pH Measurement and Control
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The Need for pH
B. Drinking Water: Rigid purification standards depend upon pH measurement and control.
C. Sewage Treatment: Successful treatment depends on pH control throughout the process.
D. Industrial Process: Petrochemical, pulp and paper, food and beverage, refining, power generation, pharmaceutical, semiconductor, automotive, steel and metal processing; all require pH measurement and control for product quality and efficiency.
E. Environmental: pH monitoring and control are critical to the continuation and quality of all plant and animal life.
F. Research & Development: Medical and industrial laboratories involved in all aspects of research and development require pH measurement.
**pH System Requirements**

1. **pH Meter:** Read the responses from the two electrodes or a combination electrode. Some pH meters have a simple single point calibration, where others may have a standardized slope (the slope is a span adjustment).

2. **Two Electrodes:** A glass electrode for measurement and a reference electrode. These two electrodes are commonly sold as a combination electrode. The OAKTON electrodes and electrodes built in the pHTestr series are combination electrodes.

   There are a few applications where the two electrodes are separate. One application is when there is high pressure in a reaction vessel and another is when the reference solution has to flow from up stream to down stream.

3. **Calibration Solutions of a Known pH Value:** These solutions are called calibration buffers. The most common buffers are 7.00 pH, 4.01 pH and 10.00 pH.

**pH Electrode Conditioning Procedures**

The pH electrodes are shipped with the electrodes moist (except for pH Testrs). Prior to using any electrode for the first time, be sure it has been conditioned or rehydrated.

**Electrode Conditioning**

1. Remove the protective cap from the bottom of the sensor, and rinse the electrode with distilled or deionized water.

2. Place the electrode in a beaker of one of the following liquids for one hour to rehydrate the electrode. The liquids listed below are in the order of their ionic ability to condition the electrode.

   A. KCl (potassium chloride) 3.8 or 4.0 molar
   B. Tap water
   C. 4.0 pH buffer
   D. 7.0 pH buffer

   NOTE: Never condition a pH electrode in distilled or deionized water. Long term exposure of the glass electrode to pure water will damage the glass by leaching pH sensitive elements out of the glass.

3. After one hour of conditioning the sensor, rinse the electrode with distilled or deionized water. You are now ready to calibrate with buffers and take measurements.

**Electrode Storage**

1. Once measurements have been made, the electrode should be stored in a manner which will keep the bulb of the electrode moist or hydrated.

   A. The protective cap of the electrode can be used to hold a small amount of liquid. Add a few drops of potassium chloride or 4.0 pH buffer to the cap or rubber boot, then place the cap on to the electrode. This method works for long and short term storage.

   B. The electrode can be placed in a beaker of either potassium chloride, 4.01 pH buffer, 7.00 pH buffer or tap water for short term storage.
C. For pHTestrs, place a small piece of sponge or paper towel in the bottom of the cap. Wet the sponge or paper towel with potassium chloride, tap water or pH 4.0 buffer and replace the cap.

**Electrode Reconditioning Procedure**

There are a number of applications which can cause the electrode to give either unstable or erroneous readings. When these errors occur, the electrode may need to be reconditioned to bring it back to proper working state.

There are three common methods of reconditioning a pH electrode:

**Method 1**

Soak the electrode in a 0.1 molar concentration of HCl (hydrochloric acid) for one hour, then rinse the electrode with deionized or distilled water. This should remove any organic protein from the glass electrode and the surface of the reference electrode. **NOTE:** Always use the proper safety practices and wear protective clothing and eyewear whenever handling hydrochloric acid.

**Method 2**

Soak the electrode in a 3.8 or 4.0 molar KCl (potassium chloride) solution heated to 50°C for one hour. Allow the KCl solution to cool down to room temperature, then rinse the electrode with deionized or distilled water. This will open and clear the reference electrode of all contaminants.

**Method 3**

Soak the electrode in a 4.01 pH buffer solution, heated to 50°C for one hour. Allow the buffer to cool down to room temperature, then rinse the electrode with deionized or distilled water. This should open and clear the reference electrode.

**Method 4**

**WARNING** - This procedure should only be attempted by qualified persons proficient with the safe handling of dangerous chemicals. Provide proper containers, fume hoods, ventilation, and waste disposal. Safety goggles and protective clothing must be worn while attempting this procedure. If possible, replace with a low cost electrode instead of attempting this reactivation procedure.

