Instrumental methods of analysis

Background:
- **Analytical Chemistry**: The Science of Chemical Measurements.
- **Analyte**: The compound or chemical species to be measured, separated or studied
- **Types of analytical methods**:
  1. **Classical Methods** (Earliest Techniques)
     a.) Separations: precipitation, extraction, distillation
     b.) Qualitative: boiling points, melting points, refractive index, color, odor, solubilities
     c.) Quantitative: titrations, gravimetric analysis
  2. **Instrumental Methods** (~post-1930’s)
     a.) Separations: chromatography, electrophoresis, etc.
     b.) Qualitative or Quantitative: spectroscopy, electrochemical methods, mass spectrometry, NMR, radiochemical methods, etc.

**Qualitative** instrumental analysis is that measured property indicates presence of analyte in matrix

**Quantitative** instrumental analysis is that magnitude of measured property is proportional to concentration of analyte in matrix
**CHOOSING AN ANALYTICAL METHOD**

1. What are the advantages or disadvantages of the technique versus other methods?
2. How reproducible and accurate is the technique?
3. How much or how little sample is required?
4. How much or how little analyte can be detected?
5. What types of samples can the method be used with?
6. Will other components of the sample cause interference?
7. Other factors: speed, convenience, cost, availability, skill required.

**Types of Instrumental Methods: Example methods**

<table>
<thead>
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<th>Type</th>
<th>Example Methods</th>
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<td>Radiation emission</td>
<td>Emission spectroscopy, fluorescence, phosphorescence, luminescence</td>
</tr>
<tr>
<td>Radiation absorption</td>
<td>Absorption spectroscopy, photometry, spectrophotometry, NMR</td>
</tr>
<tr>
<td>Electrical potential</td>
<td>Potentiometry</td>
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<tr>
<td>Electrical charge</td>
<td>Coulometry</td>
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<tr>
<td>Electrical current</td>
<td>Voltammetry - amperometry, polarography</td>
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<tr>
<td>Electrical resistance</td>
<td>Conductometry</td>
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<tr>
<td>Mass-to-charge ratio</td>
<td>Mass spectrometry</td>
</tr>
</tbody>
</table>

![Diagram of Energy Stimulus, Analyte in Matrix, Analytical Response, Data](image-url)
**Example:**  
**Spectrophotometry**

**Instrument:** spectrophotometer  
**Stimulus:** monochromatic light energy  
**Analytical response:** light absorption  
**Transducer:** photocell  
**Data:** electrical current  
**Data processor:** current meter  
**Readout:** meter scale

**Detector** (general): device that indicates change in environment  
**Transducer** (specific): device that converts non-electrical to electrical data  
**Sensor** (specific): device that converts chemical to electrical data
Part 1

Electrochemical methods of analysis

Introduction

Electrochemistry is the relationship between electrical properties and chemical reactions. The electrical properties most commonly measured involve voltage, current or resistance or combination of these. The measurements are carried out by the use of certain instruments, thus, the methods are also denoted by instrumental methods.

Classification of electrochemical methods

1. POTENTIOMETRY

Measure electrical potential developed by an electrode in an electrolyte solution at zero current flow. Use NERNST EQUATION relating potential to concentration of some ion in solution.
2. **VOLTAMMETRY**

Determine concentration of ion in dilute solutions from current flow as a function of voltage when **POLARIZATION** of ion occurs around the electrode. POLARIZATION = depletion of concentration caused by electrolysis. If using a dropping mercury electrode, method is termed POLAROGRAPHY.

3. **CONDUCTIMETRY**

Measure conductance of a solution, using **INERT ELECTRODES, ALTERNATING CURRENT, AND AN ELECTRICAL NULL CIRCUIT** - thereby ensure no net current flow and no electrolysis. The concentration of ions in the solution is estimated from the conductance.

**NOTE:**

*Methods 1 and 3*, **NO ELECTROLYSIS** of solution. Sample recoverable, unaltered by analysis.

*Methods 2* must cause **ELECTROLYSIS OF THE SAMPLE**.
1. Potentiometry

Definitions:
An electro-analytical technique based on the measurement of the electromotive force (e.m.f) of an electrochemical cell consists of a measuring (indicator) and reference electrodes.

