



Focus on pH



Spartan Controls – Emerson’s Local Business Partner



- 51 years of employee owned sales, service and support
- 12 million hours without a lost time injury
- > 400,000 ft² locally owned infrastructure
- \$50M in inventory
- 13 years running as one of Canada’s 50 Best Managed Companies

We sell, apply and service instruments, control and automation solutions in the process industries



Presentation Overview



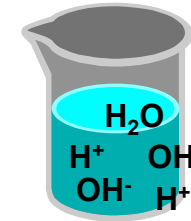
- Basic pH Theory
- Tips on the installation and use of pH sensors.
- Diagnostics can minimize maintenance
- pH issues and troubleshooting

What is pH?



pH is the unit of measurement for determining the acidity or alkalinity of a solution

The symbol (pH) represents the Hydrogen Ion (H^+) Activity in an Aqueous Solution



pH Scale vs Moles/Liter Ion Concentration

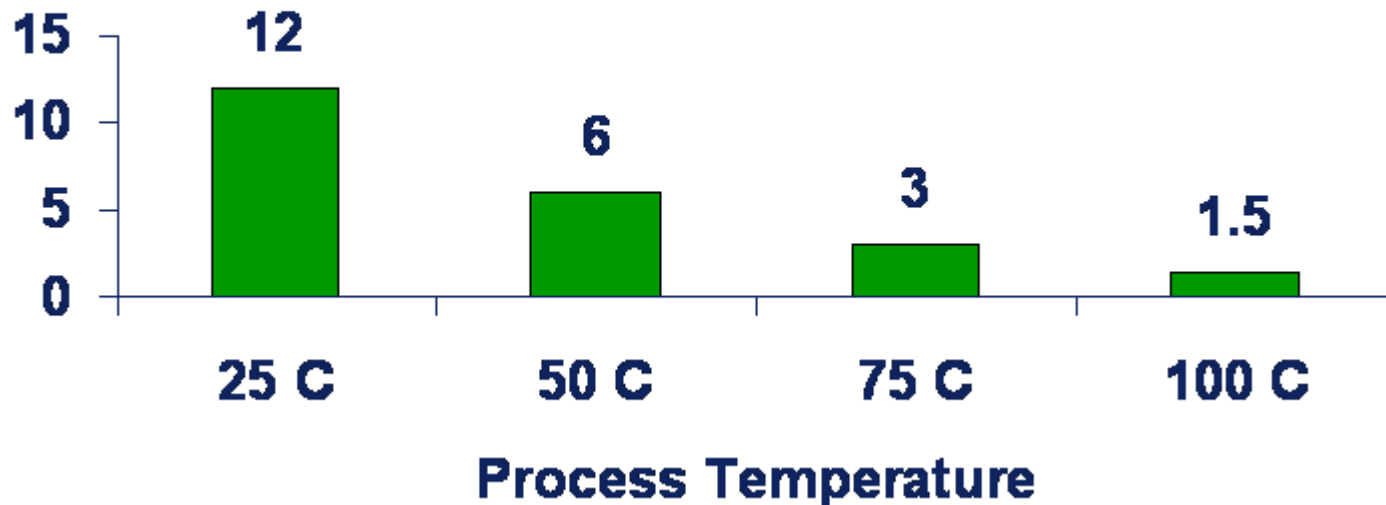
pH	Hydrogen Ion [H^+]	Hydroxyl Ion [OH^-]
0 Acidic	1.0	0.0000000000000001
1	0.1	0.000000000000001
2	0.01	0.00000000000001
3	0.001	0.0000000000001
4	0.0001	0.00000000000001
5	0.00001	0.000000000000001
6	0.000001	0.000000001
7 Neutral	0.0000001	0.0000001
8	0.00000001	0.000001
9	0.000000001	0.00001
10	0.0000000001	0.0001
11	0.00000000001	0.001
12	0.000000000001	0.01
13	0.0000000000001	0.1
14 Basic	0.00000000000001	1.0

pH Probe a Consumable

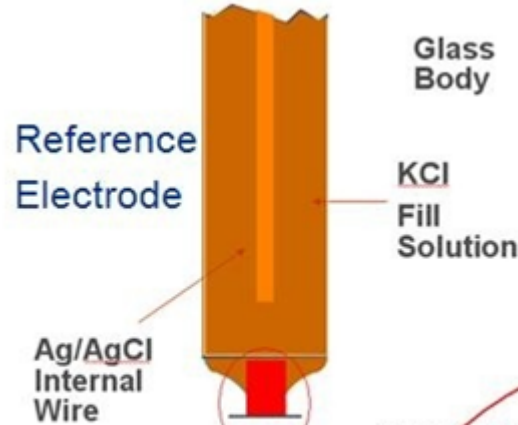
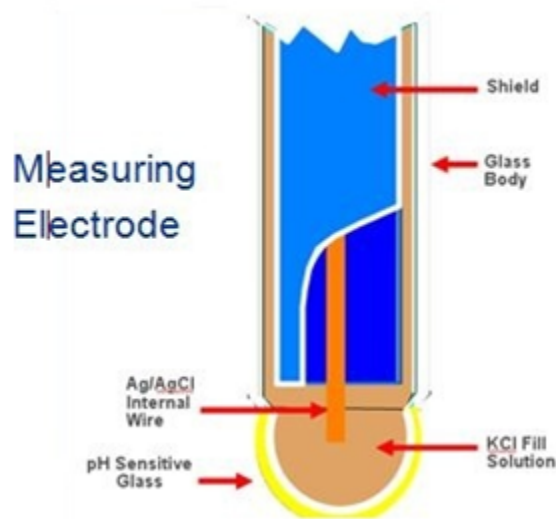


- Room Temperature and Benign Process = 1 Year Life
- Life Halved for each 25 Deg C

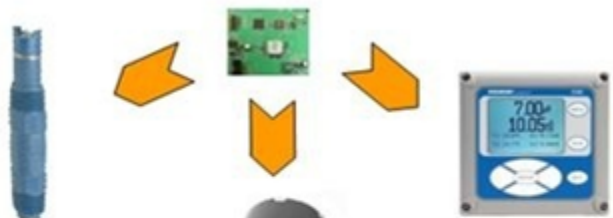
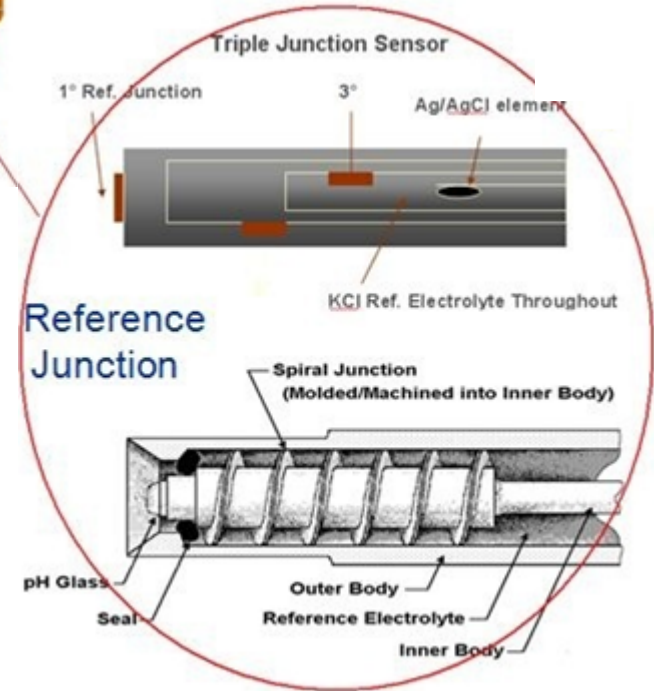
Months



What's Inside a pH Sensor



Temperature Compensator



- At 25°C the pH electrode produces 59.16 mV per pH unit
 - The impedance of a general purpose pH electrode is approximately 100 Meg ohms
 - Ohms Law
 - Voltage (E) / Resistance (R) = Current (I)
 - E / R = I
-therefore 0.05916 v / 100,000,000 ohms = 0.000000001 Amps

b

How is pH measured?...