1. Dip or Stir the electrode in freon or alcohol for 5 minutes.
2. Leave the electrode in tap water for 15 minutes.
3. Dip and stir the electrode in concentrate acid (such as HCl or H₂SO₄) for five minutes.
4. Repeat Step 2.
5. Dip and stir in strong base (NaOH) for five minutes.
6. Leave for 15 minutes in distilled or de-ionized water.
7. Now test with standard calibration buffer solutions to see if the electrode yields acceptable results. You may repeat step 3 through 6 for better response (but not more than three times). If the response does not improve, then your electrode is no longer functioning. Replace with a new electrode. Call your OAKTON distributor.
Applications for pH Electrodes
Most pH electrodes have a General Purpose glass electrode and a reference electrode which has a KCl saturated with silver, silver chloride reference solution. This combination is designed to measure most common applications where there is an aqueous solution containing at least 5% moisture and compounds which do not have a chemical reaction with silver.

Because standard electrodes have silver in the reference solution, there are a number of applications where the electrode cannot be used.

**Solutions which cannot be measured with General Purpose Electrodes:**
1. Heavy Metals
2. Proteins
3. Organics
4. Low Ion Solutions (DI water)
5. High Sodium
6. Sulfides
7. Tris Buffers

If a sample contains any of these contaminants, the pH electrode may work for only a very short period of time before it fails to operate at all. Reconditioning may restore the electrode to a useful condition but the same short term usage may occur if it is to be used in the same sample again.

If a sample contains any of these contaminants, the customer should look at other electrode combinations which are more compatible with the solutions to be measured.

The **Calomel Referenced electrode** is designed to work in solutions containing proteins, organics, low ion activity tris buffers and heavy metals.

The **Double-Junction Referenced electrode** is designed to work in the same applications as the calomel electrode as well as work at higher concentrations. This is due to the presence of two reference junctions to filter out any potential contamination to the reference electrode.

The **Teflon Junction Reference electrodes** are designed for applications where the solution being measured can clog the reference of the standard electrode. Some solutions which fit this description are oils, foods, paints, gels and pastes.

How the Typical pH Electrode Works
1. Two electrodes (glass and reference electrodes) or a combination electrode are immersed in the liquid.
2. An electrolyte solution from the reference electrode leaks out of the liquid junction at a rate of approximately 0.8 microliters per hour.
3. The electrolyte solution mixes with the liquid or standard being measured, completes an electrical circuit, and the combined solution gives an ionic charge on the glass electrode. The principle ions giving this charge are H+ (Hydrogen ion) and OH- (Hydroxide ion) which come from water (H2O). The ratio of the H+ and OH- ions is affected by the other ions in that solution, mainly ions from acids and bases.
4. If the liquid being tested is acidic, the glass electrode receives a positive ionic charge, which results in a pH value less than 7.00pH.

5. If the liquid being tested is alkaline, the glass electrode receives a negative charge, which results in a pH value greater than 7.00pH.

6. If the liquid does not give a positive or negative charge, the solution is neutral and the pH value is 7.00pH.

**Identifying the Electrode Components**

1. The General Purpose combination electrode has a glass electrode for measurement and a reference electrode. The glass electrode has a pH sensitive glass bulb at the end and a silver chloride wire located in the center of the electrode. The wire is surrounded by a KCl electrolyte solution, a liquid that can be seen from the glass bulb and through the length of the glass electrode.

   The reference electrode usually is a chamber that surrounds the glass measurement electrode. The reference electrode has a silver chloride wire which is surrounded by an electrolyte solution of potassium chloride saturated with silver chloride.

   There is a porous liquid junction in the reference electrode which allows the electrolyte solution to flow through it and make physical and electrical contact with the liquid outside of the electrode.

2. The Calomel reference combination electrode has the same glass measuring electrode as the general purpose electrode, though the reference electrode has different components. The Calomel reference electrode has a KCl wire and a column of mercuric chloride. The reference solution for the Calomel electrode is KCl, meaning there is no silver present in this reference solution.

3. The Double Junction combination electrode has the same glass measuring electrode as the General Purpose electrode.

   The reference of a double junction electrode has two parts. The upper junction has a silver chloride wire, surrounded by potassium chloride saturated with silver chloride electrolyte solution. There is one liquid junction which connects the upper reference chamber to the lower reference chamber of the reference electrode. The lower reference chamber has a more chemically inert electrolyte solution (potassium nitrate) which leaks out of the second porous liquid junction to mix with the liquid to be measured.

4. The Teflon Junction reference combination electrode has the same glass electrode as the General Purpose electrode. The reference electrode has a silver chloride wire and has layers of porous teflon from the middle of the electrode to the glass bulb. The liquid junction is also made of teflon which encircles the bulb and stem of the measuring electrode.