General Principles

<table>
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<tr>
<th>Reference electrode</th>
<th>salt bridge</th>
<th>analyte solution</th>
<th>indicator electrode</th>
</tr>
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<tbody>
<tr>
<td>$E_{\text{ref}}$</td>
<td>$E_j$</td>
<td>$E_{\text{ind}}$</td>
<td></td>
</tr>
</tbody>
</table>

$E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}} + E_j$

Reference cell:
A half-cell having a known electrode potential

Indicator electrode:
Has a potential that varies with variations in the concentration of an analyte

Electrochemical Cell:

1.) Basic Set-up:
a) Two electrodes
b) electrolytes solution
c) external connection between electrodes (wire)
d) Internal connection via contact with a common solution or by different solutions connected by a salt bridge.

**Salt bridge** – acts to isolate two halves of electrochemical cell while allowing migration of ions and current flow.
- usually consists of a tube filled with potassium chloride
- Separate species to prevent direct chemical reactions.

**Electrochemical cell**
It is composed of a container or two containing a pair of electrodes (metallic or otherwise) in contact with an electrolyte solutions. These electrodes are anode at which the oxidation occurs and cathode at which reduction occurs. A conductive junction is used to connect the two electrolyte solutions in the two containers of the cell.

**Electrochemical cells can be classified into:**

1. **Galvanic or voltaic cell**
   An electrochemical cell which spontaneously produces current (or energy) when the electrodes are connected externally by a conducting wire
   
   **e.g. Daniell cell**
   For the galvanic cell shown in the following figure the copper electrode is the cathode. The cathode half reaction is

   \[
   \text{Cu}^{2+} + 2e^- = \text{Cu}^0
   \]
The zinc electrode is the anode. The anodic reaction is:

\[ \text{Zn}^0 = \text{Zn}^{2+} + 2e^- \]

Electrons are supplied from the zinc electrode to the external circuit to the copper electrode and copper deposited on the electrode surface. The two electrodes solutions are connected by a junction which allows transference of charges without mixing of the two electrodes solutions

The potential difference i.e. electro-motive force of the obtained cell is

\[ E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \]

Where \( E_{\text{cathode}} \) and \( E_{\text{anode}} \) are the electrode potential of the cathode and anode. E.g. Daniell cell \( E_{\text{cell}} = E_{\text{Cu}} - E_{\text{Zn}} \)

Schematic representation of cells:

A cell such a Daniel cell can be represented as follows:

\[ \text{Zn} / \text{Zn}^{2+} (C_1) \ || \ | \ \text{Cu}^{2+} (C_2) / \text{Cu} \]
2. Electrolytic cell

In this cell an electrical energy is forced from outer external source to the cell and cause chemical changes of the electrolyte solutions i.e. electrical energy is converted to chemical energy. Electrolysis occurs, e.g. plating with silver or platinum.

Potentiometry

It is a method of analysis in which we determine the concentration of an ion or substance by measuring the potential developed when a sensitive electrode is immersed in the solution of the species to be determined.

\[ M^0 = M^{n+} + ne \]

Applying Nernest equation.

\[ E_{25} = E_0 - \frac{0.059}{n} \log \frac{1}{[M^{n+}]} \]

Since \( E_0 \) for the given electrode is constant so, \( E_{25} \) will vary by change of \([M^{n+}]\).
Thus, by measuring $E_{25}$ one can calculate the concentration of the ion. e.g

$$E_{Ag/Ag^+}^{25} = E_{Ag/Ag^+}^0 - 0.059 \log \frac{1}{[Ag^+]^0}$$

The electrode used to determine $[M^{n+}]$ is known by the indicator electrode as it indicates $M^{n+}$ concentration.

The potential of the indicator electrode cannot be measured alone, it must be connected with another electrode with known constant potential which is known by reference electrode. Both the two electrodes form the two half-cells of electrochemical cell, the electromotive force [e.m.f.] of which is the algebraic difference of the two electrode potentials [cathode – anode].