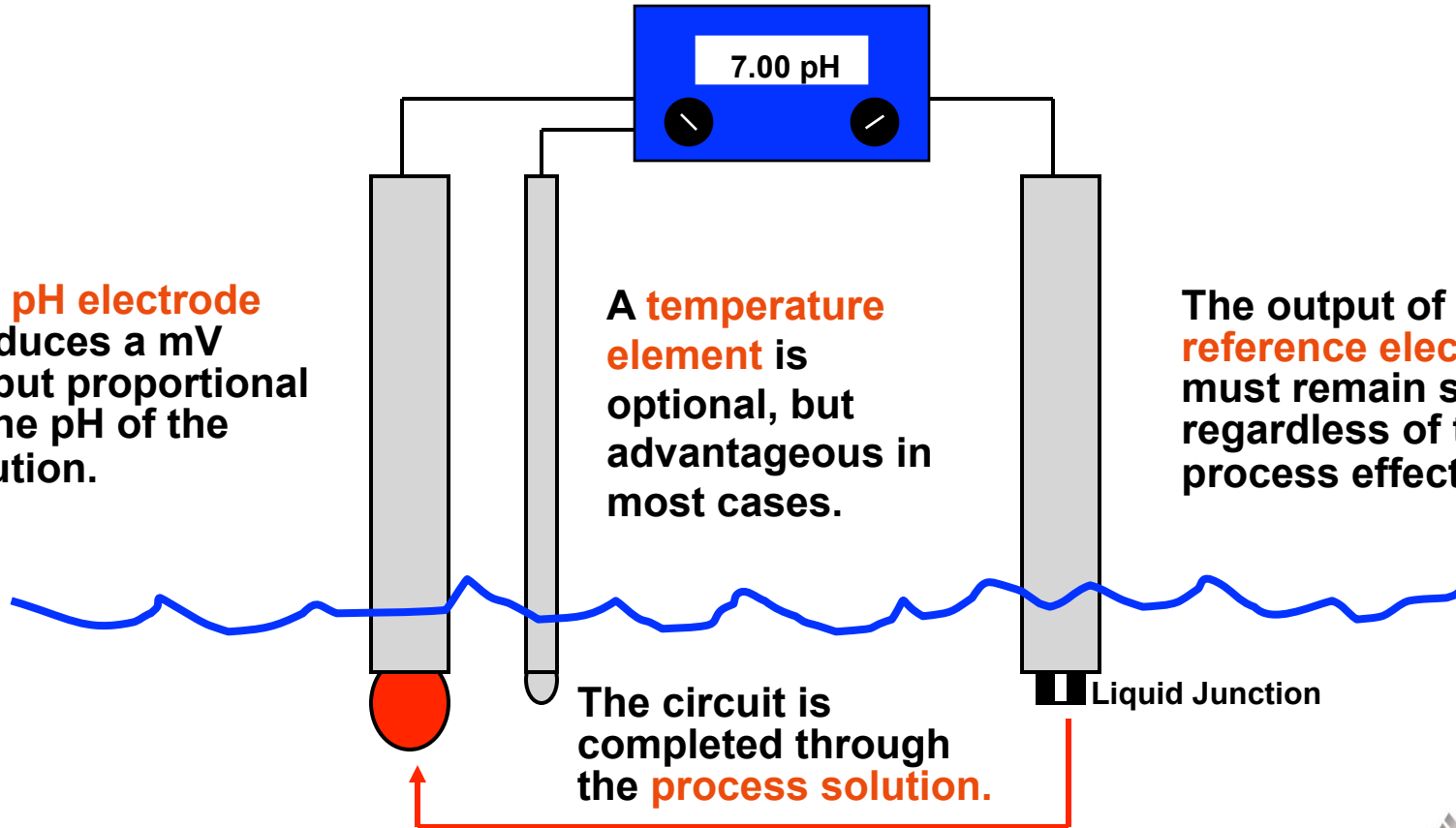


The **pH meter** is a high impedance volt meter

The **pH electrode** produces a mV output proportional to the pH of the solution.

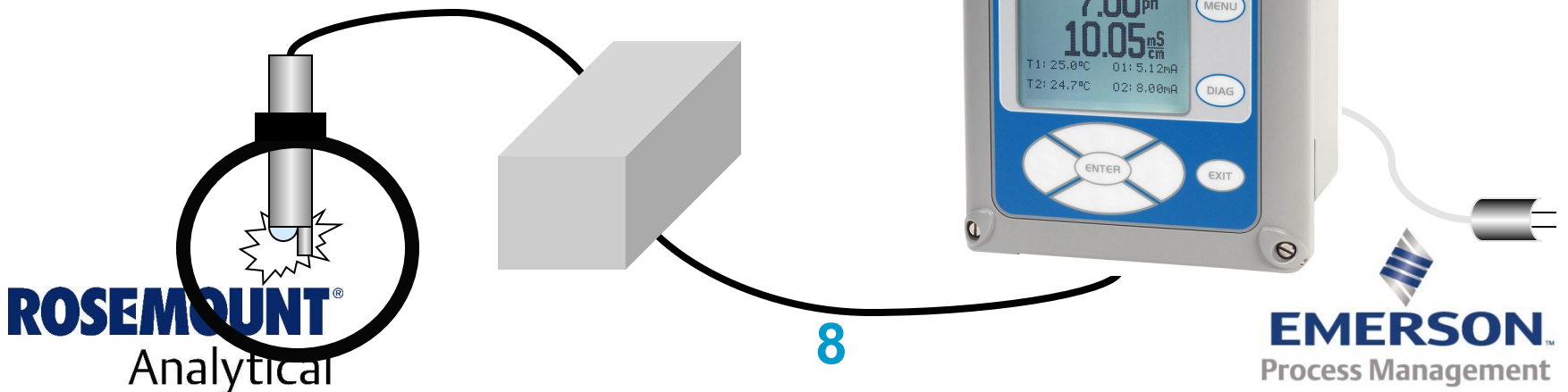
A **temperature element** is optional, but advantageous in most cases.

The output of the **reference electrode** must remain stable regardless of time or process effects.



pH measurement

pH measurement starts with the sensor making an electro-chemical reaction with a solution. Please, keep your pH sensors wet!!

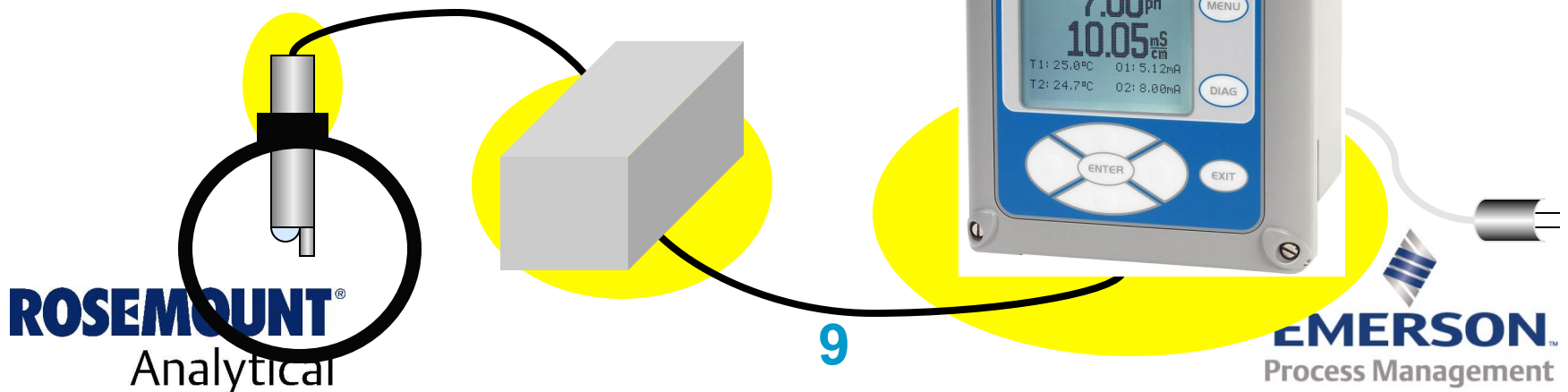


pH measurement



pH measurement starts with the sensor making an electro-chemical reaction with a solution.

The signal is then processed through a preamplifier. The preamplifier can be physically located in the sensor body, the j-box, or in the analyzer's electronics. Do not use integral preamp if the process > 80 degrees C.



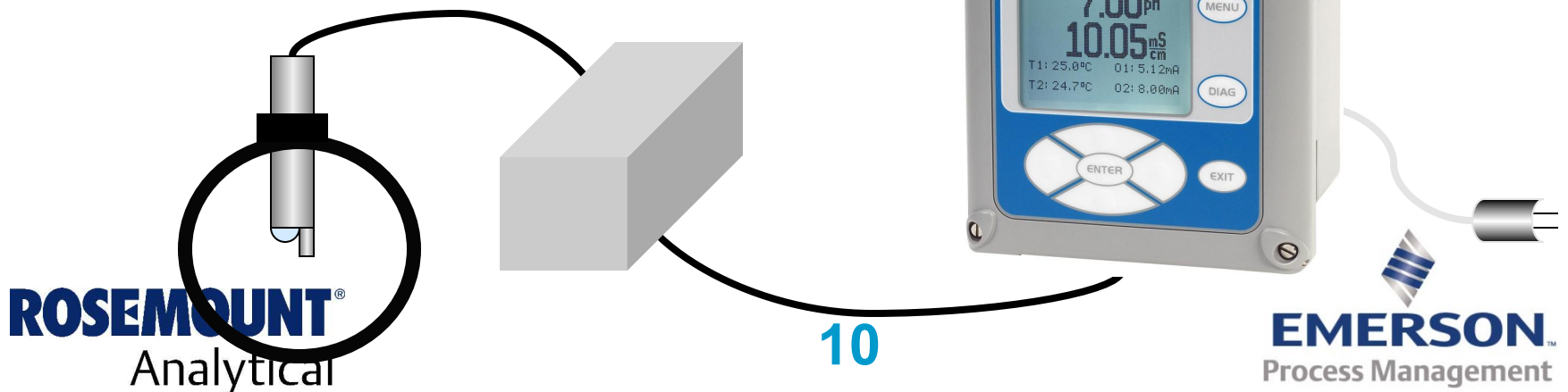
pH measurement



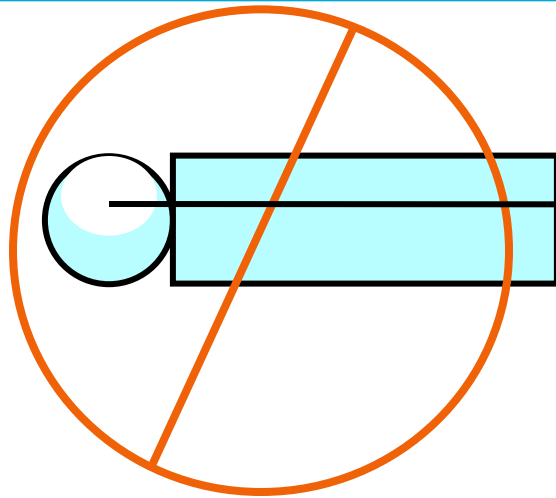
pH measurement starts with the sensor making an electro-chemical reaction with a solution.

The signal is then processed through a preamplifier. The preamplifier can be physically located in the sensor body, the j-box, or in the analyzer's electronics.

