Chapter 2 : Electrochemical methods

Electrochemical analytical techniques are based on the measurement of electrical potential, current, or charge to determine an analyte's concentration or to evaluate its chemical reactivity. Collectively, this field of analytical chemistry is known as electrochemistry, as it originates from the study of electron transfer processes in oxidation–reduction reactions.

2.1 pH measurement

2.1.1. pH definition

The term pH is derived from a combination of "p" for the word power and "H" for the symbol of the element hydrogen. Together the meaning is the power of hydrogen. pH serves as a convenient way to compare the relative acidity or alkalinity of a solution at a given temperature. A pH of 7 describes a neutral solution because the activities of hydrogen and hydroxide ions are equal. When the pH is below 7, the solution is described as acidic because the activity of hydrogen ion is greater than that of hydroxide ion. A solution is more acidic as the hydrogen ion activity increases and the pH value decreases. Conversely, when the pH is above 7, the solution is described as basic (or alkaline) because the activity of hydroxide ion is greater than that of hydrogen ion.

2.1.2. pH measurement methods

There are two methods for measuring pH: colorimetric methods using indicator solutions or papers, and the more accurate electrochemical methods using electrodes and a millivoltmeter (pH meter).

a. Colorimetric methods

Determination of pH using the color of acid–base indicators is a very simple technique that can be carried out rapidly and reproducibly. Approximate pH values can be obtained very quickly using pH papers. Under optimum conditions, accurate values of pH can be obtained by colorimetric methods. No doubt, these methods will be used for many years to come, but must become less favored with the advent of portable, cheap, easy-to-use electrochemical pH meters. (See Spectroscopy: Visible Spectroscopy and Colorimetry.)

Color change of acid–base indicators Indicators are natural or artificial dyestuffs that are weak acids or bases (acids and bases that are only partially dissociated) and have different colors in their acidic and basic forms.0028

- **Colorimetric Measurements of pH**

Indicator papers For approximate determination of pH values, indicator papers may be used. Of particular value are 'nonbleeding' indicator papers. These contain dyestuffs strongly bound to the cellulose, so that the dye does not bleed into the test solution. These indicator papers are available, covering very narrow pH ranges, enabling moderately accurate pH values to be obtained very cheaply, conveniently, and quickly.

- **Comparison method**

This is carried out by adding similar quantities of an indicator to the test solution and a reference solution, and if the two solutions have the same color, they are assumed to have the same pH. The accuracy of the method, therefore, depends on the accuracy of the pH of the reference solution.

The indicator used must have a color at the pH of the test solution intermediate between the acidic and basic forms. The approximate pH of the solution is first detemined using a 'universal,' or full-range, indicator, when an appropriate indicator for the measurement can be chosen. A quantity of the test solution is measured into a tube and a measured amount of indicator added. Tubes of buffer solutions covering the pH range of the indicator are treated in the same way. The colors of the tubes are viewed through the length of the tube against a white background. The accuracy of the method will depend on the differences of pH of the buffer solutions. These are typically 0.2, and the pH of the unknown solution can then be measured to within +0.1.

- **The Lovibond Comparator**

The need to use buffer solutions is eliminated by using a Lovibond 2000 comparator, in which the color of the test solution is compared with colored glasses. Standard colored glass rings are fitted into a disk that can be rotated and the colored glasses compared with the test solution. For accurate results, the sample solution and discs must be viewed against north daylight or in white light.

Table-1 : Indicators, pH ranges and color changes.

Sl. No	Indicator	Ideal range (acid) pH		Color	
				Acid	base
1	Thymol Blue	1.2	2.8	Red	Blue
2	Congo Red	3.0	5.0	Blue	Red
3	Methyl Orange	3.0	6.3	Red	Yellow
4	Bromocresol Green	4.0	5.6	Yellow	Blue
5	Methyl Red	4.2	6.2	Pink	Yellow
6	Bromothymol Blue	6.0	7.6	Yellow	Blue
7	Phenol Red	6.8	8.2	Yellow	Red
8	Phenolphthalein	8.0	10	Colorless	Pink
9	Thymolthalein	8.8	10.5	Colorless	Blue
10	Neutral red	6.8	8.0	Red	yellow

