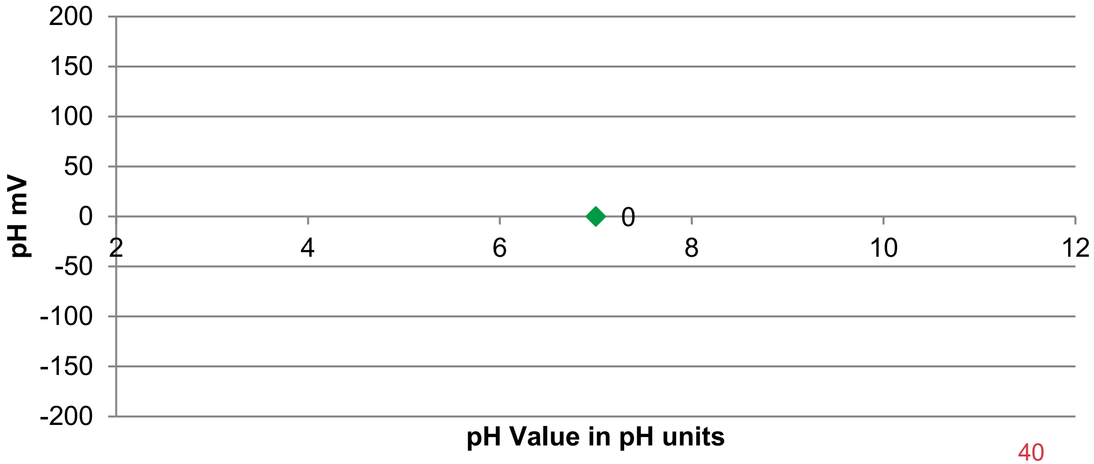


Immerse sensor in pH 7

Allow pH mV time to stabilize
- Temp, mV
- Auto-stable indicator



pH Calibration - Point 1



Accept the calibration point

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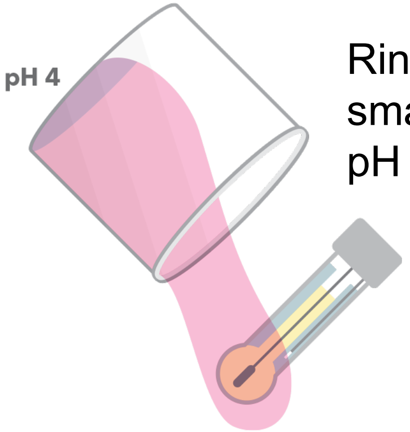
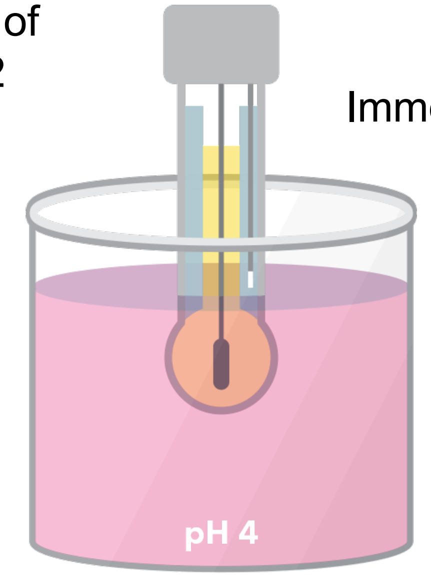
pH – 3 point Calibration   Point 2

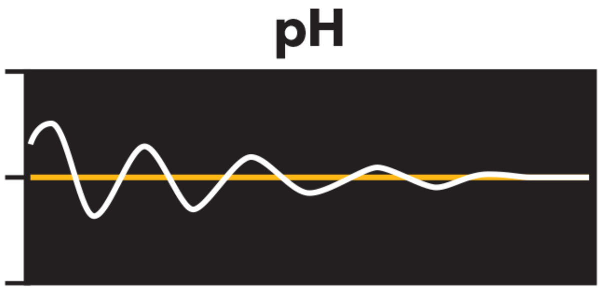


Rinse sensor with small amount of pH 4 buffer x2



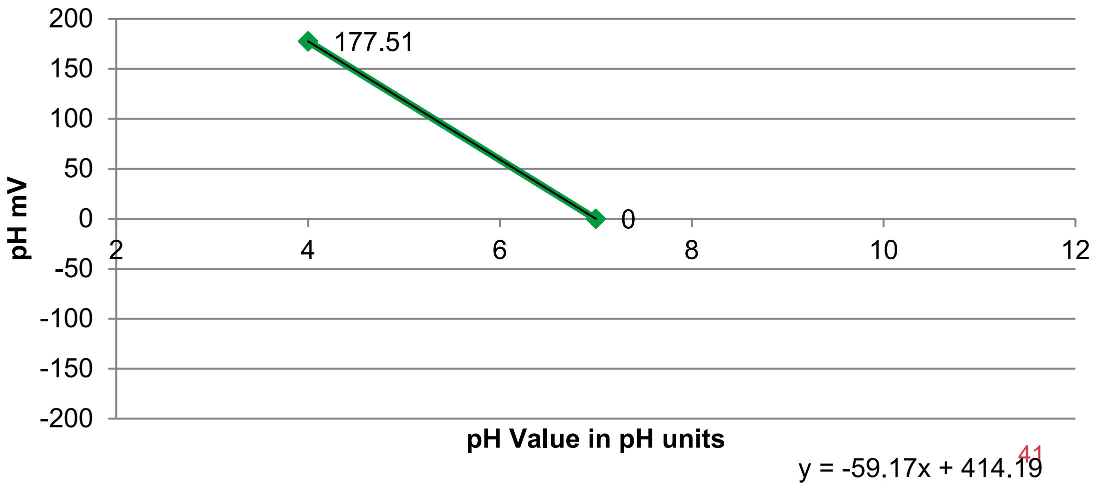
Immerse sensor in pH 4

Allow pH mV time to stabilize
- Expect pH4 mV to be 165-180 mV **higher** than pH7