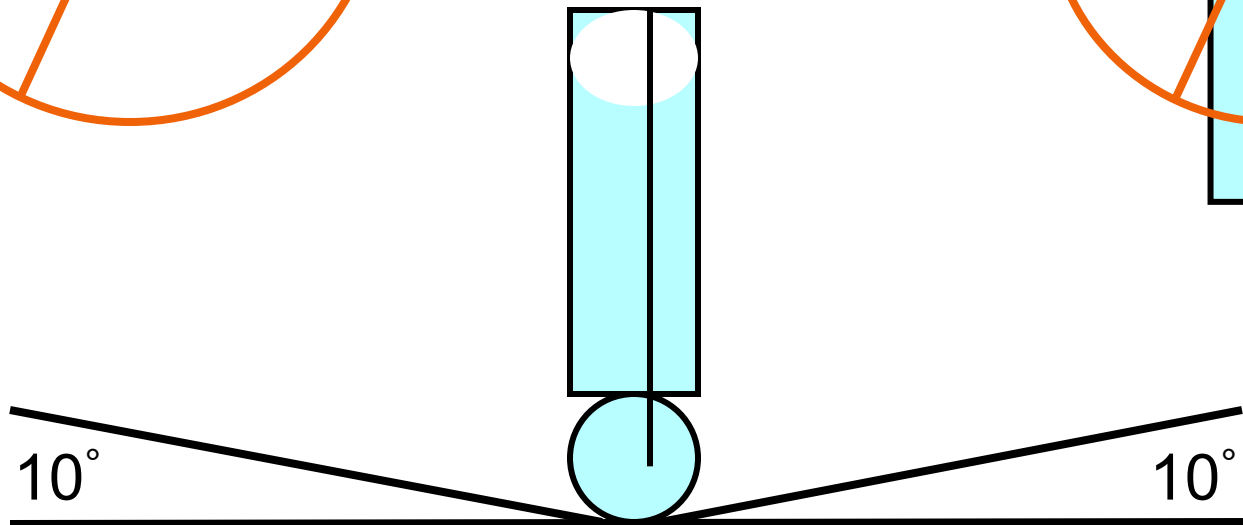
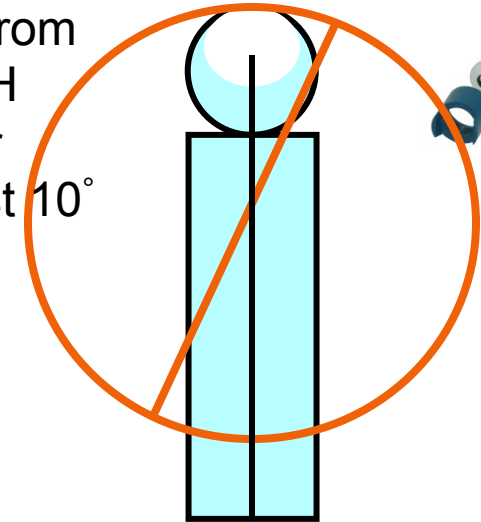
Finally, the millivolt input signal and the temperature signal are processed through the microprocessor, and a pH value is displayed.



pH sensor mounting



To prevent the air bubble from blocking signal from the pH sensitive glass, the sensor should be mounted at least 10° above horizontal.



pH sensors generally have an air bubble sealed inside to allow for expansion and contraction of the fill solution.

Mixing and Reagent Addition



- If the sensor does not see a representative sample of the process, it won't measure correctly.
- Don't try to do all the neutralizing in a pipe!
- pH reagents can be more viscous than water and require time to mix and react.
- If the pH reading appears noisy it may be installed in an area that is not well mixed....move the probe farther downstream of the reagent additive point.

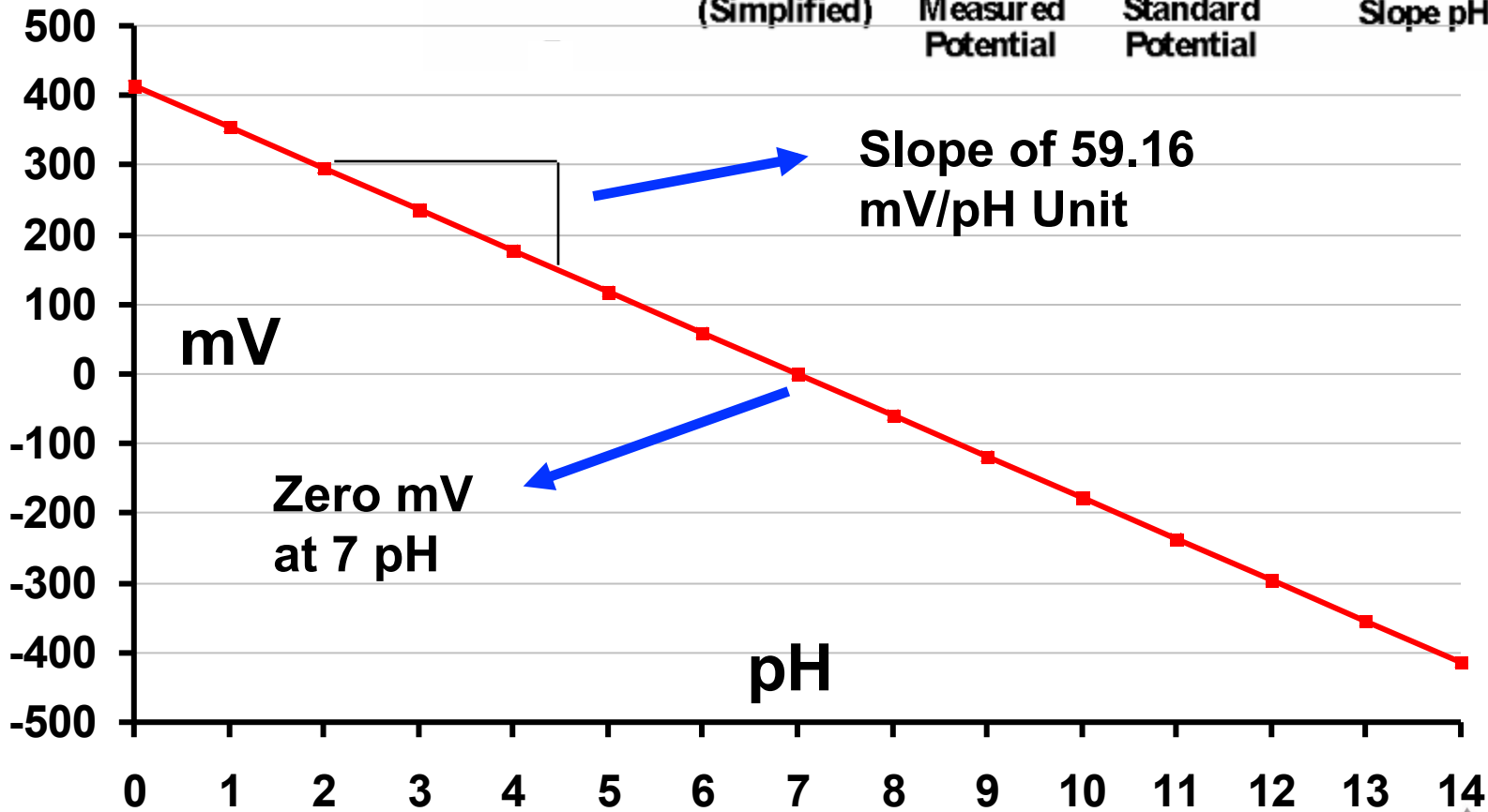


Theoretical Response of a pH Sensor



$$\text{Nernst Equation: } E = E^{\circ} - s \times \text{pH}$$

(Simplified) Measured Potential Standard Potential Slope pH



Temperature compensation



- Sensor slope is affected by temperature... so we measure temperature to compensate for it.
- Auto temp comp...calculation done at the analyzer... is Standard.
- Some processes change their pH with temperature (example...high pH buffers)
- Can lead to errors between process pH and grab sample measurements at different temperatures

Calibration with Buffer Solutions

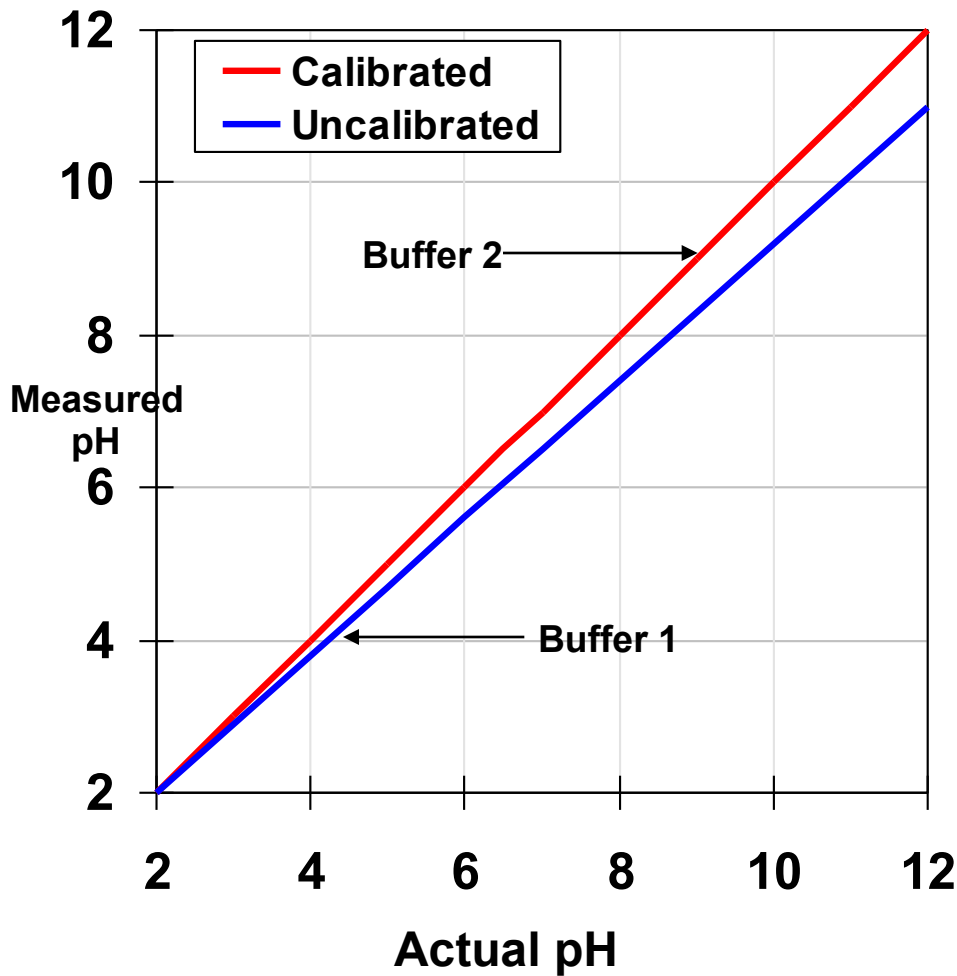


- Solutions of known pH that can withstand moderate contamination or dilution without significant pH variation. **Automatic buffer recognition in some analyzers adjusts buffer values for different temperatures**
- Buffers 4 and 7 are most recommended, however can use 10 as well depending on the pH value of interest.