Since the reference electrode potential is constant the change in e.m.f. of the cell is due to the change of the indicator electrode potential which in turns is due to the change in the concentration of the ion to be determined.

To measure e.m.f. developed between the reference and indicator electrodes we must have an electrical device which is known by potentiometer.
A) Reference electrode

It must:
1. Have a constant potential which will not change with the passage of small current.
2. Its potential must be definite and known in case of direct potentiometry.

To express any electrode we have to mention:
a- Redox reaction at the electrode surface.
b- Half-cell and Nernst equation.
c- Sketch of its design.
d- Any necessary conditions for its preparation.
e- Any necessary precautions for its use.

1. Normal Hydrogen Electrode: (N.H.E.)
It’s a primary reference electrode. Its potential is considered to be zero.

✓ Electrode reaction:
\[ 2H^+ + 2e \overset{\text{Pt, balck}}{\longrightarrow} H_2 \]

✓ half cell: \( \text{pt, } H_2 / H^+ (1N) \)

✓ Design: \[ E_0 = \text{zero} \]
1. It is difficult to be used and to keep H₂ gas at one atmosphere during all determinations.
2. It needs periodical re-plating of Pt. Sheet with Pt. Black. Thus for these limitation we use secondary reference electrodes.

3. Calomel electrode (secondary reference electrode)

✓ Half reaction:

\[
\begin{align*}
Hg_2^{2+} + 2e & \iff 2Hg^0 \\
Hg_2Cl_2 + 2e & \iff 2Cl^- + 2Hg^0
\end{align*}
\]

✓ Half cell:

Hg/Hg₂Cl₂, saturated KCl, 0.1N or 1N KCl

✓ The Nernst equation for the electrode: The potential of the electrode depends on the chloride ion concentration obtained from potassium chloride in the solution. This effect is illustrated as follows:

\[
E_{25} = E^0_{Hg/Hg} + \frac{0.059}{2} \log \frac{1}{[Hg^{2+}]}^2
\]
The \( \text{Hg}_2^{2+} \) found is that produced from the ionization of the very small amount of the sparingly soluble \( \text{Hg}_2\text{Cl}_2 \):

\[
\text{Hg}_2\text{Cl}_2 \rightleftharpoons 2 \text{Hg}^{2+} + 2\text{Cl}^{-}
\]

\[
\text{Sp}_{\text{Hg}_2\text{Cl}_2} = [\text{Hg}_2^{2+}]^2 [\text{Cl}^{-}]^2
\]

\[
[Hg_2^{2+}]^2 = \frac{\text{Sp}_{\text{Hg}_2\text{Cl}_2}}{[\text{Cl}^{-}]^2}
\]

\[
E^{25}_{\text{Hg/Hg}_2\text{Cl}_2} = E^\circ - \frac{0.059}{2} \log \frac{[\text{Cl}^{-}]^2}{\text{Sp}_{\text{Hg}_2\text{Cl}_2}}
\]

Since \( \text{Sp}_{\text{Hg}_2\text{Cl}_2} (K_{sp} = 1.8 \times 10^{-18}) \) is constant value and the chloride ion concentration with very little approximation is that the same as KCl concentration so as the concentration of KCl increases the concentration of \( \text{Hg}_2^{2+} \) decrease and accordingly the electrode potential decreases. Calomel electrode prepared in saturated KCl, 1M KCl and 0.1M KCl has potentials of:

<table>
<thead>
<tr>
<th>KCl</th>
<th>E volt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated</td>
<td>0.241</td>
</tr>
<tr>
<td>1M</td>
<td>0.280</td>
</tr>
<tr>
<td>0.1 M</td>
<td>0.334</td>
</tr>
</tbody>
</table>

However, once it is prepared in either one of these solutions it has a definite constant potential.