b. Electrochemical Method

pH is measured electrochemically by determining the electromotive force (emf) of a cell consisting of a pH-sensitive electrode and a reference electrode. The hydrogen electrode was originally used, but after Cremer's discovery in 1906 that the potential across a glass membrane depends on hydrogen ion concentration, the glass electrode became the standard pH electrode. A glass electrode consists of a thin glass bulb containing a solution of constant pH (usually hydrochloric acid or a phosphate buffer with potassium chloride) and an internal silver/silver chloride electrode. The pH response arises from the exchange of hydrogen ions across the glass membrane, forming silanol (Si–OH) layers. Special sodium or lithium glass is used for this purpose.

To maintain accuracy, the pH-sensitive tip must be kept hydrated and is stored in a pH 7 buffer containing potassium chloride. Glass electrodes show a good linear response over the pH range 2–9, and up to pH 14 under low salt conditions.

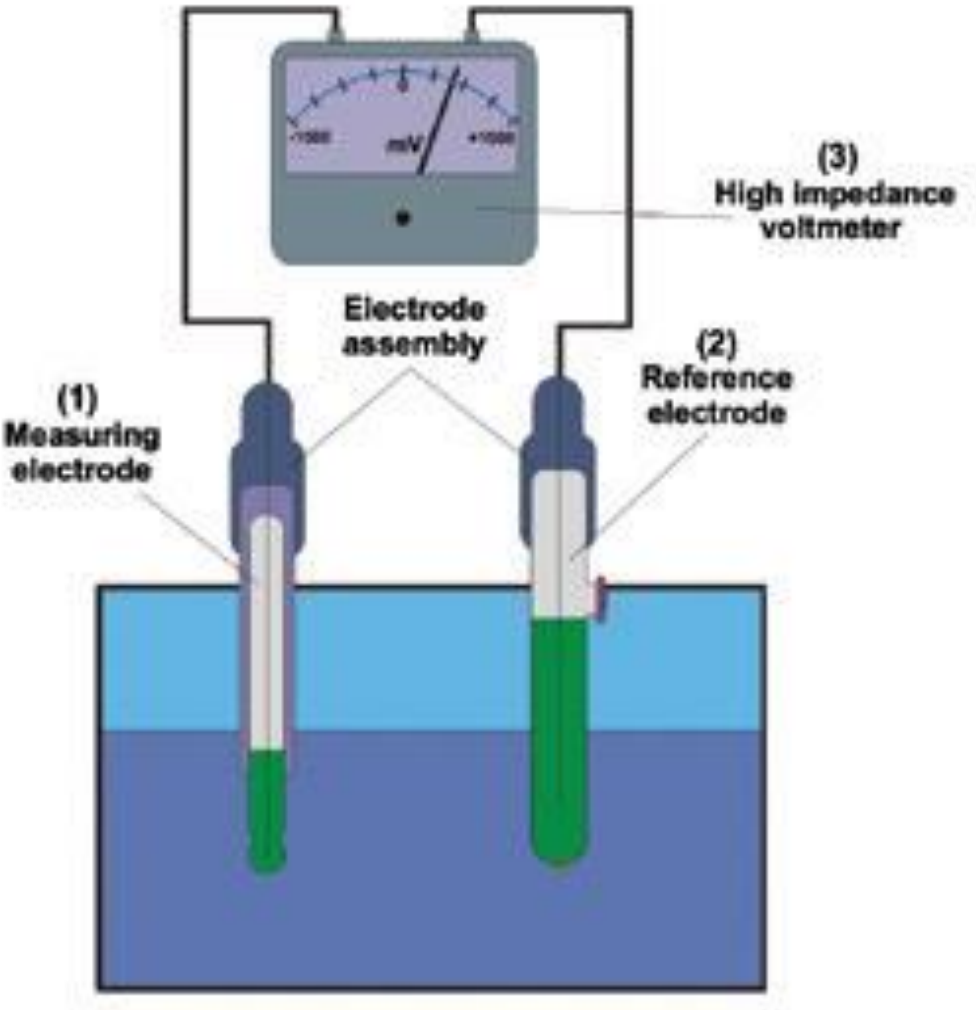

Figure 1: The pH measuring system.