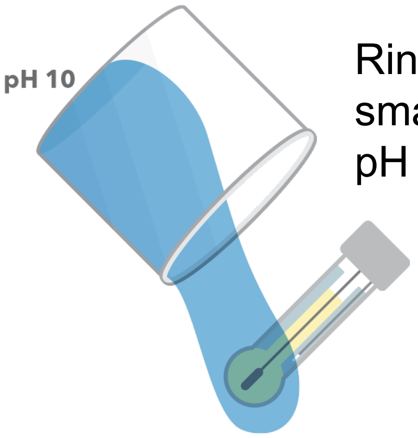


Accept the calibration point

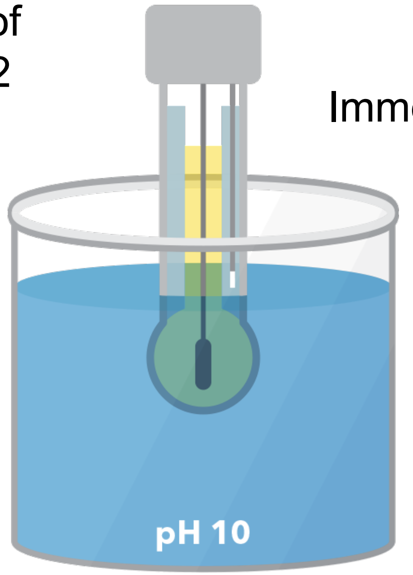
pH Calibration - Points 1 and 2



pH – 3 point Calibration Point 3



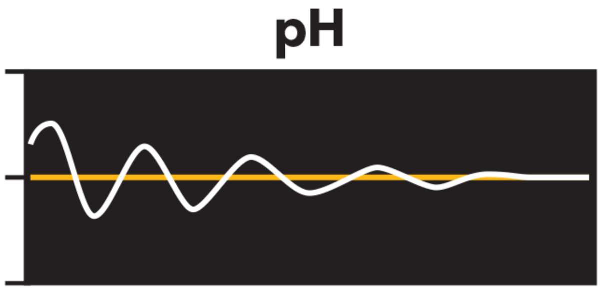
Rinse sensor with small amount of pH 10 buffer x2



Immerse sensor in pH 10

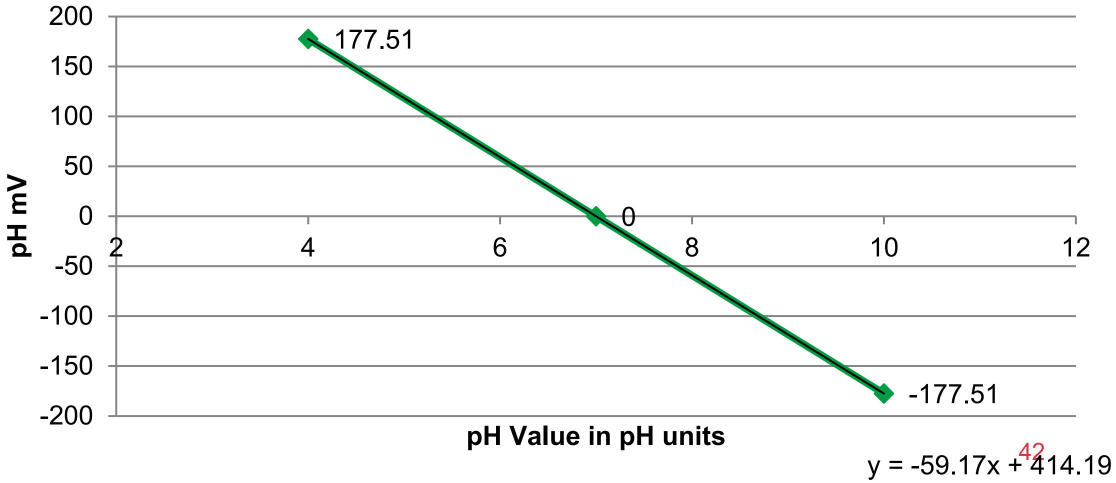
Allow pH mV time to stabilize

- Expect pH4 mV to be 165-180 mV **lower** than pH7



Accept the calibration point

pH Calibration - Points 1 and 2 and 3



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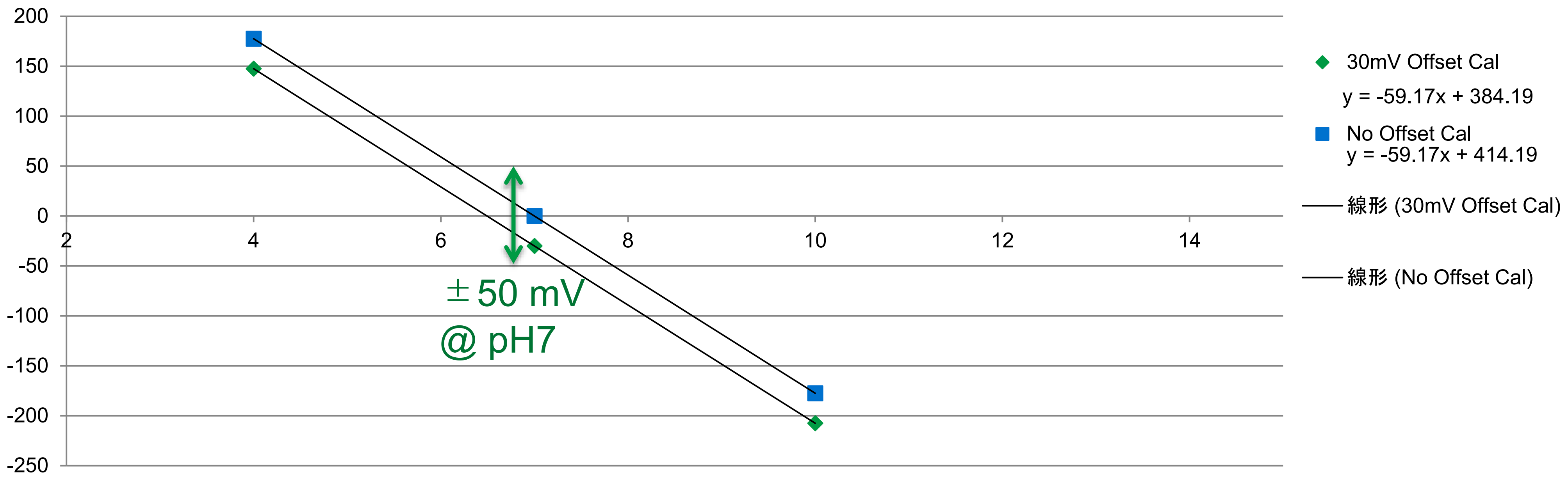
Example Calibration Results: Good Results