3. \( \text{Ag/AgCl, saturated KCl electrode:} \)

It is a secondary reference electrode, which has a constant definite potential:
✓ **Half reaction:**

\[
\text{AgCl}(s) + e^{-} \rightleftharpoons \text{Ag}(s) + \text{Cl}^{-}
\]

✓ **half cell**

Ag/AgCl, saturated KCl || or 1 N KCl || or 0.1 N KCl ||

✓ **design**

✓ **The Nernest equation for the electrode:** the potential of the reaction depends on the chloride ion concentration:

\[
E_{\text{Ag/Ag}^+} = E^0 - 0.059 \log \frac{1}{[\text{Ag}^+]}
\]

Because the concentration of Ag\(^+\) obtained from the ionization of the very small amount of AgCl dissolved from the sparingly soluble AgCl:

\[
\text{Sp}_{\text{AgCl}} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{Cl}^-]}
\]

\text{Sp}_{\text{AgCl}} is a constant value the chloride ion concentration is that of potassium chloride [KCl] so, as KCl concentration increases the potential of the electrode decreases. It is prepared in saturated KCl, 0.1N or 1N KCl. However, in either of these solutions it has a constant potential.
Disadvantage of silver-silver chloride electrode

1. It is more difficult to prepare than SCE.
2. AgCl in the electrode has large solubility in saturated KCl

Advantage of Ag/AgCl electrodes over SCE.

1. It has better thermal stability.
2. Less toxicity and environmental problems with consequent cleanup and disposal difficulties.

B- Indicator electrodes

An indicator electrode is that which it’s potential is sensitive to the concentration of one of the products of reaction. In potential changes rapidly with the change of concentration of a particular ion.
It must be:
(a) Give a rapid response and
(b) Its response must be reproducible.

Now, when it is connected with a reference electrode with constant potential the change in e.m.f. of the cell reflects the change of the ion under examination.
These electrodes are classified into two classes
1. Metallic electrodes where the redox reaction takes place at the electrode surface.
2. **Membrane (specific or ion selective) electrodes:** where charge exchange takes place at a specific surfaces and as a result a potential is developed.

### Metallic indicator electrodes

1. **First-order electrodes for cations:**
   A first order electrode is comprised of a metal immersed in a solution of its ions, such as silver wire dipping into a silver nitrate solution. e.g. in determination of Ag⁺ a rode or wire of silver metal is the indicator electrode, it is potential is:

   \[
   E^{25}_{Ag/Ag^+} = E^0_{Ag/Ag^+} - 0.059 \log \frac{1}{[Ag^+]}
   \]

   \[
   Ag^+ + e = Ag(s) \quad E^0 = + 0.800V
   \]

   It is used for determination of Ag⁺ with Cl⁻, Br⁻ and CN⁻.

2. **Second order electrodes for anions**
   A metal electrode can sometimes be indirectly responsive to the concentration of an anion that forms a precipitate or complex ion with cations of the metal.
Ex. Silver electrode

The potential of a silver electrode will accurately reflect the concentration of iodide ion in a solution that is saturated with silver iodide.

\[
\text{AgI(s)} + e = \text{Ag(s)} + \text{I}^- \quad E^o = -0.151 \text{V}
\]

\[
E = -0.151 - (0.05916/1) \log [\text{I}^-]
\]

\[
= -0.151 + (0.05916/1)pI
\]

3. Inert electrodes

Chemically inert conductors such as gold, platinum, or carbon that do not participate, directly, in the redox process are called inert electrodes. The potential developed at an inert electrode depends on the nature and concentration of the various redox reagents in the solution.

\[
\text{Ag(s)} \mid \text{AgCl(sat’’d), KCl(xM) \mid \mid Fe}^{2+},\text{Fe}^{3+} \mid \mid \text{Pt}
\]

\[
\text{Fe}^{3+} + e = \text{Fe}^{2+} \quad E^o = +0.770 \text{V}
\]

\[
E_{\text{cell}} = E_{\text{indicator}} - E_{\text{reference}}
\]

\[
= \{0.770 - (0.05916/1) \log \left[\text{Fe}^{2+}\right]/\left[\text{Fe}^{3+}\right]\} - \{0.222 - (0.05916/1) \log [\text{Cl}^-]\}
\]
Membrane indicator electrodes

The potential developed at this type of electrode results from an unequal charge buildup at opposing surface of a special membrane. The charge at each surface is governed by the position of an equilibrium involving analyte ions, which, in turn, depends on the concentration of those ions in the solution.

