

Chapter-3

pH Metry

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Introduction

A pH meter is a instrument that measures the hydrogen-ion movement in water-based suspensions, showing its acidity or alkalinity expressed as pH. It is also called a “potentiometric pH meter” because it measures the variation in electrical potential between a pH electrode and a reference electrode. In 1909, the concept of pH or "potential of hydrogen ion." was introduced by Sorensen to allow easier notation for the wide range of $[H^+]$ found in chemical systems. H^+ ion concentration means gm of hydrated ion present as H_3O^+ per litre of fluid denoted by cH or of OH^- ion activity by cOH . As example water contains 1/1000000 gm of H^+ ion in one litre which is expressed as 10^{-7} H^+ ion concentration.

The pH of a solution is the logarithm of hydrogen ion concentration with a negative sign.

$$pH = -\log [H^+] \quad (1)$$

The pH is 7 at 25.C which is neutral because water contains equal amount of H^+ and OH^- ions. Any solution having pH below 7 is acidic and above 7 is alkaline. Sorenson developed a scale based on the pH value and different concentration of H_3O^+ in a solution which is called Sorenson's pH scale.

PH SCALE

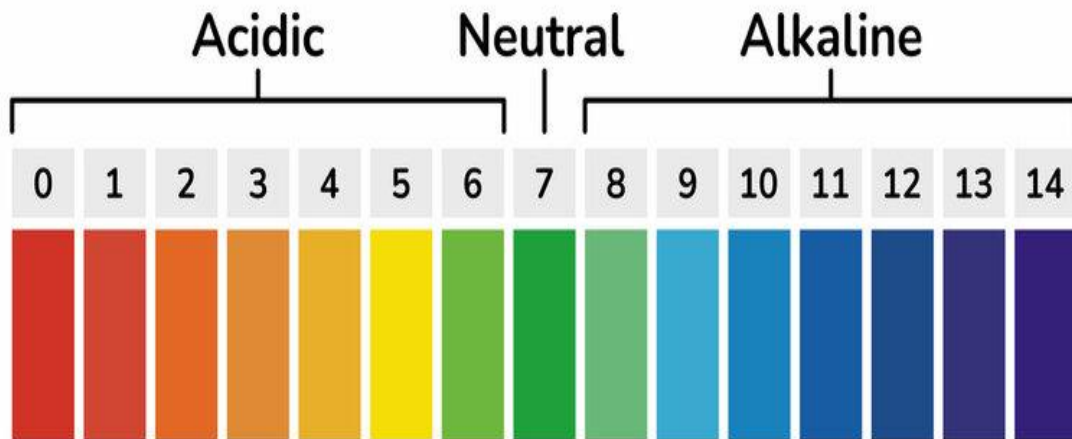


Figure 1: PH Scale

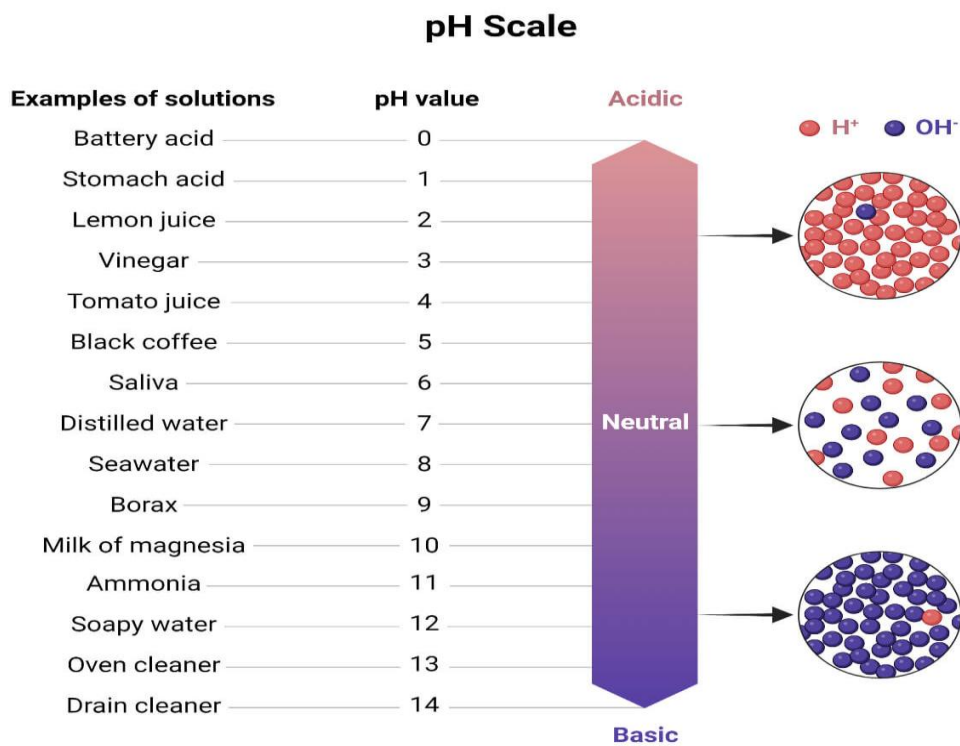


Figure 2: pH of Different Solutions

Determination of pH

Two methods are widely used for determination of pH:

- Electrometric method
- Potentiometric titration method
- Colorimetric method

Measuring pH using an Indicator

This category basically consist of two methods, one uses buffer solution to immerse indicator in the test liquid and compares its color to a standard color that correspond to a known PH. The alternate procedure entails preparing pH test paper that has been soaked in indicator, submerging the paper in test liquid, and comparing the color of the paper to the standard color. Although easy to use, this approach is subject to error. One cannot anticipate a high level of accuracy. A variety of errors can occur, such as:

- Test liquid errors caused by high concentration of salt.
- Test liquid error caused by variation in temperature
- Test liquid error caused by organic substances

Electrochemical Method

