



CHM 221 (ANALYTICAL CHEMISTRY)

**INTRODUCTION TO
ELECTROANALYTICAL TECHNIQUES**

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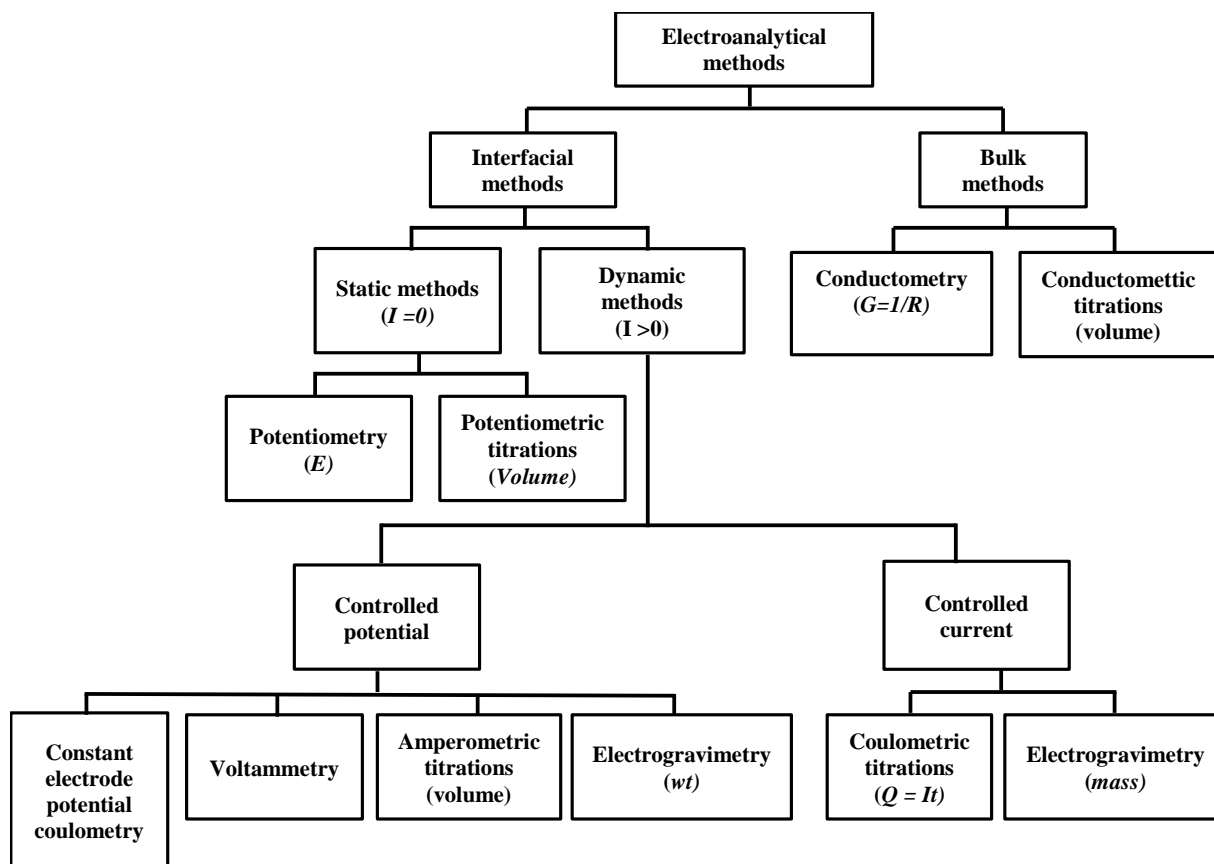
ELECTROANALYTICAL TECHNIQUES

Electroanalytical techniques are concerned with the interplay between electricity and chemistry, namely the measurement of electrical quantities such as current, potential or charge and their relationship to chemical parameters such as concentration.

Although there are only three principal sources for the analytical signals, that is, potential, current, and charge, a wide variety of experimental designs are possible. The simplest division is between **bulk methods**, which measure properties of the whole solution, and **interfacial methods**, in which the signal is a function of phenomena occurring at the interface between an electrode and the solution in contact with the electrode.

The measurement of a solution's conductivity, which is proportional to the total concentration of dissolved ions, is one example of a bulk electrochemical method. A determination of pH using a pH electrode is one example of an interfacial electrochemical method.

The use of electrical measurements for analytical purposes has found large range of applications including environmental monitoring, industrial quality control and biomedical analysis.



Classification of Electroanalytical Techniques

In static methods, no current passes between the electrodes, and the concentrations of species in the electrochemical cell remain unchanged, or static. The largest division of interfacial electrochemical methods is the group of dynamic methods, in which current flows and concentrations change as the result of a redox reaction.