1. Glass electrodes for pH-measurements:

This is the most used one for measuring the pH. It is one of the ion selective electrodes, which is specific for hydrogen ion. In this type of electrode the membrane consists of a thin envelope of soft glass sealed into the end of a hard-glass tube. The tube is filled with a dilute solution of HCl in which a silver wire is immersed thus forming a silver-silver chloride reference
The acid also provides a solution of hydrogen ions of constant activity “a”.

This electrode can be represented by the half-cell:

\[ \text{Ag(s)} \mid \text{AgCl(sat’d), Cl}^-(\text{inside}), \text{H}^+(\text{inside}) \mid \text{glass membrane} \mid \text{H}^+(\text{outside}) \]

\[ E = E^\circ - (0.05916/1) \log [\text{Cl}^-] + (0.05916/1) \log ([\text{H}^+(\text{outside})]/[\text{H}^+(\text{inside})]) \]

\[ E = Q + (0.05916/1) \log [\text{H}^+(\text{outside})] \]
Theory of operation
When a thin membrane of glass of special composition separates two solutions of different hydrogen ion concentration a potential is developed on this membrane depending on the concentration of hydrogen ion (more accurately on its activity in the two solution.)

Composition of glass membranes
70% SiO$_2$ 30% CaO, BaO, Li$_2$O, Na$_2$O, and/or Al$_2$O$_3$

Ion exchange process at glass membrane-solution interface:

\[
\text{SiO}^-\text{Na}^+ \text{(solid)} + \text{H}^+ \text{(solution)} \leftrightarrow \text{SiO}^-\text{H}^+ \text{(solid)} + \text{Na}^+ \text{(solution)}
\]

This potential, due to change, i.e. ion exchange that takes place between H$^+$ and one of the component ion of the glass matrix H$^+$, is exchanged in the form of H$_3$O$^+$ thus hydration of the membrane is necessary. Changes will be concentrated on
both surfaces at different concentration depending on the different H⁺ activities in the two solutions. As result of this change imbalance a potential is developed. It is given by the following equation:

\[ E = K + 0.059 \left( \text{pH}_1 - \text{pH}_2 \right) \]

- **K** = constant known by the asymmetry potential.
- **\( \text{pH}_1 \)** = pH of the internal solution 1.
- **\( \text{pH}_2 \)** = pH of the external solution 2.

The final equation is:

\[ E = K - 0.059 \text{pH} \]

Where **K** is a constant formed of four components:

1. Asymmetry potential
2. E of the 2 reference electrodes
3. pH of the internal solution
4. Liquid junction potential

**Salt bridges and liquid junction potential:**

Connection between two electrodes is made by a junction which allows transference of charges without mixing of the two electrodes solutions. This is done by the use of salt bridge which may be in the form of a bend or inverted U shape tube being filled with an agar gel prepared in saturated potassium chloride (KCl) or potassium nitrate (KNO₃) solution. The bridge may be in the design of the electrode itself as a wick saturated with KCl or disc filled with KCl. The bridge has two boundaries one between it and the solution of the cathode and the other with that of the anode solution. A potential is developed at both
boundaries of the junction, which is known by liquid junction potential. It is due to the difference in rates of migration of both anions and cations of the bridge salt and electrolytes in the electrodes solutions. This difference results in unequal charge distribution at the boundaries thus producing a potential.

To reduce the liquid junction potential to only few millivolts one has to:

1. Use a sat for preparation of the junction which its cation and anion have very near mobilities, so that they move by the same rate e.g. KCl and KNO₃. (K⁺ =74, Cl⁻ = 73 and NO₃⁻ = 76)
2. Use high concentration of the salt for preparation of the bridge, to reduce the effect of difference in rates of migration of other ions in the electrode solutions.

**Advantages of glass electrode:** It can be used in presence of oxidizing, reducing, complexing and catalytic poisonous substances. Also in reactions involving volatile constituents' noble metals....

**Disadvantage:**
1. Delicate, it can’t be used in presence of dehydrating agent e.g. conc. H₂SO₄, ethyl alcohol....
2. Interference from Na⁺ occurs above pH 12 i.e. Na⁺ exchange together with H⁺ above pH 12 and higher results are obtained.
3. It takes certain time to come to equilibrium due to resistance of glass to electricity.