Errors resulting from dipping an electrode into water. Because of its solution pressure, it tends to dissolve during the metals atoms dissolution. They depart from the electrode with a negative charge due to their loosely bound valence electrons. Because there is now a negative charge on the electrode. Now that the positively charged metal ions have already entered solution, it draws them in. Perhaps a few of the positively charged metal ions will find their way back to the negatively charged electrode. Metal ions have a tendency to reattach themselves and atoms have a tendency to escape the metal. Eventually achieves balance and reaches equilibrium. There are some positively charged metal ions in solution at equilibrium, and the electrode's and the metal ions opposite charges cause a potential difference

Principle of pH Meter

The working principle of the pH meter depends on the ion exchange via the glass membrane from the sample solution to the inner solution (pH 7 buffer) of the glass electrode. In order to transmit electric signals to the pH meter and display the pH value of the solution, a pH meter is equipped with a pH probe.

An electrode for the sensor and reference electrode both are present in the pH probe. Saturated potassium chloride solution is placed in one, and a pH 7 buffer is placed in the other. The sensor electrode bulb comprises of a porous glass membrane coated with metal salts and silica.

Metal ion are replaced by hydrogen ions around the bulb when the probe is immersed in a sample solution to measure pH. The glass or sensor electrode and the sample solution both experiences some metal ion transfer. The reference electrode potential provide a steady voltage because of its minimal sensitivity or total insensitivity to pH fluctuations. This cause a potential difference or hydrogen ion activity which produces some electricity that is coaght by the silver wire. By contrasting the generated voltage with the reference electrode, the pH meter interprets the voltage of this electric flow as the pH value.

The concentration of hydrogen ions increases with increasing acidity of the solution, which cause increase in the voltage. This increased voltage decrease the pH measurement on the pH meter. In same manner, Similarly increase in the concentration of hydroxyl ions is caused by increasing alkalinity and reduces hydrogen ions, reduces the voltage and raises the pH reading in the pH meter.