- Rules of buffering
 - Use fresh buffer
 - Rinse between buffers
 - Allow reading to settle



pH Buffer Calibration



Two Point Calibration

- Verifies Sensor Response to pH Change
- Determines Slope**
- Determines Zero Offset**

Single Point pH Calibration (Standardize)



- Performed on-line by grab sample evaluation
 - ❑ *Only Determines Zero Offset*
 - ❑ *Use calibrated portable analyzer*
 - ❑ *Take sample at or near pH sensor installation point*
 - ❑ *Analyze grab sample ASAP if not immediately*
- Calibrates pH sensor in process environment
 - ❑ *Does not verify that sensor is operational*
 - ❑ *Compensates for small offsets in the liquid junction potential due to flow, pressure, temperature, conductance, etc...*

pH Maintenance



- How often should you buffer calibrate a pH sensor?
- Depends on the process, however every 2 weeks is a good start
- Whenever your process reading is off by more than 0.2 to 0.5 pH units from a grab sample (adjusting for temperature effects).
- In practice it depends on how precise the reading needs to be and how old the sensor is...as the sensor gets older it will need calibration more.

Retraction assemblies



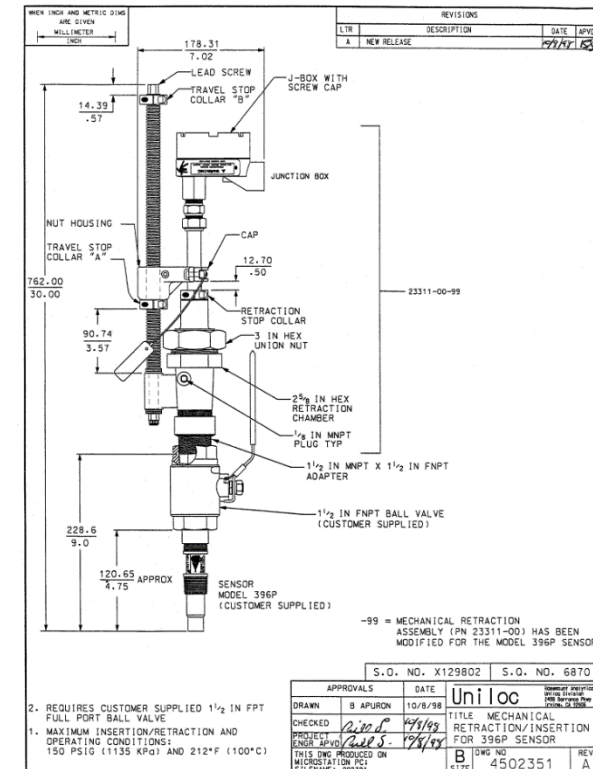
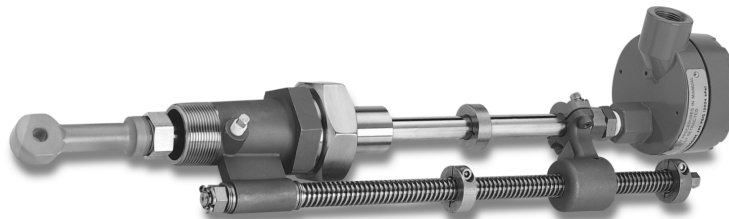
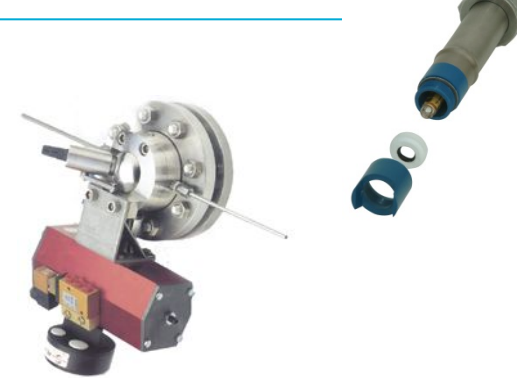
- Retractable sensors have retraction pressure spec of 64 psig –limited by strength of average human being

- Options:

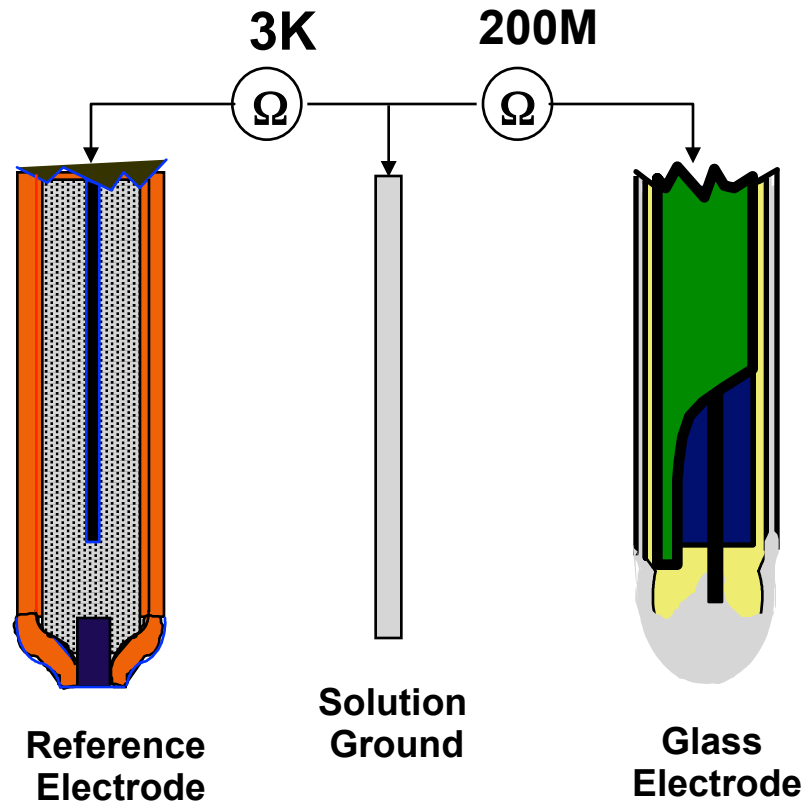
- Reduce pressure when installing sensor

- PASVE rotary valve

- Special 228 retraction mechanism



Typical pH Sensor Impedances



What is Glass Impedance?



- The glass impedance is a resistance measurement of the glass electrode
- Expressed in Meg ohms (MΩ)
- Glass impedance increases with age and cold process temperatures
- Glass impedance decreases with breakage, and high process temperatures
- Temperature compensation for glass impedance is approximate

What is Reference impedance?



- The reference impedance is a conductance measurement of reference electrode and the liquid junction
- Reference impedance is expressed in kilohms ($k\Omega$)
- Reference impedance increase with coating, plugging

When does the sensor need to be cleaned?



- The reference impedance increases as the open surface area of the liquid junction decreases.
- A large (typically double or triple) change in reference impedance indicates that the sensor should be removed and cleaned.
- In early stages, periodic standardization may be sufficient to keep the sensor reading correctly
 - Note: the **Offset** updates after a two-point calibration or a standardization is performed

pH Glass Electrode Cleaning

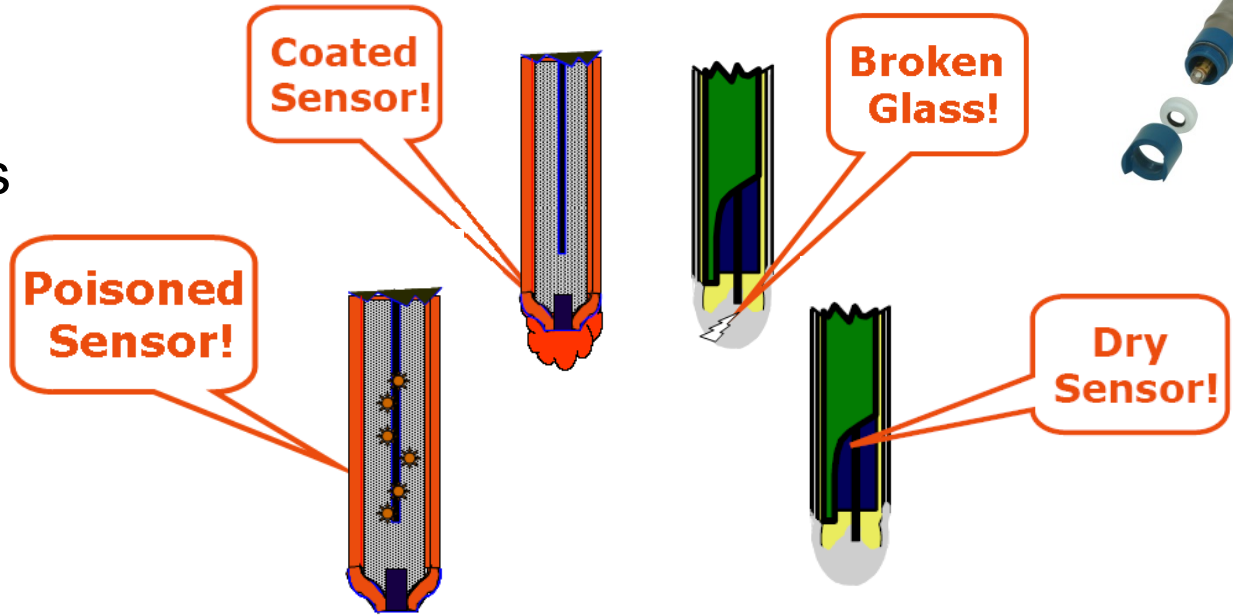


- **Alkaline or scale coating**
 - 5% HCl solution or vinegar
- **Acidic coatings**
 - Weak caustic <4%NaOH
- **Oil, grease or organic compounds**
 - Detergent
 - Organic solvent compatible with sensor materials
- **Don't use a small brush (toothbrush) with abrasive powder (baking soda) to clean the sensor unless no other method is working.**