2. Combination electrodes
A typical modern pH probe is a combination electrode, which combines both the glass and reference electrodes into one body. The combination electrode consists of the following parts:
1. a sensing part of electrode, a bulb made from a specific glass
2. sometimes the electrode contains a small amount of AgCl precipitate inside the glass electrode
3. internal solution, 0.1 M HCl
4. internal electrode, usually silver chloride electrode or calomel electrode
5. Body of electrode, made from non-conductive glass or plastics.
6. reference electrode, usually the same type as 4
7. Junction with studied solution, usually made from ceramics or capillary with asbestos or quartz fiber.
The pH electrode is best thought of as a tube within a tube. The inside most tube (the inner tube) contains an unchanging saturated KCl and a 0.1 M HCl solution. Both the inner tube and the outer tube contain a reference solution but only the outer tube has contact with the solution on the outside of the pH probe by way of a porous plug that serves as a salt bridge

2. **Hydrogen electrode:**

- **Electrode reaction:**
  
  \[
  H^+ + 2e \rightarrow Pt.balck \rightarrow \frac{1}{2} H_2
  \]

  \[
  E = \text{zero} - 0.059 \log \frac{1}{[H^+]} \]

- **Nernest equation**
  
  \[
  E = -0.059 \text{ pH} \]

- **Design:**
  When it is connected with NHE as reference electrode the e.m.f. of the cell:

  \[
  E_{cell} = \text{zero} - (-0.059 \text{ pH})
  \]

  \[
  = 0.059 \text{ pH}
  \]

  \[
  \text{pH} = E / 0.059
  \]
Disadvantages:
1. It cannot be used in solution containing oxidising agent which will oxidise \([ \frac{1}{2} \text{H}_2 = \text{H}^+ + e ]\) or reducing substances which will reduce \([ \text{H}^+ + e = \frac{1}{2} \text{H}_2 ]\) especially in presence of platinum black.
2. It cannot be used in reactions involving volatile constituent's e.g. \(\text{CO}_2\), as it will be bubbled out by the \(\text{H}_2\) gas.
3. It cannot be used in presence of catalytic poisons which will affect Pt black which catalysis the electrode reaction.
4. It needs re-plating with Pt black.
5. It is not easy to keep \(\text{H}_2\) gas at one atmospheric pressure during all measurements.

3. Antimony electrode \(\text{Sb}/\text{Sb}_2\text{O}_3\)

Electrode reaction:
\[
\text{Sb}_2\text{O}_3 + 6 \text{H}^+ + 6 e^- = 2 \text{Sb} + 3 \text{H}_2\text{O}
\]

Nernst equation
\[
E_{\text{Sb}/\text{Sb}_2\text{O}_3} = E^0 - \frac{0.059}{6} \log \frac{[\text{Sb}]^2}{[\text{Sb}_2\text{O}_3][\text{H}^+]^6}
\]

or
\[
E^{25} = E^0 - \left( \frac{0.059}{6} \log \frac{[\text{Sb}]^2}{[\text{Sb}_2\text{O}_3]} \right) - \left( \frac{0.059}{6} \log \frac{1}{[\text{H}^+]^6} \right)
\]
\[ E^{25} = E^0 - 0.059 \text{ pH} \]

- **Design**
  
  It is prepared by allowing a rod of antimony to cast for two or three weeks in air. It should be standardized before use.

- **Advantages**
  
  Easy to use, cheap and durable.

- **Disadvantages**
  
  1. Can only be used within pH range 2 – 8 at lower pH Sb\(_2\)O\(_3\) dissolves and at higher pH Sb\(^0\) dissolves.
  2. It cannot be used in presence of oxidizing agents, reducing agents, complexing agents and noble metals.

- **4. Quinhydrone electrode**

  Quinhydrone is an organic molecular compounds formed by the addition of quinone and hydroquinone in equimolar proportion.

  It is slightly soluble in water and is partially dissociated in aqueous solution to quinone and hydroquinone.
Quinone and hydroquinone constitute a conjugate redox pair.