**Choosing the Electrode**

1. The General Purpose pH electrodes are designed to work in most common applications where there is an aqueous solution containing at least 5% moisture and compounds which do not react with silver.
2. The Calomel reference electrode is designed to work in solutions containing proteins, organic material, tris buffers, low ion activity and heavy metals. These compounds have a reaction with silver causing the general purpose electrode to clog and give erroneous readings.

3. The Double Junction electrode is designed to work in the same application as the Calomel electrode as well as work at higher concentrations of problems materials. This if due to the presence of two reference junctions to filter out any potential contaminants to the reference electrode.

4. The Teflon Junction electrode is designed to be used in applications where the solution being measured can clog the reference junction of the normal electrode. Some solutions which fit this description are oils, foods, paints and pastes.

**Testing the pH Meter**

1. Connect the electrode to the pH meter, turn the meter on, then press the “mode” button until the display reads “pH”. Connect the ATC probe if applicable.

2. Rinse the electrode with DI water, dip in a pH 7.00 buffer. Verify the measured temperature of the buffer. Perform pH 7.00 calibration according to the meter's instructions.

If you cannot calibrate to pH 7.00 and you are not sure you have a good electrode, disconnect the electrode, place one end of a paper clip to the outside of the meters' BNC connector and the other end of the paper clip to the center connection hole of the BNC connector. This will short out the input to the meter and give it a 0.0mV signal, equivalent to pH 7.00. If you are not able to adjust to pH 7.00 with the input shorted out, there is a problem with the meter. The meter should be returned for servicing. If you can calibrate to pH 7.00 with the input shorted out, then your electrode is not working properly and requires reconditioning or replacement. See “Testing the pH Electrode”.

**Testing the pH Electrode**

1. Connect the electrode to the pH meter, turn the meter on and press the mode button until the display reads “pH”. Connect the ATC probe.

2. Rinse the electrode with DI water, then immerse in a 7.00pH buffer. Verify the temperature, then perform a pH 7.00 calibration according to the meter's instructions.

3. Press the mode button until the display is in the millivolt mode. Read the millivolt value. It should be within +/- 20 millivolts of 0.0 mv. If the mV reading is greater than +/- 20 mV the electrode needs reconditioning or replacement.

4. Press the mode button until you reach the pH mode, then remove the electrode from the 7.00pH buffer. Rinse the electrode with DI water then place the electrode in a 4.01 or a 10.00pH buffer. Perform a pH 10.00 or pH 4.01 calibration according to the meter's instructions.

5. Press the mode button to reach the millivolt mode, observing the millivolt reading. If the millivolt value is greater than +/- 12mv of +/- 177mv, the probe should be reconditioned or replaced.
The pH Scale

Figure 1: How pH relates to Acid and Base. Adding Acid tips the scale pointer to the left and the pH number gets smaller. Adding Base tips the scale to the right and the pH number gets larger. A pH number of 7.0 is neutral.

Figure 2: The relationship of pH values to relative acidities and alkalinitides of common chemicals and foods.
The pH Measurement ("Glass") Electrode

- COAX CABLE
- CAP
- BACK SEAL
- FOIL SHIELD
- OUTER BODY
- Ag/AgCl ELEMENT
- FILL SOLUTION, KCl BUFFERED TO 7.0 pH
- pH SENSITIVE GLASS MEMBRANE BULB

The pH Reference Electrode

- ELECTRICAL LEAD
- CAP
- BACK SEAL
- OUTER BODY
- Ag/AgCl ELEMENT
- ELECTROLYTE, KCl SATURATED WITH AgCl
- LIQUID JUNCTION
The Calomel Reference Electrode

- **Electrical Lead**
- **Cap**
- **Back Seal**
- **Outer Body**
- **KCL (Potassium Chloride) Element**
- **Mercuric Chloride (Hg/HgCl)**
- **Potassium Chloride (KCL) Electrolyte**
- **Liquid Junction: Porous Ceramic Ground Glass Porous Fiber Porous Teflon Wood**

The pH Double Junction Reference Electrode

- **Ag/AgCl Element**
- **Inner Chamber Electrolyte**
- **Inner Chamber Liquid Junction**
- **Outer Chamber Electrolyte**
- **Outer Chamber Liquid Junction**
The Combination pH Electrode

General Construction and Component Layout

- COAX CABLE
- BACK SEALS
- OUTER BODY
- FILL SOLUTION (pH 7.0), KCl
- Ag/AgCl ELEMENT
- REFERENCE Ag/AgCl ELEMENT
- REFERENCE ELECTROLYTE, KCl
- REFERENCE LIQUID JUNCTION (Peripheral)
- pH SENSITIVE GLASS MEMBRANE