Diagnostics

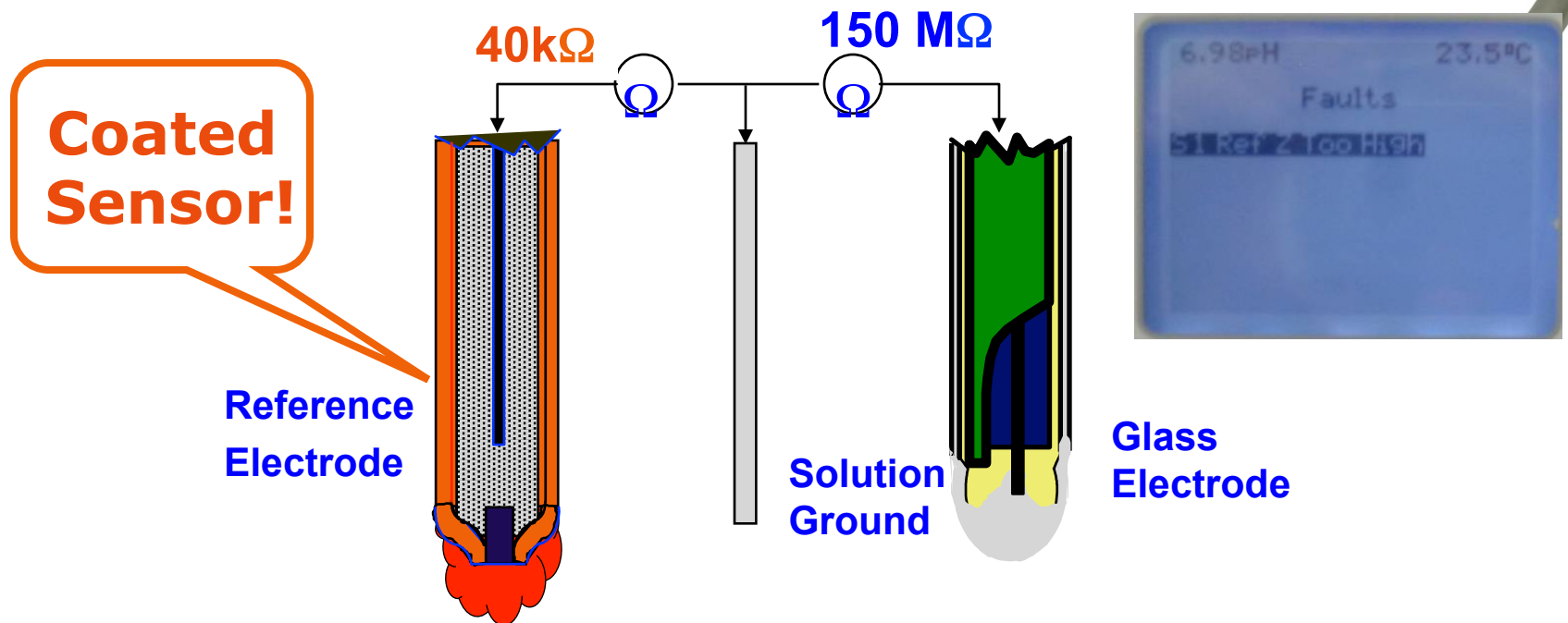


- Cracked Glass
- Aged Glass
- Coating
- Poisoning



- History of impedance behavior of electrodes will allow yourself to avoid unnecessary cleaning or buffer calibration

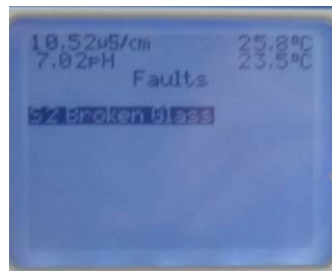
Diagnostics - Coated Sensor



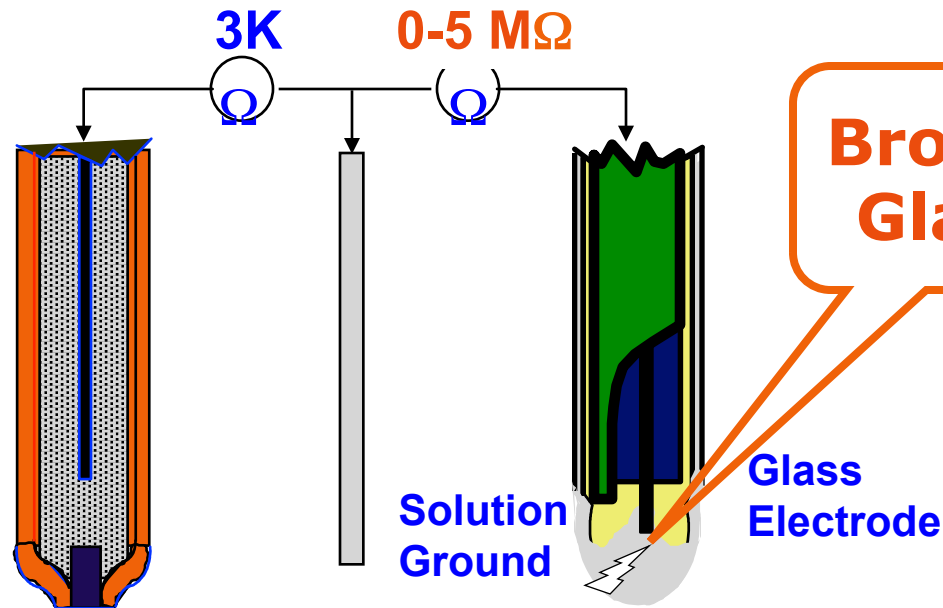
■ Coated Sensor Fault (Ref Z Too High)

- pH Reference electrode normally has low impedance of 1-10 KilOhm
- Reference coating slowly builds up around the junction
- Recommended setting of 20 KilOhm should not generally cause false alarms, but sensors can vary

Diagnostics - Broken Glass



Reference
Electrode

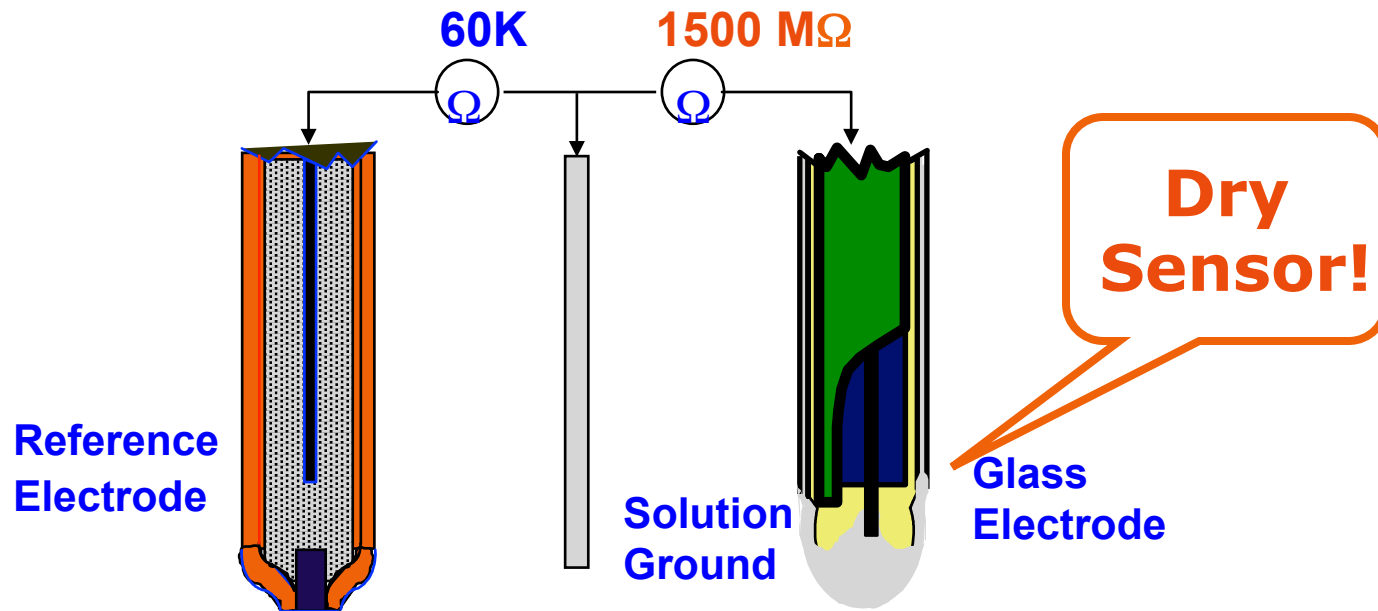


Glass
Electrode

■ Broken Glass Fault (Glass Fault Low)