If an inert electrode such as platinum wire is immersed in the system potential is developed and given by Nernst equation:

\[
E_{Q/H_2Q} = E_{Q/H_2Q}^o - \frac{0.059}{2} \log \frac{[H_2Q]}{[Q][H^+]^2}
\]

\[
E_{Q/H_2Q} = E_{Q/H_2Q}^o - \left( \frac{0.059}{2} \log \frac{[H_2Q]}{[Q]} \right) - \left( \frac{0.059}{2} \log \frac{1}{[H^+]^2} \right)
\]

\[
E_{Q/H_2Q} = E_{Q/H_2Q}^o - 0.059 \text{pH}
\]

To measure the hydrogen ion concentration about 0.1 g of quinhydrone is added to the solution, the quantity must be sufficient to saturate the solution and have some undissolved.
quinhydrone. After stirring for two minutes the redox potential is measured by dipping a platinum electrode and connects it with a suitable reference electrode.

- **Advantages**
  1. It is not affected by catalytic poisons.
  2. It gives satisfactory results in presence of carbonic acid.
  3. Easy to prepare and use.
  4. It comes to equilibrium rapidly.

- **Disadvantages:**
  1. It cannot be used in presence of oxidising agents which oxidise hydroquinone to quinone also reducing agents that reduce quinone to hydroquinone. This affects the ratio of $[H_2Q]/[Q]$ and makes the equation un-applicable.
  2. The upper limit of the electrode use is pH 8 above which hydroquinone, which is, weak acids dissociates and affect the pH.
  3. Atmospheric oxygen slowly oxidizes hydroquinone. It needs to be used freshly.
1. Direct potentiometric measurements
The **calibration curve method** in which we plot the potential of the cell versus a series of standard solutions of extra pure grade of substance to be determined. Then measure the potential obtained when using the The most important application of this method is the determination of pH.

2- Potentiometric titration
In this method we measure simultaneously the potential \([E_{25}]\) developed when a sensitive electrode is immersed in the solution to be titrated after successive addition of the titrant i.e. we add certain amount of the titrant then measure the potential and repeat the process. Then we plot a curve representing the \(E_{25}\) against ml of titrant from which we can determine the end point i.e. the method is a mean for determination of the end point.

It is used for all types of volumetric analysis: acid base, precipitmetry, complexometry and redox

It is used when it is not easy or impossible to detect the end point by ordinary visual methods i.e:

1. For highly coloured or turbid solutions.
2. For very dilute solutions \(10^{-3}, 10^{-6}\) M.
3. When there is no available indicator

**End point determination:**

Several methods can be used to determine the end point for a potentiometric titration.

a) **Normal curve:** it is a plot of potential against volume of titrant.

b) **First derivative curve:** it is a plot of the change in potential per unit change in volume \((\Delta E/\Delta V)\) against volume of titrant.

c) **Second derivative curve:** it is a plot of the change in the change in potential per unit volume \((\Delta^2 E/\Delta V^2)\) against volume of titrant.

<table>
<thead>
<tr>
<th>Vol of AgNO₃ ml</th>
<th>E vs. SCE, V</th>
<th>(\Delta E/\Delta V), V/ml</th>
<th>(\Delta^2 E/\Delta V^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.062</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>15.0</td>
<td>0.085</td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>0.107</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>22.0</td>
<td>0.123</td>
<td>0.015</td>
<td></td>
</tr>
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<tr>
<td>28.0</td>
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</table>
Application of potentiometric titration in:

**a) Neutralization reactions:**

The electrode system is glass / calomel electrode. The instrument used is pH-meter which is a potentiometer, the millivolt scale of which is converted to pH scale by dividing the potential over 0.059. The value of asymmetry potential (K) is balanced by means of potentiometer which feeds a value of (-K) when using a buffer of exact known pH and adjust the scale to the pH value of the buffer. The titration curve is a plot of pH values obtained during the titration versus the volume of titrant. All the possible titration curve discussed before in neutralization reactions can be obtained by applying potentiometric titrations.
**b) Precipitation reactions:**

For a precipitation titration the indicator electrode is often the metal from which the reacting cation is derived. The most widely used volumetric precipitation reagent is silver nitrate, which is employed for the determination of the halogens, the halogenoids, mercaptans, sulfides, arsenates, phosphates and oxalates. The titration curves obtained in determination of different halides and their mixtures with silver nitrate is shown below.