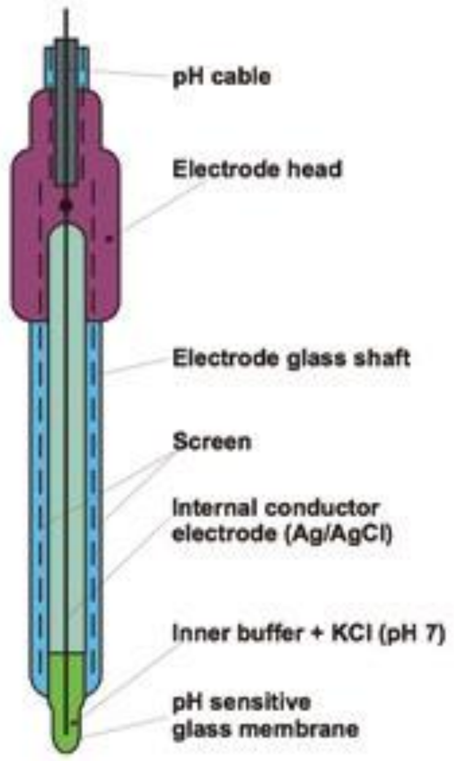

Figure 2 : The construction of a glass electrode.

1.2.3. Applications of pH Measurement

-Biomedical Engineering

-pH monitoring is valuable in wound assessment, indicating healing progress and bacterial infection.

-Biomedical pH meters use glass electrodes, reference electrodes, and CO_2-sensitive systems with a linear pH–emf relationship.

-Advanced pH sensors include fluorescent nano-micellar probes for cancer diagnostics and PMMA optical fibre sensors for wound monitoring.

-Industrial Applications

-pH measurement is essential for controlling chemical reactions and ensuring product quality.

-Widely applied in chemical, agricultural, fishery, water management, and public sectors.

-Pharmaceutical Industry

-pH influences drug solubility, stability, absorption, and release rate.

-Proper pH reduces tissue irritation in injectables and improves drug effectiveness.

-Many drugs require specific pH conditions (e.g., aspirin dissolves in acidic stomach pH).

-Drug delivery systems must maintain near-neutral pH for tissue compatibility.

-Food and Beverage Industry

-pH affects food safety, quality, taste, texture, and shelf life.

-High-pressure food processing increases acidity.

-Proper pH prevents bacterial growth (e.g., salami pH < 5.3).

-pH indicates meat quality and animal welfare.

-Electricity and Electrochemistry

-pH control is vital in electroplating, etching, anodizing, and battery manufacturing.

-Poor pH regulation leads to surface defects, poor adhesion, and reduced durability.

2.2. Conductivity measurement

2.2.1. Definition

Conductivity is the ability of a material to permit an electric current. In solutions, the current is carried by cations and anions. Electrical conductance is governed by several factors, namely, concentration, mobility of ions, valence of ions, and temperature. Conductivity SI units are ($\Omega^{-1} . m^{-1}$), otherwise called "Siemens" ($S. m^{-1}$). Solutions of ionic salts or of compounds that ionize in solution are often called "electrolytes". Ions formed in electrolytes carry the electric current in solution. Electrolytes might be strong or weak depending on the nature of cations and anions that make them up. Strong electrolytes dissociate completely in water. Upon imposing an electric field, ions of strong electrolyte can basically travel freely in aqueous solutions.

A conductivity meter measures the amount of electric current or conductance in a solution. A conductivity system measures conductance by means of electronics connected to a sensor immersed in a solution.

2.2.2. Principle of conductivity meter

The common laboratory conductivity meters employ a potentiometric method and four electrodes. Often the electrodes are cylindrical and arranged parallel. The electrodes current is applied to outer pair of the electrodes. Conductivity could in principle be determined using the distance between the electrodes and their surface area .Generally for accuracy a calibration is employed using electrodes of well- known conductivity. Conductivity is the ability of a material to conduct electric current. The principle by which instruments measure conductivity is simple -two plates are placed in the sample, a potential is applied across the plates (normally a sine wave voltage), and the current that passes through the solution is measured.