Construction and Working

- 1. A High Input Impedance Meter:** This is the essential part that holds the microprocessor which processes displays measurements and small electrode voltages in pH units on display. pH of the solution can be readed by the microchip, calculates the measurement temperature, and translates the amplifier voltage value.
- 2. The Combined Electrode:** Where the actual measurement is made, it consist of two electrodes. The combination electrode is composed of two electrodes, a reference electrode and a measuring or sensor electrode, both of which are submerged in the same solution. A defined pH value can only be obtained if the reference electrode has a defined stable voltage that is independent of the measured solution. As indicator electrodes for pH measurement, a variety of electrodes that are reversible to hydrogen ions are employed. There includes the commonly used hydrogen electrodes, antimony, glass electrode and quinhydrone. Commonly calomel electrode is used as reference electrode.
- 3. Amplifier:** The measurement of pH value requires the use of an amplifier, sometimes referred as a voltage amplifier. In the same manner a thermometer improves calculations regarding temperature, the amplifier will increase the accuracy of the PH reading. This component will guarantee that the voltage

count is within the pH range of 0-14, allowing for an accurate measurement of the acidity, basicity and neutrality in a solution.

- 4. Thermometer Probe:** As pH is directly influenced by solution temperature, some pH meters have the ability to measure the temperature of the solution being sampled and incorporate that information into the meter reading. This feature is called as ATC or “Automatic Temperature Compensation”.