**c) Complex formation titration:**

Similar to precipitation reactions both metal and membrane electrodes can be used to detect end point for reactions that involve formation of soluble complexes. By far, the most important reagent for complexometric titrations are a group of amino carboxylic acids of which EDTA is the most widely used one (H₄Y).

The indicator electrode commonly used in EDTA potentiometric titration is mercury as a second order electrode. When using it a
drop of 0.005-M mercuric editate complex is added to the solution to be determined before titration.
The electrode reaction:
\[ \text{HgY}^- + 2e^- = \text{Hg}^0 + \text{Y}^4^- \]
For which:
\[
E = 0.21 - \frac{0.059}{2} \log \frac{[\text{Y}^4^-]}{[\text{HgY}^{2-}]} 
\]

The complex is very stable, thus its concentration remains essentially constant over a wide range of \([\text{Y}^4^-]\) concentration.
To relate the electrode potential to EDTA concentration:
\[
E = K - \frac{0.059}{2} \log [\text{Y}^4^-] 
\]
\[
= K + \frac{0.059}{2} \text{pY}^4^- 
\]
Where \( K \) is a constant
\[
K = 0.21 - \frac{0.059}{2} \log \frac{1}{[\text{HgY}^{2-}]} 
\]

Many cations and their mixtures can be determined by this electrode e.g. a mixture of Bi\(^{3+}\), Cd\(^{2+}\) and Ca\(^{2+}\) can be determined by EDTA at different pH using the mercury electrode. At pH 1.2 Bi\(^{3+}\) reacts and at the end point sharp change in potential occurs, then adjust pH at 4 where Cd\(^{2+}\) only reacts, similarly at the end point distinct change in
potential occurs now raise the pH to the basic side using ammonia/ ammonium chloride buffer, EDTA forms stable complex with calcium. The titration curve will be a plot of the electrode potential versus milliliter of EDTA.

![Graph](image)

*Titration and derivative curves for determination of Ca\(^{2+}\) with EDTA.*

**d) Redox titration:**

A platinum electrode responds rapidly to many important oxidation couples and develops a potential that depends upon the concentration ratio of the reactant and the products of such half reactions. A plot of the measured potential during the titration versus ml. titrant will give the titration curve where the change in the potential becomes larger at the equivalence point as the equilibrium constant of the reaction is great sharp inflection at equivalence point occurs:
For example for reaction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ with $\text{Ce}^{4+}/\text{Ce}^{3+}$

$$\log K_{\text{eq}} = \frac{n \left( E^0_{\text{oxidising}} - E^0_{\text{reducing}} \right)}{0.059}$$

$$\log K_{\text{eq}} = \frac{1.45 - 0.77}{0.059}$$

$$K_{\text{eq}} = 4.17 \times 10^{11}$$

Table: Summary of potentometric titration electrode systems

<table>
<thead>
<tr>
<th>Titration</th>
<th>Ind.elec.</th>
<th>Ref. elec</th>
<th>Equations</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid – base</td>
<td>Glass</td>
<td>Calomel or Ag/AgCl</td>
<td>$E = K + 0.0591 , \text{pH}$</td>
<td>Acid-base titration</td>
</tr>
</tbody>
</table>
| Redox           | Pt        | Calomel or Ag/AgCl | $E = E^0 + 0.0591/n \, \log [\text{Ox}]/[\text{red}]$ | $\text{Ce}^{4+}, \text{MnO}_4^-$...
| Precipmetry     | Silver    | Calomel     | $E = E^0 + 0.0591 \, \log [\text{Ag}]$ | Halides                |
| Complexometry   | Hg/Hg(II) | Calomel     | $E = E^0 + 0.0591 \log [K_1 - \text{pM}]$ | Metal-EDTA titration   |

K glass electrode constant and $K_1$ constant derived from Hg(II)-EDTA equilibrium