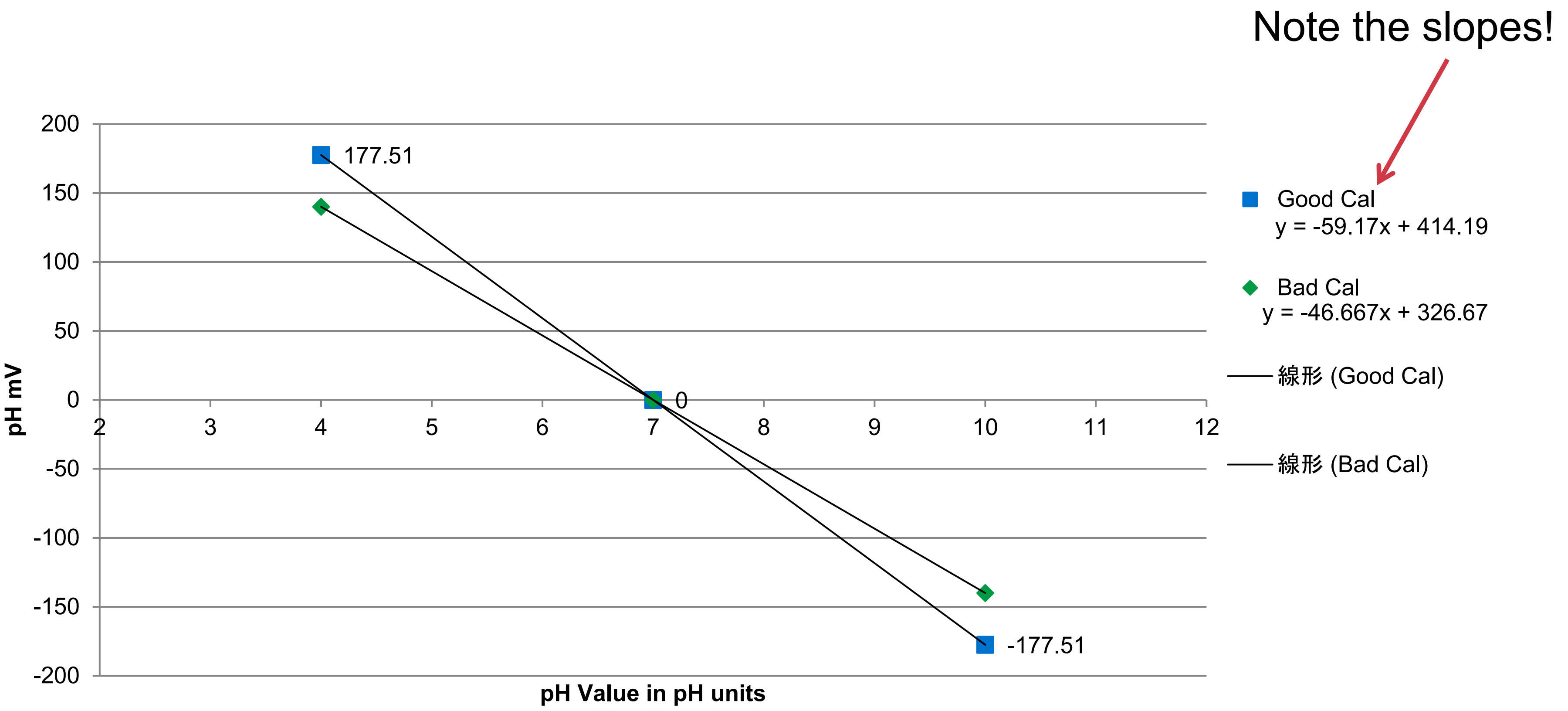


pH 7 – 0 mV
pH 4 – 177 mV ← a good calibration
pH 10 – (-177 mV)

pH 7: -30 mV
pH 4: 207 mV ← also a good calibration
pH 10: (-147 mV)

Example Calibration Results: Bad Results

If you have a low slope (-55 mV or lower), then that is considered a poor response.



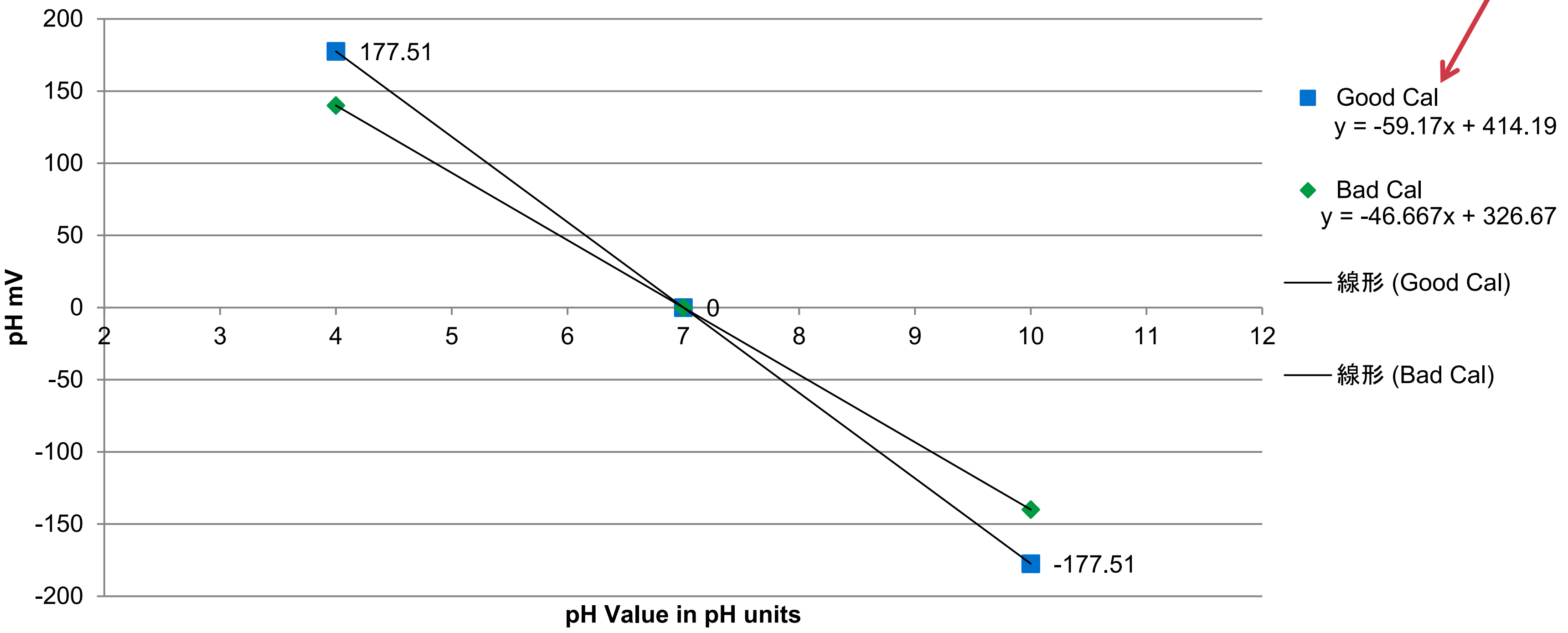
Example Calibration Results: Bad Results

If your instrument says you are ‘out of range’, (mV)

DO NOT ACCEPT THE CALIBRATION!

If you accidentally accept, restore calibration to defaults (for YSI sensors)

Note the slopes!