- pH Glass electrode normally has high impedance of 50-500 Megohm
- Recommended setting of 10 Megohm will detect even hairline cracks
- Glass can be cracked at the tip or further back inside the sensor (and not easily visible)

Diagnostics - Non-Immersed Sensor



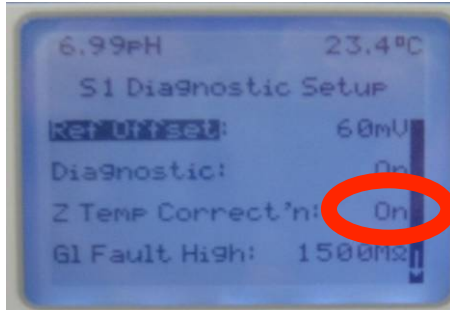
■ Dry Sensor Fault (Glass Z Too High)

- pH Glass electrode normally has impedance of 50-500 Megohm
- When sensor is dry there is no continuity between the electrode(s) and the solution ground so impedance reading is very high
- Recommended setting of 1000 Megohm will not cause false alarms
- May also detect problem with horizontal orientation

GI Temperature Effects

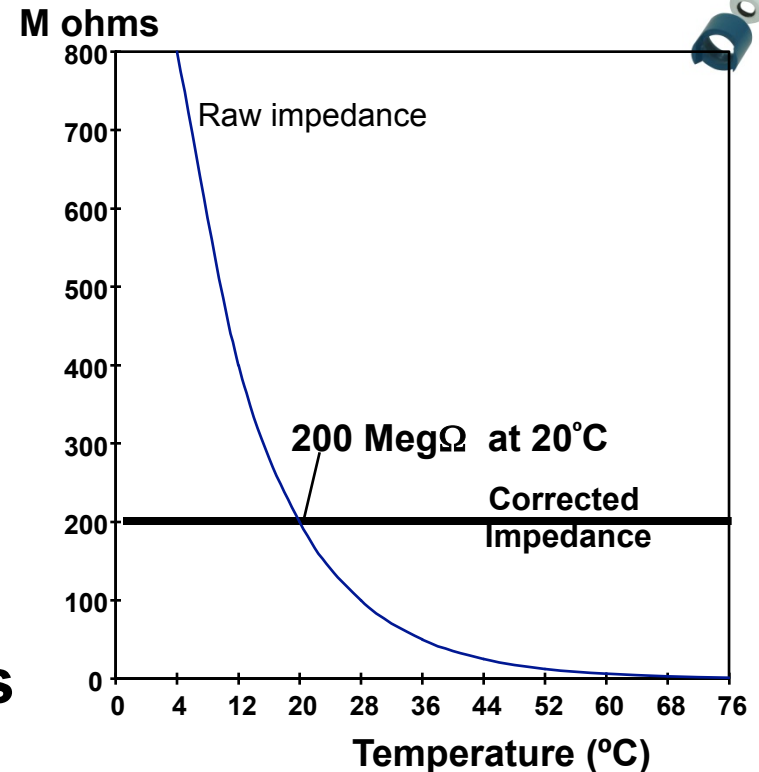


- Always use temperature correction



- When online temperature is not available, enter the operating temperature manually
- If rapid temperature changes occur, false alarms may be generated.

Glass Impedance vs. Temperature



Reference Electrode Plugging



Over 80% of sensor failures are reference related:

- Reference Junction Blocked

- The Liquid Junction can become plugged by precipitation or coating, creating an open measuring circuit.
 - Precipitation occurs by the reaction of a contaminant with a constituent of the reference fill solution.
- Plugging of the liquid junction by precipitation of of:
 - Sulfide ion in the process and silver ion in the reference fill
 - Heavy metals, lead, mercury, and silver, in the process, with chloride ion present in the fill solution
- Plugging causes the reference impedance to increase

Reference Electrode poisoning



Over 80% of sensor failures are reference related:

- Fill Solution Depleted or Poisoned
- The potential of the reference can be changed (poisoned) by contamination from the process.
 - Reaction with the silver ion concentration in the reference, causes a potential change within the reference.
 - The amount of poisoning can be viewed on the offset diagnostic feature. The reference offset updates every time a standardization or a two point calibration is performed.

Addressing the Problems



- Provide a high Porosity Liquid Junction for minimal to No Junction Potential
- Protect the Ag/AgCl wire from Poisoning
- Stop Depletion of the KCl, especially in High-Temperature applications.
- Attack the Poisoning, Coating and Fouling Problems that cause drift and offsets



Challenging Process Conditions



- **Temperature**... sustained elevated temperatures and temperature cycling are tough on glass and reference
- **Poisoning**... sulfide, cyanide, and other reducing agents attack the reference element and can damage the reference from the inside
- **Scaling**... the reference junction gets clogged with calcium scale and mineral deposits
- **Coating**... oils and greases blind the sensor
- **Heavy Metals**... react with the Cl⁻ in the reference electrolyte, precipitate and clog the junction
- **Water**... bio-films and algae can blind a sensor similar to oils and greases... requires a different solution yet
- **High Purity / Low Conductivity Water**... junction potentials frustrate accurate, stable measurements

>80% of pH Problems are
Reference Electrode Problems

Semi Rebuildable Sensor

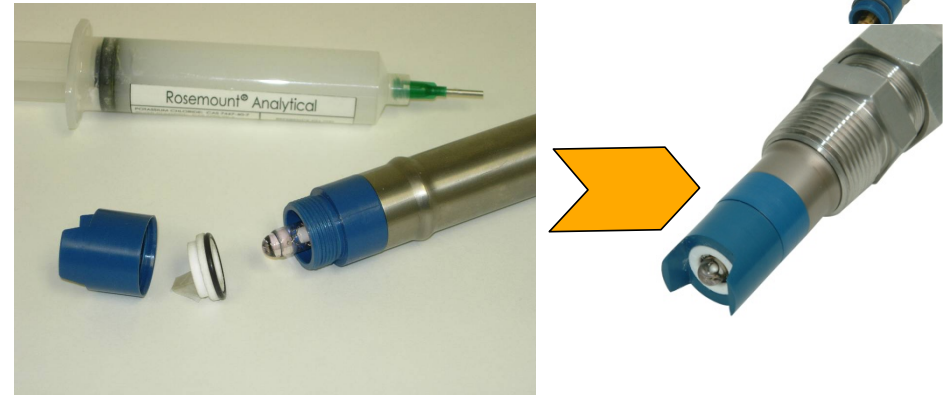


Re-buildable / Extended Life



Fill kits available to match the application:

- Poisoning
- Coating
- High Temperature
- Scaling
- Heavy Metals
- Bio-films & Algae



ROSEMOUNT[®]
Analytical

Advanced Technology: SMART pH



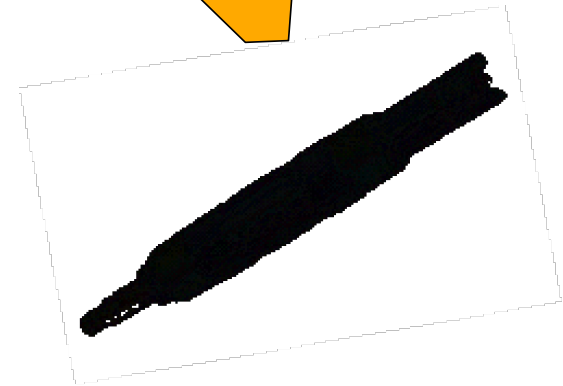
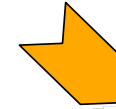
Smart Preamp in sensor

■ Plug and Play

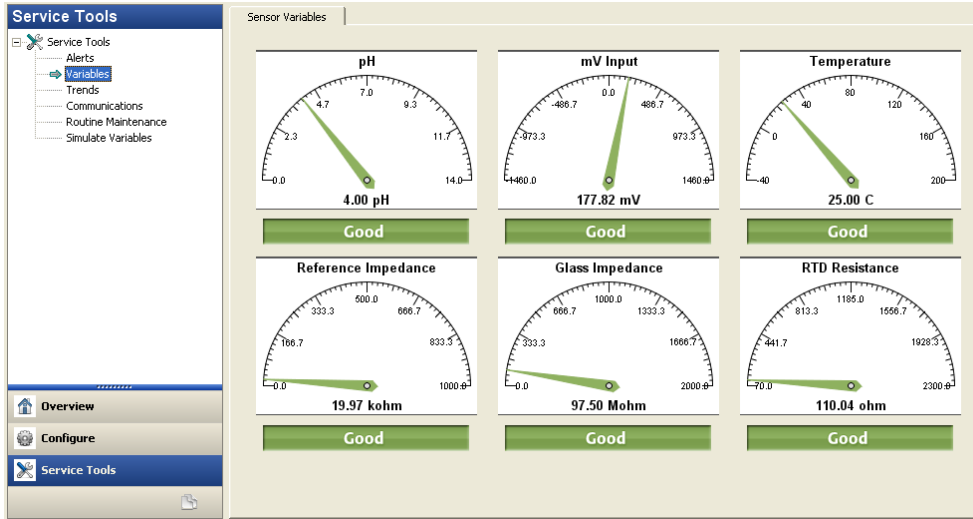
- Factory pre-calibrated
- Calibrate **in lab** instead of in field
- Can restore to factory values

■ SMART technology

- Automatically trend diagnostics
- Capture intermittent sensor problems
- SMART signal superimposed on mV signal