2.2.3. Types of conductivity meter

a. Contacting type conductivity meter

A contacting type conductivity meter measures the electrical conductivity of a solution using metal electrodes, typically stainless steel or titanium, placed in direct contact with the electrolyte. The analyzer applies an alternating voltage to create an electric field that causes dissolved ions to move, generating an ionic current proportional to the ion concentration. Conductivity reflects the presence and amount of charged particles in a solution and is influenced by ion type, ion concentration, temperature, and sensor geometry. The measured conductance is corrected using a factory-determined cell constant to obtain accurate conductivity values. Some sensors use two electrodes, which are suitable for high-purity water applications in semiconductor, power generation, and pharmaceutical industries, while four-electrode sensors improve accuracy by separating current injection and voltage measurement. Conductivity meters are widely used to assess water quality, evaluate total dissolved solids (TDS), and monitor the condition of natural and industrial water systems.

Figure 3 : Contacting type conductivity meter.

b. Inductive conductivity meter

An inductive conductivity meter, also known as a toroidal or electrodeless conductivity sensor, measures the conductivity of a solution without direct electrode contact. It consists of two wire-wound toroidal coils encased in a corrosion-resistant plastic or polymer body: a drive coil and a receive coil. When an alternating voltage is applied to the drive coil, it generates a magnetic field that induces a voltage in the surrounding conductive liquid, causing ions to move and produce an ionic current proportional to the solution's conductance. This current, in turn, induces a signal in the receive coil. The measurement is influenced by the cell constant and the conductivity of the solution. Inductive sensors are particularly suitable for corrosive, dirty, or high-conductivity solutions because they avoid direct electrode contact and reduce fouling or polarization effects.

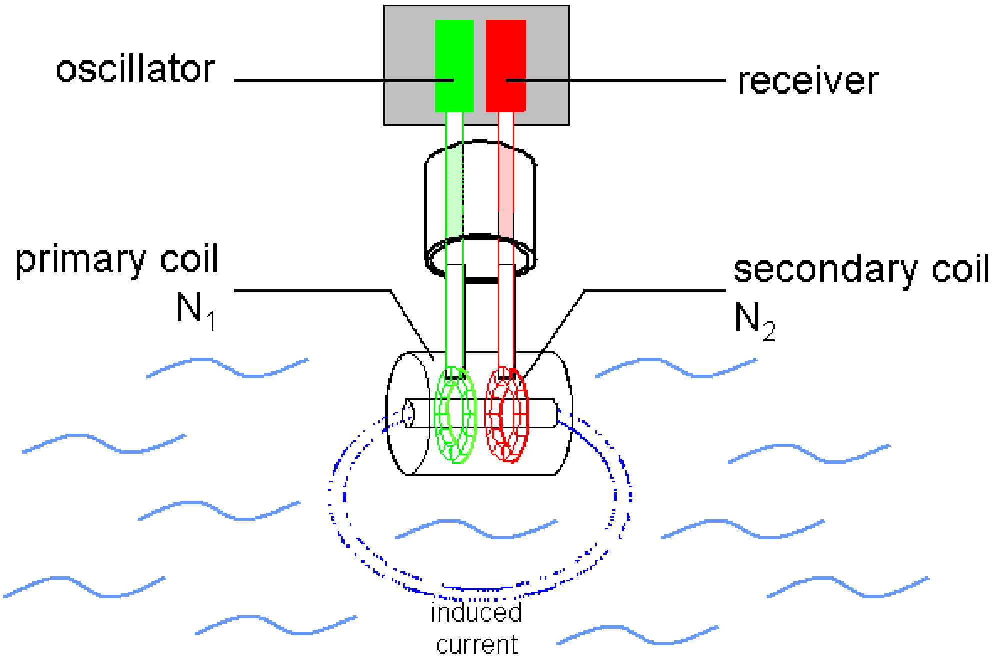

Figure 3 : Inductive conductivity meter.

2.2.4. Applications

-Monitoring water quality in public water supplies

-Quality control in hospitals

-Boiler water monitoring in power plants and industrial systems

-Water quality control in industries such as brewing

-Estimation of total dissolved solids (TDS) when solution composition is known

-Assessment of drinking water purity

-Control of freshwater and saltwater aquarium conditions

-Maintenance of appropriate salinity for fish, snails, and shrimp breeding