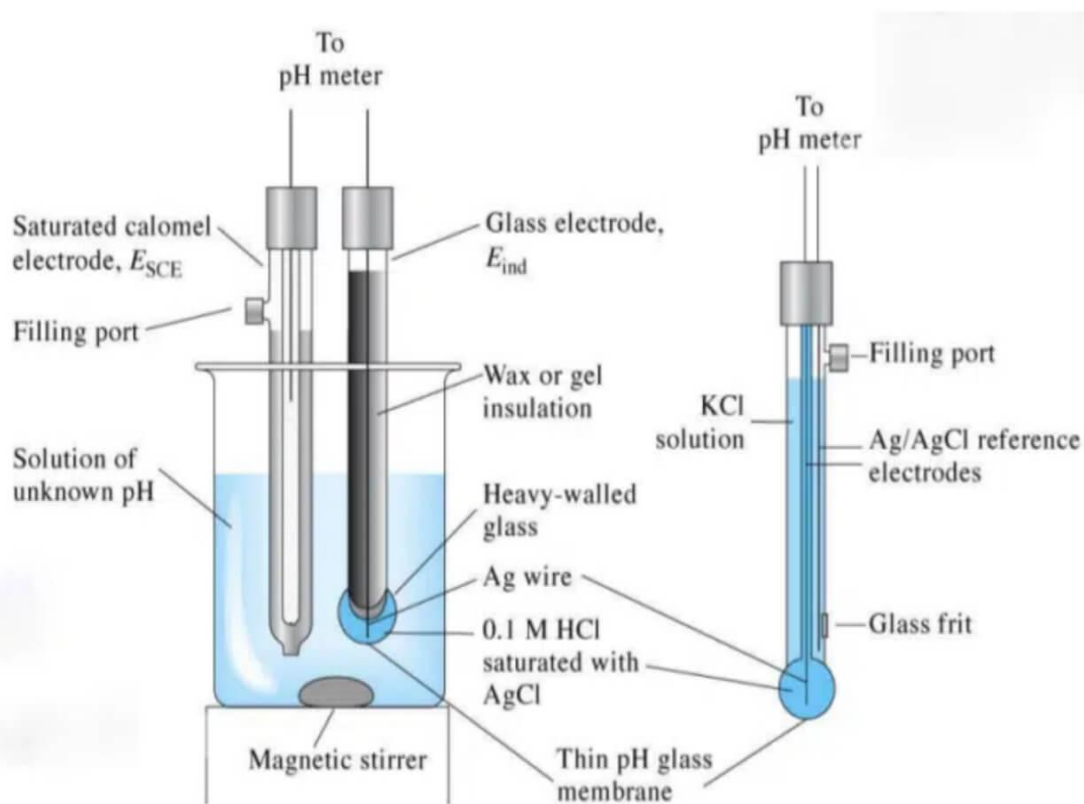
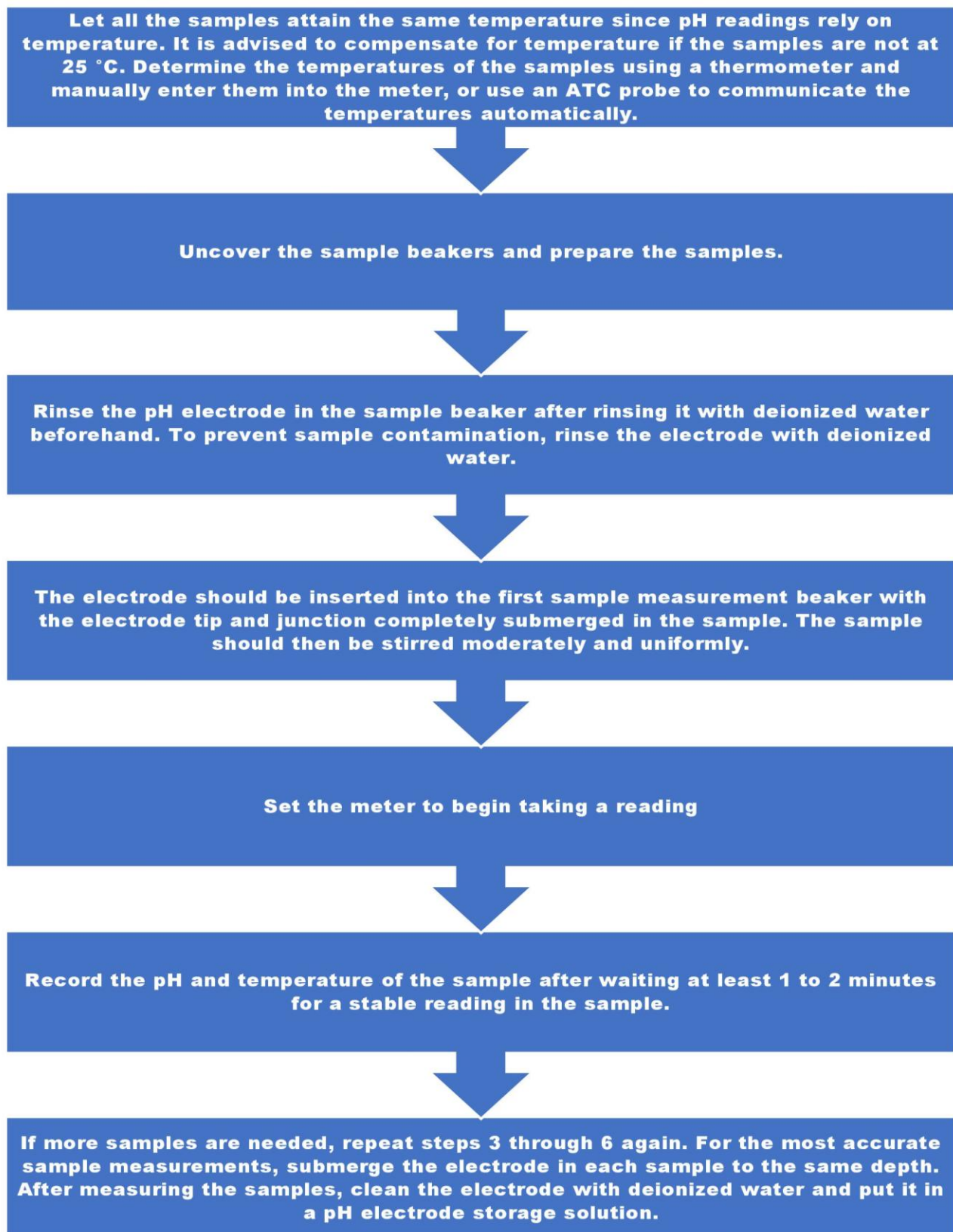