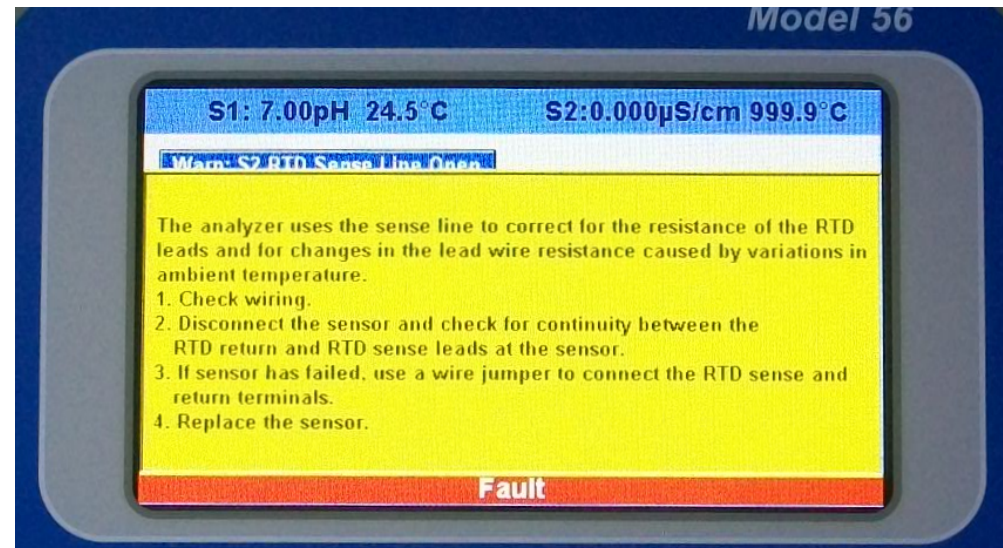
Diagnostic Software provides a window on the process: Key Indicators of Sensor Performance



Software Can Display Live Readings of All Transmitter Variables Available at a glance.

Some Instruments provide Graphical Information Right on the Instrument Display Itself.

ROSEMOUNT[®]
Analytical



Example: Coated pH Sensor Troubleshoot in shop



File Actions Help

Overview

- Overview
- Overview

Alerts

Active

Failed - Fix Now **Press Troubleshoot Button**

Reference Impedance Too High

The reference impedance is above the high fault setpoint. The reference electrode may be coated or plugged.

Recommended Actions:

1. Clean or replace sensor.
2. Check sensor wiring.
3. Increase the setpoint value.
4. Set the reference impedance level to high.

Alert Tracker Finds Issue. Next step open device.

Reference Impedance

High Fault Setpoint 40 kohm

58 kohm

Advisory

Output 1 Fixed

Analog output 1 is either being tested, calibrated, or accidentally left on hold. A fault condition could also set the analog output to a fixed value.

PV Loop current 22.000 mA

Recommended Action:
If there is no active fault, wait for test or calibration to be done or take output 1 out of hold mode.

Device last synchronized: 10/6/2015 10:53:32

Send Close Print

pH Sensor Application Guide



Designed for general use in most industries.

For processes that require a high performance or special application sensor, there's a more specific Rosemount Analytical solution.



2

Non-Coating with Possible Poisoning

Processes containing sugar, ammonia, chloride or sulfides
Chemical
Wastewater
Pulp and Paper
Refining
Metals



3

Sanitary

For ultra-clean SIP and CIP Processes
Food and Beverage
Pharmaceutical
Life Sciences



4

Heavy-Duty Industry

For dirty applications and processes with viscous coating
Metals and Mining
Chemical Refining
Oil Refining
Pulp and Paper



5

Low-Conductivity

Power Generation
Boiler water
Boiler feedwater



6

High-Temperature and Pressure

Processes requiring high performance
Oil Refining
Chemical
Pulp and paper
Water and Wastewater
Metals and Mining



7

Special Use

Hydrofluoric Acid Processes
Non-glass applications



Troubleshooting



- How to troubleshoot pH issues

Troubleshooting a pH loop



- All pH loops have the same basic components
- There are several steps that can be taken to troubleshoot a pH loop
 - Verification of compatible components
 - Verification of proper wiring
 - Isolation to finding the problem component.



Basic Troubleshooting



Determine the extent of the problem

- What is the primary value indication (realistic, steady or erratic)
- What is the temperature (realistic, steady or erratic)
- Where is the sensor (in the process, in a beaker filled with a grab sample, or in a beaker filled with standard / buffer)
- Are the sensor and analyzer / transmitter compatible

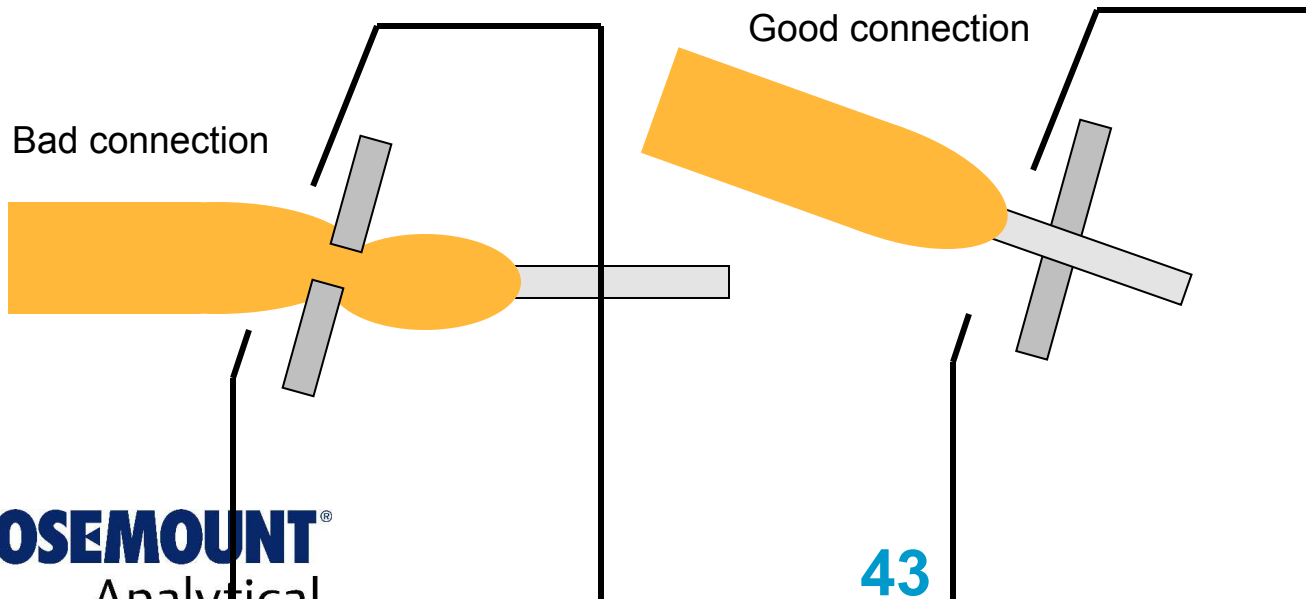
Checking the wires



Verify that the wire is in the correct terminal spot, and the bare wire makes proper contact with the terminal.

Check that the terminal is NOT clamped down on the insulation of the wire; otherwise, poor or no contact will result.

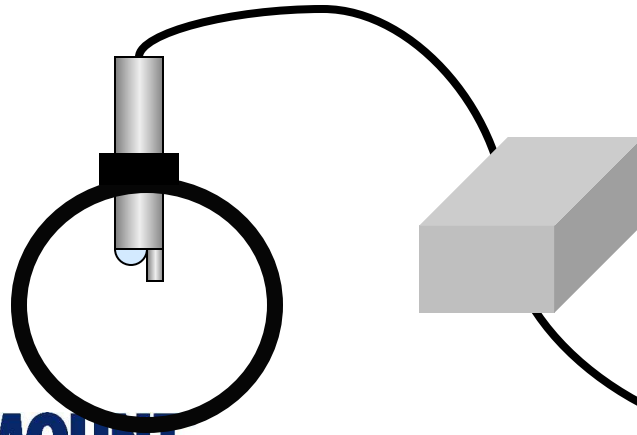
Verify that some of the bare wire is visible, guarantying proper connections



Isolation Steps

A pH measurement loop is comprised of 6 distinct components.

- 1) Process solution
- 2) The Sensor
- 3) The connecting cable
- 4) A preamp
- 5) The Analyzer
- 6) A power source



ROSEMOUNT
Analytical

44

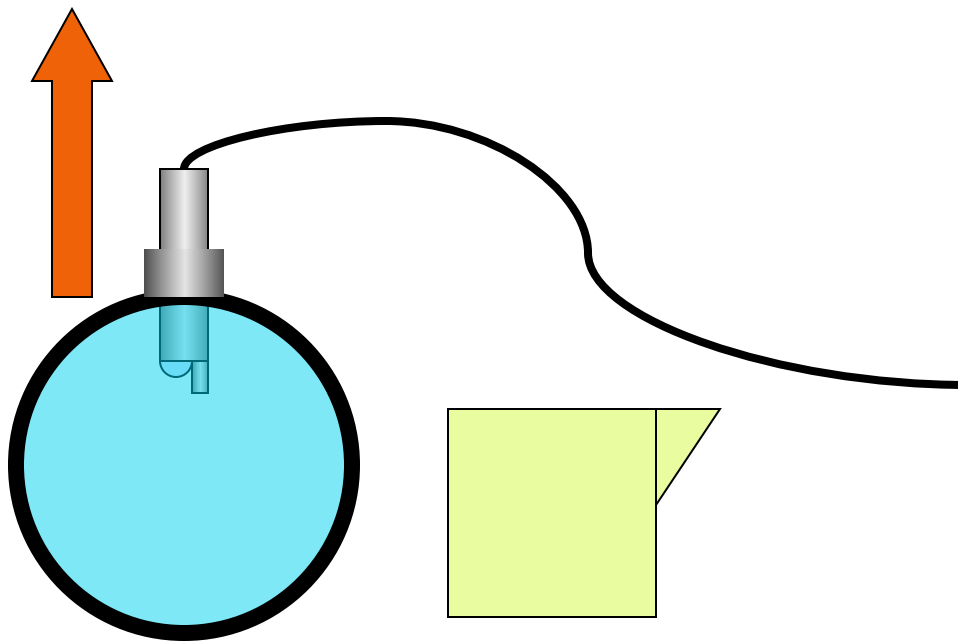


EMERSON
Process Management

Step 1 Remove sensor from the process



The first step is to isolating the sensor from the process. Remove the sensor from the process to see if the erratic readings go away.