ORP Calibration

- ORP: simple, 1-point calibration
- Zobell Solution
  - Be sure to use the supplied documentation to match the temp to the ORP value!
  - YSI uses KCl reference
- ORP is a relative measurement, so we don't need to establish a slope, just a zero-point
  - ORP Change is more important than ORP value

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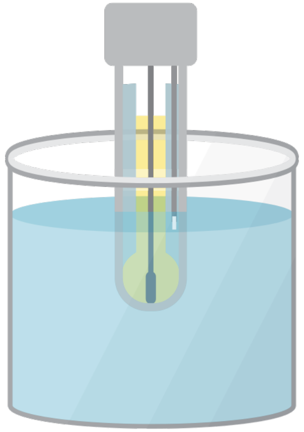
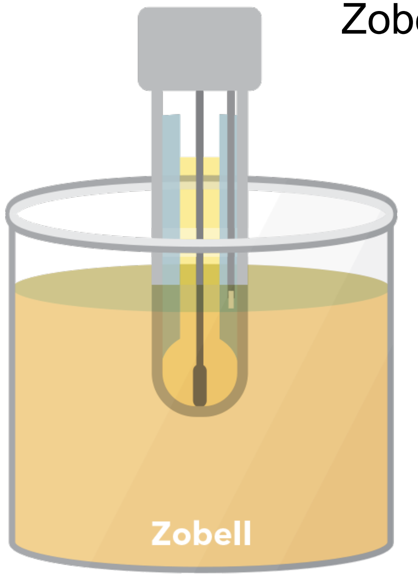
ORP – 1 point Calibration

Set ORP value on calibration screen
According to the temperature + supplied documentation

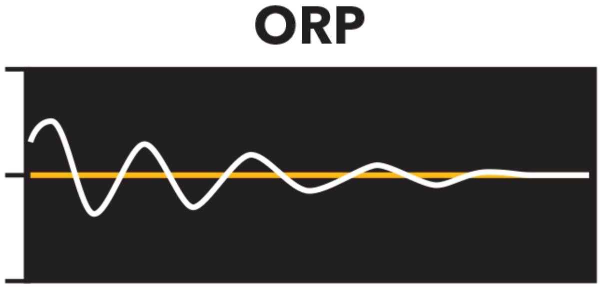
Rinse sensor



Immerse sensor in Zobell solution



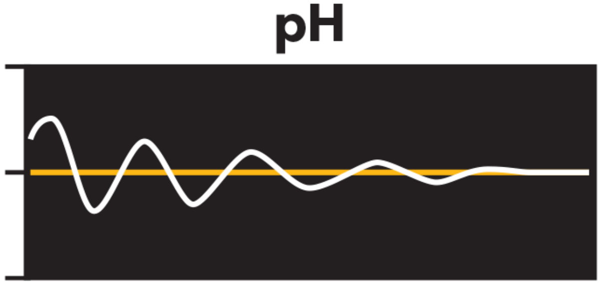
Allow ORP mV time to stabilize



Accept the calibration point

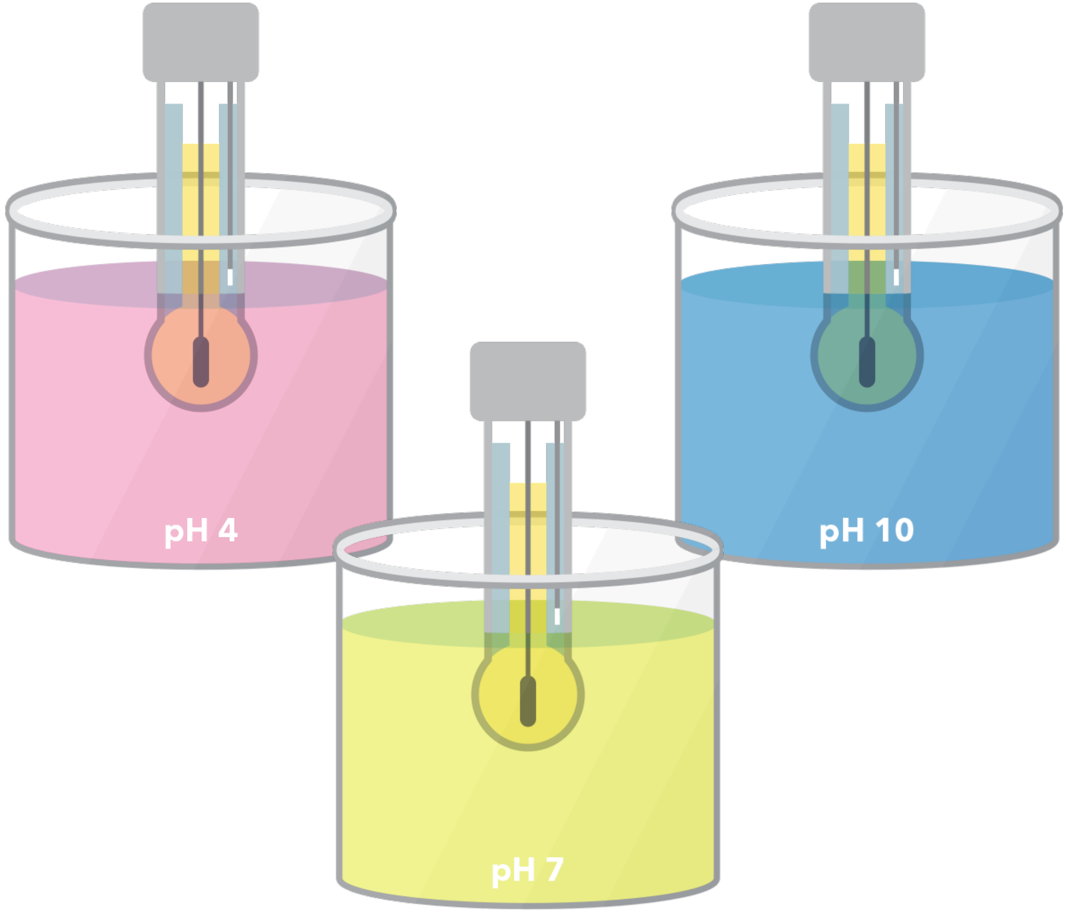
Troubleshooting Your pH/ORP Sensors

- Clues that there is a problem:
  - Slow stabilization during calibration or won't calibrate



Troubleshooting Your pH/ORP Sensors

- Buffers: Are your buffers expired?
- Don’t Reuse Buffers
- Buffer Selection
- Don’t use TRIS buffers
  - TRIS buffer reacts with the silver wire, creating a precipitate and clogging the reference junction



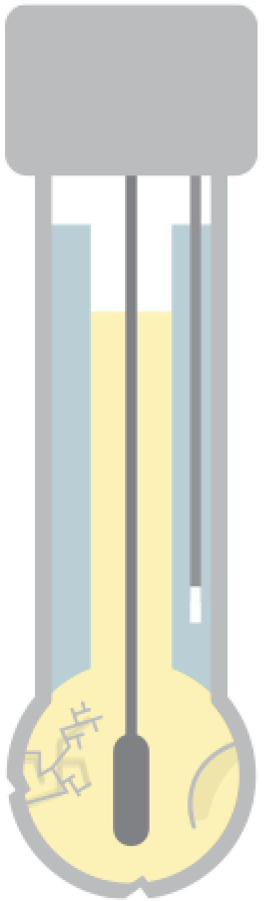
Troubleshooting Your pH/ORP Sensors

- Fouling: Check to see if the bulb is dirty, or if the reference junction is blocked

- Cracked Bulb –invisible?