Figure 3: Working of pH Meter

pH Meter Operating Procedure



Factors Affecting pH Measurement

- 1. Glass Membrane:** Typically, the pH electrode is composed of glass. The pH readings can be considerably changed by coatings applied to the glass surface. A variety of coatings, such as pollutants, deposits that are poorly soluble, solids, biofilms, lime, or oils, can prevent the measured medium from accessing the glass surface. As a result, routine cleaning of the glass surface is necessary. But, this shouldn't be carried out "mechanically," as vigorous cleaning could harm the glass's surface. Thiourea solution, cleaning solutions containing tensile, or diluted acids should be used to accomplish this "chemically."
- 2. Diaphragms:** A diaphragm made of a Teflon ring, a tiny hole, and porous ceramic is present in the pH electrode. Although blockage by soluble compounds can result in low pH and increased resistance, this serves to prevent the leaching of electrolytes. This issue can be avoided by using the cartridge reference system.
- 3. Reference Electrolyte and Reference Electrode:** The reference electrode made of silver or silver chloride may corrode if electrode poisons are present in the measurement medium, which could alter the potential difference. By limiting the electrolyte's access to the reference electrode with a two-chamber electrode, this can be avoided
- 4. Measurement Medium:** Measuring medium Issues can also arise from the pH meter's medium. The measurement medium's electrical resistance may rise when deionized, distilled, or demineralized water is used, which could affect the pH readings. This problem can be fixed, though, by discharging a significant volume of potassium chloride into the solution via solid potassium chloride in the electrode.
- 5. Contacts:** Cables are typically used to connect the electrodes. Since different manufacturers produce different cables, incompatibilities between various pH meters from different manufacturers may occur. To stop moisture from entering, an O-ring can be inserted into the connection between the electrode and cable.
- 6. pH Connection Cable:** The instrument may be damaged by short circuits, which can lead to inaccurate pH readings. Therefore, the pH meter and all of its electrical connections should have elevated insulation resistance. The pH meter solely employs coaxial cables, and the connecting cables feature a semiconducting layer in addition to the copper shielding.

- 7. Effect of Temperature:** Temperature plays a significant role in pH measurement. This is due to the temperature-dependent nature of chemical reactions and pH values. Temperature has an impact on the voltage signal that a pH meter measures. Adding a temperature sensor to the pH meter is recommended in environments with fluctuating temperatures. Utilizing a temperature-corrected slope, the sensor calculates pH.
- 8. Effect of Moisture and Pressure:** The reference's glass material may be harmed by high pressures or sudden variations in pressure. Evaluating this problem can be aided by fitting the glass membrane with special fittings and choosing special electrodes. Also, the glass membrane may be impacted by drying out from a lack of moisture.
- 9. Mechanical Disruptions:** Particles in the medium may cause abrasions on the pH electrode's glass surface. This may shorten its life and cause the readings to change. Glass membranes with unique or flat surfaces have been created to lessen the effects of this issue. Moreover, shocks and vibrations that put stress on the materials can shorten their lifespan. This can be fixed by moving the installation location.
- 10. Electrical Disruptions:** The pH meter may lose its slope or signal due to electrical faults or short circuits. Checks should be made on all electrical components, including cables, installation, shielding, and grounding, both during and after installation.
- 11. Electrode Aging:** pH electrodes have a limited lifespan, and over time they can become less sensitive or drift in their readings.

Applications of pH Meter

- To assess the rainwater, swimming pools, and drinking water quality.
- To determine the kind of biological conditions by measuring the pH of biological fluids like blood, urine, etc.
- pH meter help in evaluation of soil in the agriculture industry. Major crops require an alkaline climate, hence a pH meter is necessary. They are also used to measure the pH of the soil, which will help to maximize soil yields and returns.
- pH meters are primarily used by the food industry.
- It is employed in the chemical industry to neutralize wastewater from the petrochemical, paper, steel, and pulp, pharmaceutical, and biotechnology sectors.
- It is employed to detergent manufacturing.

- To know pH of buffer solutions
- To maintain the pH of reaction conditions

Advantages

- pH Calibration is low-priced and robust
- Small size pH Meters are user friendly
- Accounts are reliable and specific

Disadvantages

- Heat affects the output readings
- pH Calibration utilizing glass electrodes need to be clean as deposition on the electrodes influences the readings
- Direct reading cannot be taken due to high electrical resistance potential, hence amplification of the signal becomes necessary