pH 7 buffer

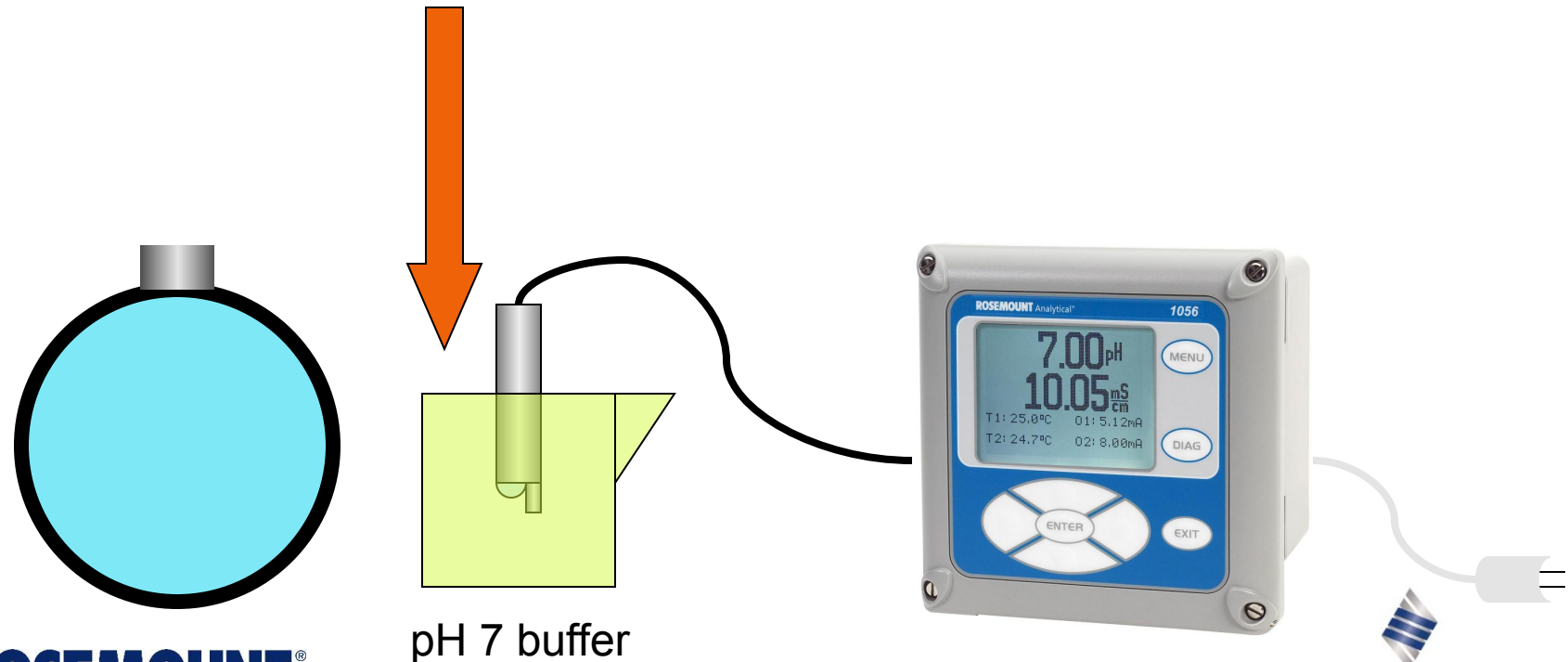


Step 2 place sensor in known solution



The first step in isolating the problem component is to remove the sensor from the process. If the problem is process-related, then this procedure will prove it.

Next, place the sensor into a solution of known value (buffer or standard). Confirm the reading is steady and reflects the proper value of the buffer or standard.



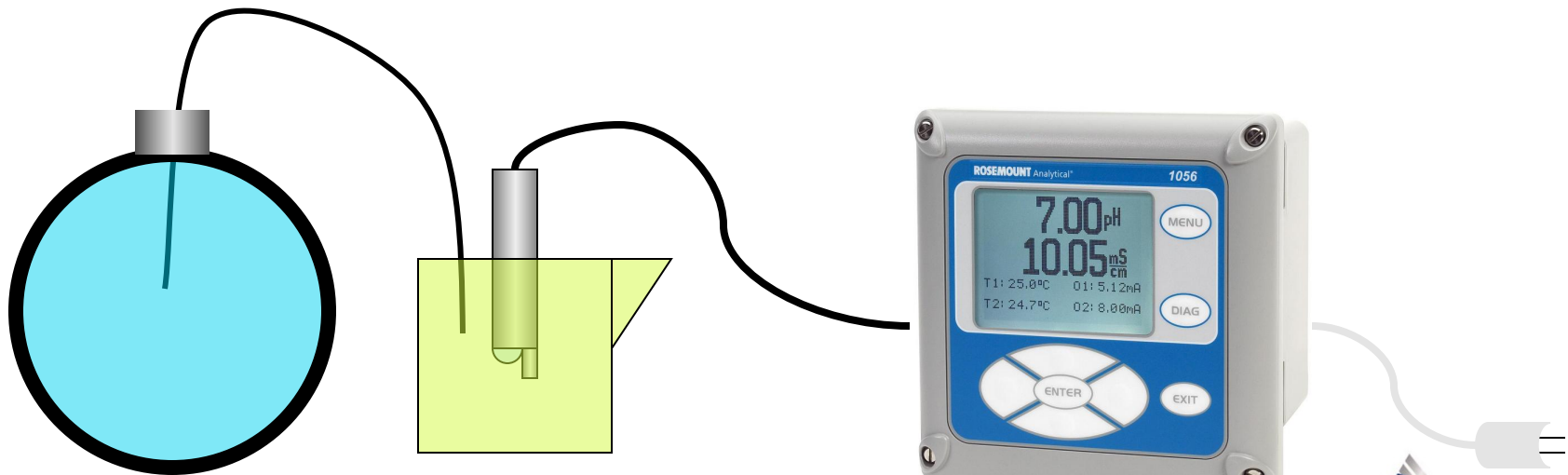
Step 3 Check for process interference



The first step in isolating the problem component is to remove the sensor from the process. If the problem is process-related, then this procedure will prove it.

Next, place the sensor into a solution of known value (buffer or standard) to confirm the reading is steady and the reading reflects the value of the buffer / standard.

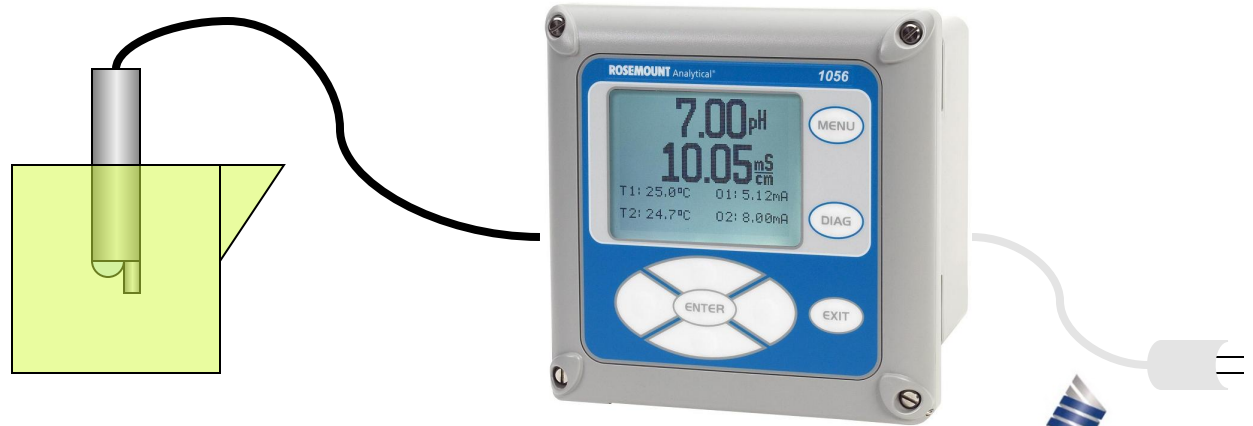
Confirm the interference is process related, by making an electrical connection from the process to the beaker. If it is a process related problem the interference will start up again.



Step 4 Remove sensor



If the source of problem has not been determined by step one, simulate an input to the analyzer.



Step 5 Simulate an input

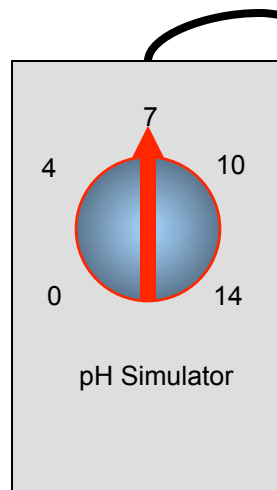


Simulating an input signal will confirm the analyzer's status.



Step 6 Use a different power source

Remove the loop from the factory floor and place on a bench top. Use a separate power source to determine if the analyzer is still working correctly. If the unit is still bad return it to the factory for repair or replacement.





Troubleshooting Conclusion

If a problem with the pH loop is detected use these steps to determine the source of the problem.

- Remove sensor from the process
- Place the sensor in a known solution
- Simulate an input directly into the analyzer
- Remove the analyzer from its power source.



Overall Summary



- pH sensors include a glass electrode and a reference electrode
- Buffer calibration is the primary method of checking the sensor
- Most measurement problems are due to the reference electrode
- Sensor installation is key to success