- (Lab only) Reference fill hole is not left open

- Did the bulb dry out?
- Was the sensor stored immersed in DI water?
- Temperature



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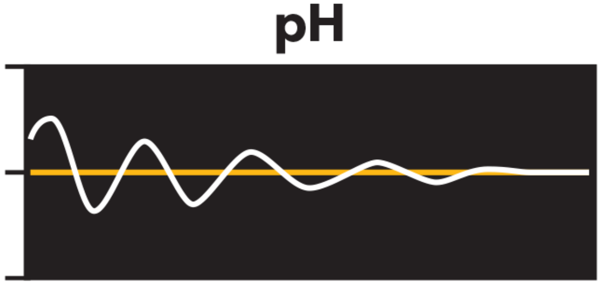
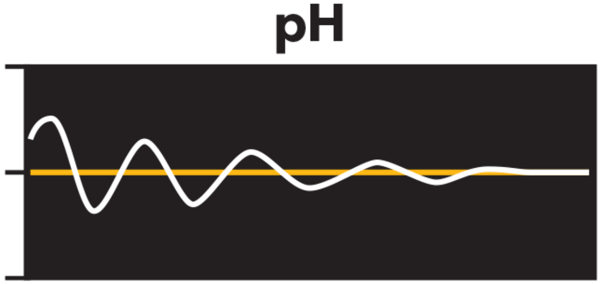
Troubleshooting Your pH/ORP Sensors

- Clues that there is a problem:
  - Slow stabilization during calibration or won't calibrate
  - Long time to get stable measurements



Troubleshooting Your pH/ORP Sensors



- Clues that there is a problem:
  - Slow stabilization during calibration or won't calibrate
  - Long time to get stable measurements

- pH and ORP probes are consumables
- Check to see if the probe is expired
  - Don't purchase pH/ORP probes too far ahead of time
  - Check with manufacturer to see the recommended replacement times for probes/modules!

Prevent Fouling - Sonde

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

Choose the correct pH/ORP module!

- Guarded
- Unguarded

Calibration of pH and ORP: Summary

For the best calibrations:

- Perform the calibration in a lab, or at least inside
- Use fresh, unexpired solutions to perform the calibration
- Don’t reuse calibration solution
- For pH: Perform a 2 or 3 point calibration, not a 1 point
    - ORP only requires 1 calibration point
- Assure that the sensor’s junctions and bulbs are free of blockages and fouling.
- Use pH mV to troubleshoot

pH and ORP: Applications

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When your pH sensor is not going to be used for the next month or more, how do you store it?

Storage of Your pH/ORP Sensor

Short-Term

- Keep the pH/ORP probe installed on your sonde/bulkhead for short-term storage
- Keep some water in the cup!

Long-Term

For long-term storage, you may want to uninstall the probe from the instrument and keep the bulb soaked in 3M KCl solution

  - 3M KCl has high ionic content, which is a good place for pH glass electrodes!

- **Never let the pH/ORP probe dry out!**
- **Never store the pH/ORP probe submerged DI water!**

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Sampling Considerations: pH and ORP

- Consistent location/depth
- Calibrate as close to deployment time as possible

Sampling Considerations: ORP

- ORP is a parameter that is best measured with others
- Different depth could mean different ORP!
- Stability will be greater in standard than it will be in the field!
- To report the ORP value as “EH” or “E_h”, add 200 mV
  - EH value = ORP + 200 mV
  - For example,
    if ORP = 100 mV → EH = 300mV

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pH and ORP in Conjunction with Other Parameters

- You may need a lot of data to show how pH and ORP is track with other parameters
- It can be useful to have many other parameters to compare

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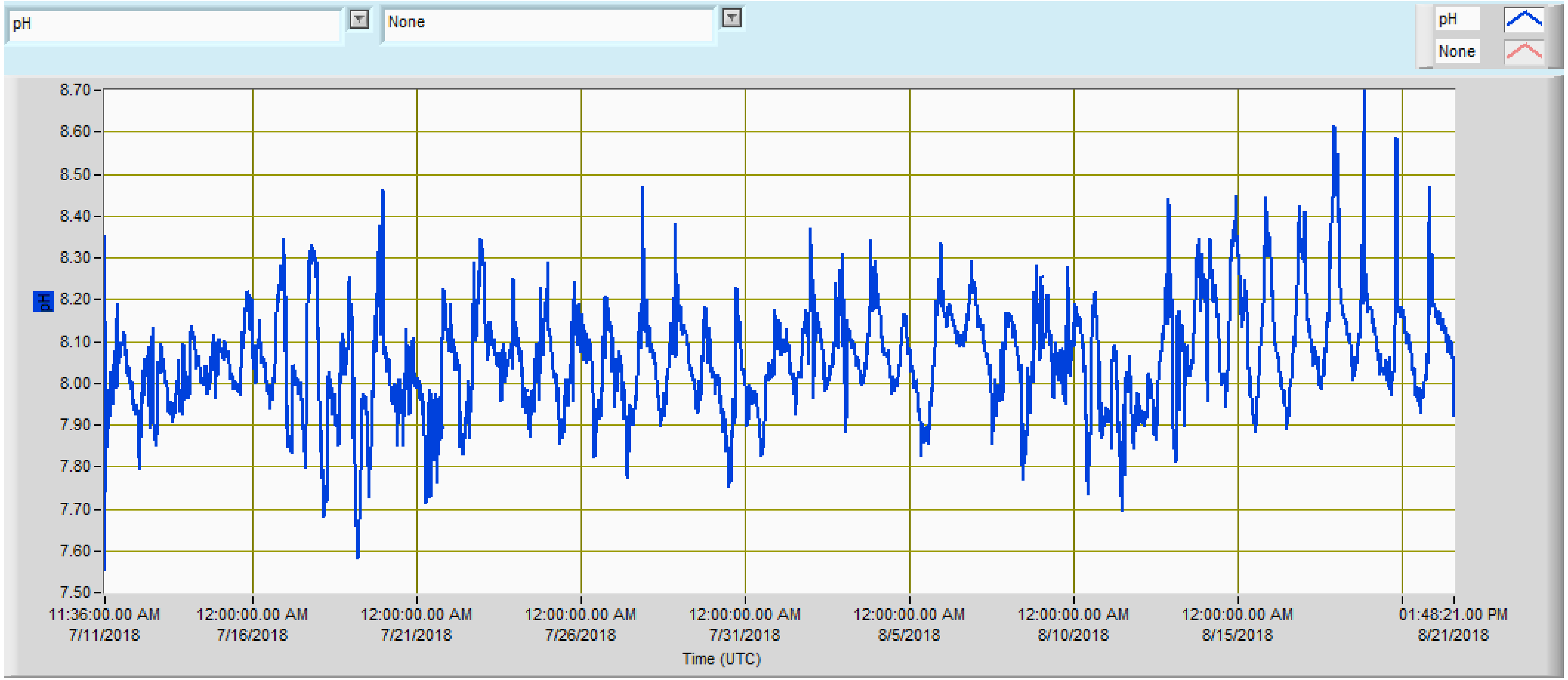
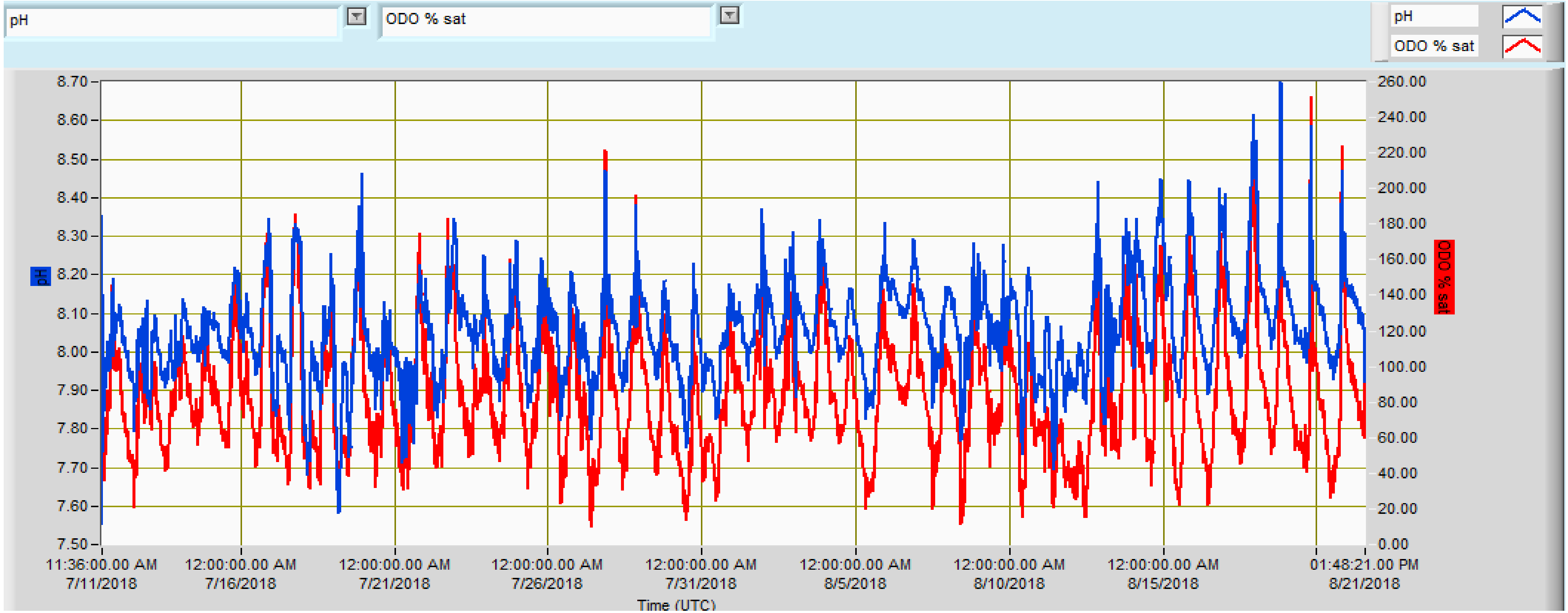
Florida Site: pH Alone

- **pH in blue**



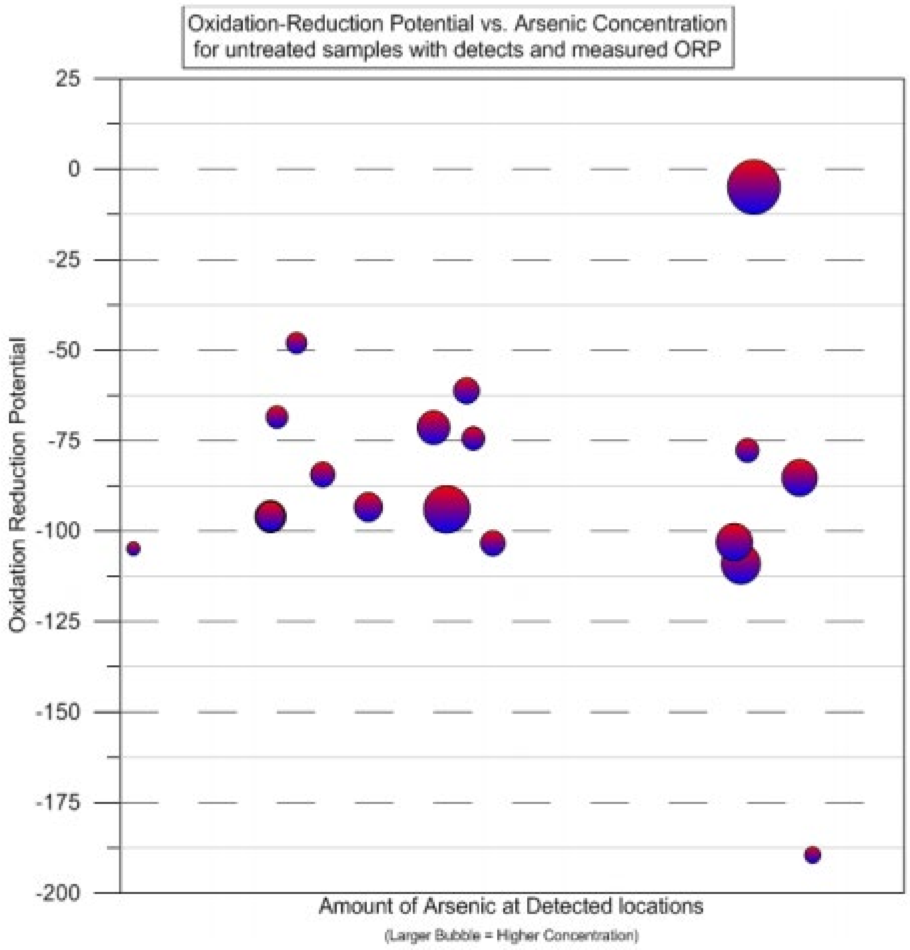
Florida Site: pH and DO

- **pH in blue**, **DO % Saturation in red**



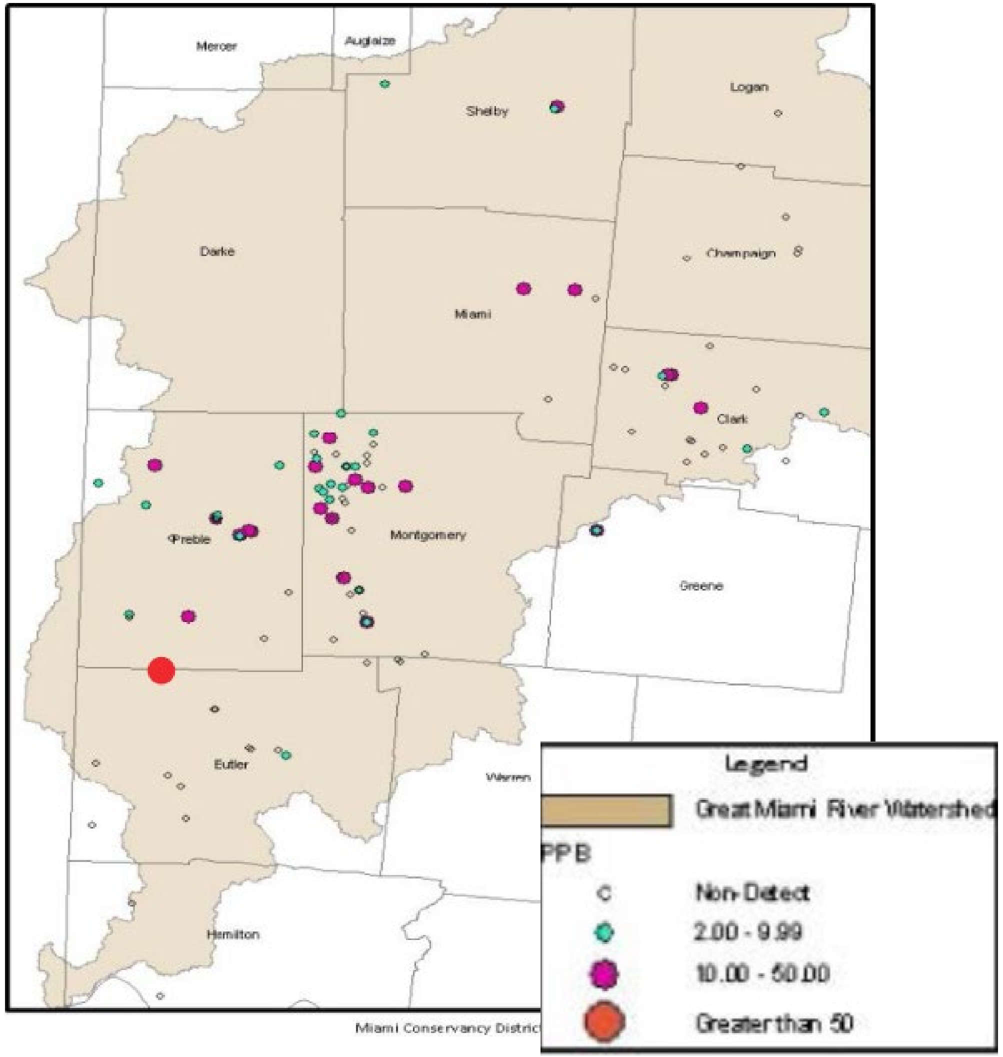
Great Miami River Watershed – Arsenic and ORP

- Initially a study to test for Arsenic in wells
- Where Arsenic was confirmed, the ORP sensor was then used for additional testing
- Samples with detectable concentrations of arsenic tended to have negative oxidative reduction potentials suggesting anoxic conditions in the aquifer supplying the well.



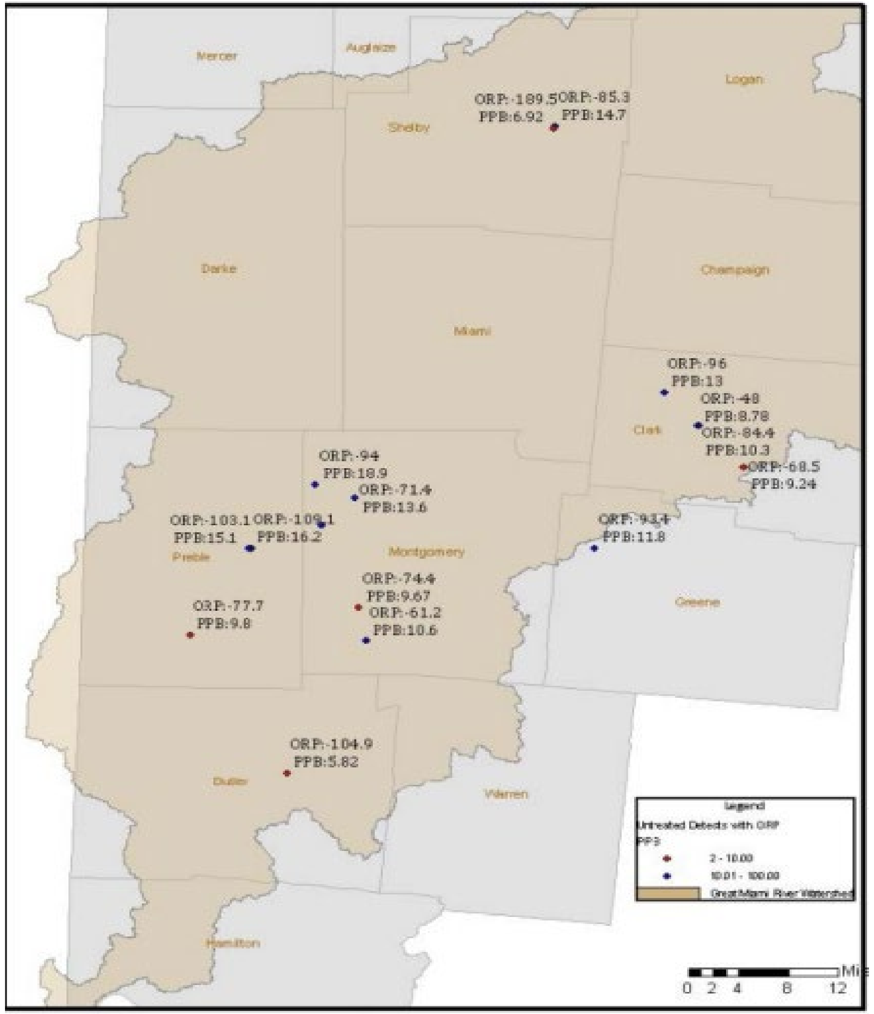
Great Miami River Watershed – Arsenic and ORP

Map of Arsenic Results



Miami Conservancy District

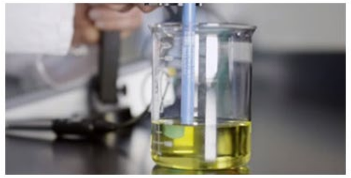
Map of ORP Results



Miami Conservancy District

More on the Blog!

- For a popular and extensive look into common problems with pH probes and their calibration, check out our ongoing water blog!
- **Check out YSI Water Blogged for more information and water news!**
- **YSI.com/blog**



The Ultimate pH Primer - Are you Familiar with Hydrogen?

Patrick Higgins | Apr 08, 2014

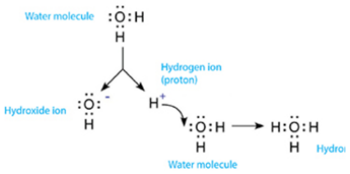
	pH	H+ Activity		OH-
	0	1.E+00	1	0.0000000000
	1	1.E-01	0.1	0.0000000000
	2	1.E-02	0.01	0.0000000000
acid	3	1.E-03	0.001	0.0000000000
	4	1.E-04	0.0001	0.0000000001
	5	1.E-05	0.00001	0.000000001
	6	1.E-06	0.000001	0.00000001
neutral	7	1.E-07	0.0000001	0.0000001
	8	1.E-08	0.00000001	0.000001
	9	1.E-09	0.000000001	0.00001

Why is the pH Scale Logarithmic?

Chris Cushman | Feb 13, 2015

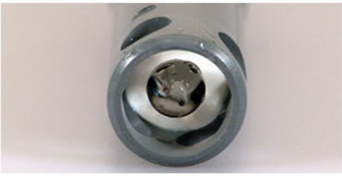
How To Choose a pH Electrode

Chris Cushman | Jul 06, 2015



Is pH the Measurement of Hydrogen Ion Concentration or Ion Activity?

Chris Cushman | Jan 30, 2015



pH Measurement Methods - Advantages and Disadvantages

Patrick Higgins | Oct 14, 2014

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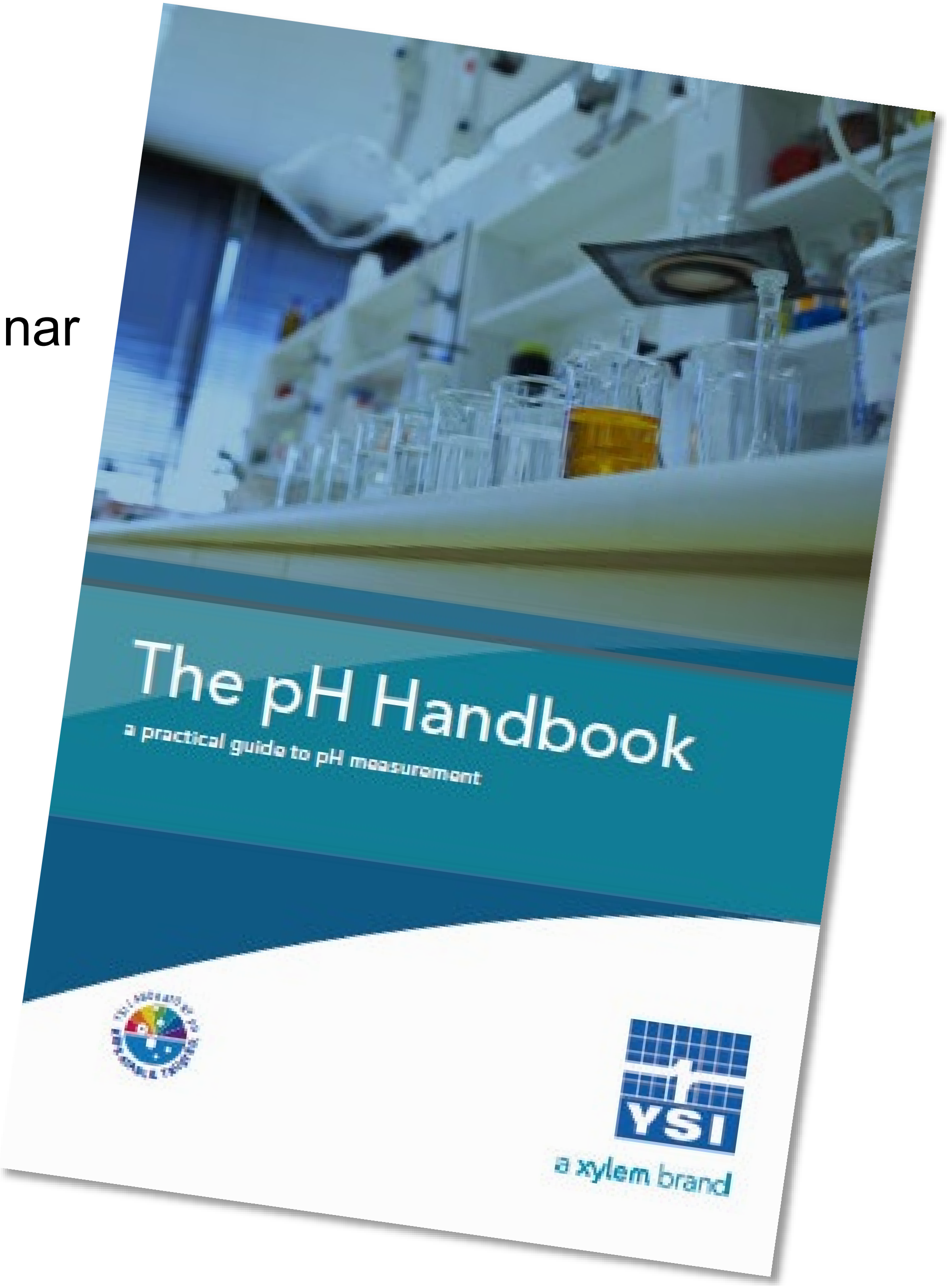
pH Handbook

Check out the YSI pH Handbook!

Tons of data that expands on the themes in this webinar

It's free!

YSI.com/pH-handbook



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Do you want someone from YSI to contact you to discuss pH/ORP sensors?

Questions?

Contact us:

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info@ysi.com

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info.apac@xyleminc.com

June 16th / www.xylem-analytics.asia

cleveland water alliance

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