Why Electroanalytical Techniques?

Electroanalytical methods have certain advantages over other analytical methods:

1. Electrochemical analysis allows for the determination of different oxidation states of an element in a solution, not just the total concentration of the element.
2. Electroanalytical techniques are capable of producing exceptionally low detection limits and an abundance of characterization information including chemical kinetics information.
3. Selective for particular redox state of a species e.g. Ce^{3+} vs. Ce^{4+} .
4. Its low cost.
5. Fastness

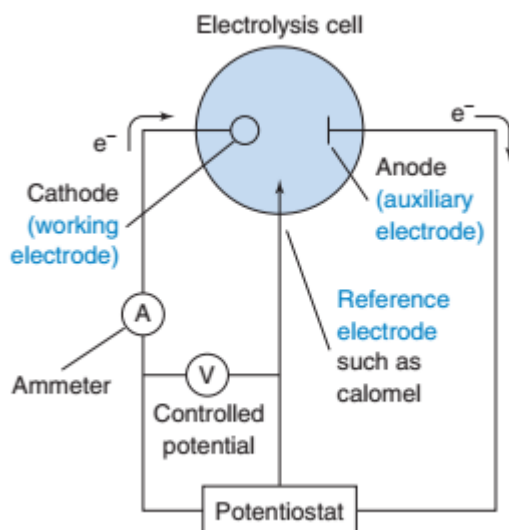
Controlling and Measuring Current and Potential

An **electroactive species** is one that can be oxidized or reduced at an electrode. We regulate the potential of the working electrode to control which electroactive species react and which do not. Metal electrodes are said to be **polarizable**, which means that their potentials are easily changed when small currents flow. A reference electrode such as calomel or is said to be **nonpolarizable**, because its potential does not vary much unless a significant current is flowing.

Ideally, we want to measure the potential of a polarizable working electrode with respect to a nonpolarizable reference electrode. How can we do this, if there is to be significant current at the working electrode and negligible current at the reference electrode?

The answer is to introduce a third electrode. The **working electrode** is the one at which the reaction of interest occurs. A calomel or other **reference electrode** is used to measure the potential of the working electrode. The **auxiliary electrode** (the *counter electrode*) is the current-supporting partner of the working electrode. Current flows between the working and the auxiliary electrodes. Negligible current flows through the reference electrode, so its potential is unaffected by ohmic potential, concentration polarization, and overpotential. It truly maintains a constant reference potential.

In **controlled-potential electrolysis**, the voltage difference between working and reference electrodes in a three-electrode cell is regulated by an electronic device called a **potentiostat**.



Controlled potential electrolysis with a three-electrode cell

Although many different electrochemical methods of analysis are possible, there are only three basic experimental designs:

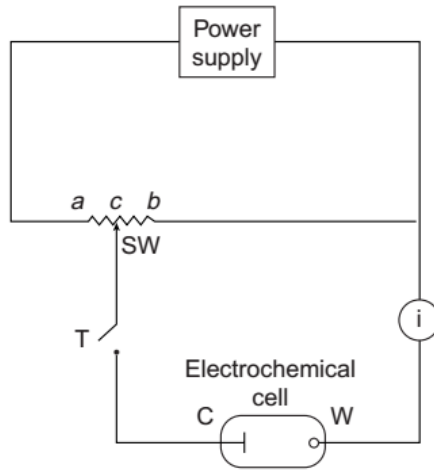
1. measuring the potential under static conditions of no current flow;
2. measuring the potential while controlling the current; and
3. measuring the current while controlling the potential.

Each of these experimental designs, however, is based on **Ohm's law** that a current, i , passing through an electric circuit of resistance, R , generates a potential, E ; thus

$$E = IR$$

Potentiometer

A potentiometer is a device for measuring the potential of electrochemical cell without drawing a current or altering the cell's composition.

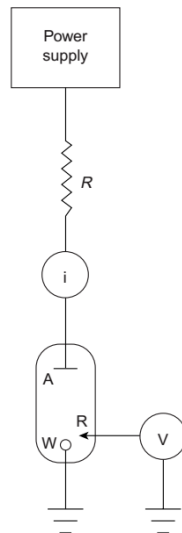


Schematic diagram of a manual potentiostat: C = counter electrode; W = working electrode; SW = slide-wire resistor; T = tap key; i = galvanometer

Galvanostats

A galvanostat is used for dynamic methods, such as constant-current, in which it is necessary to control the current flowing through an electrochemical cell.

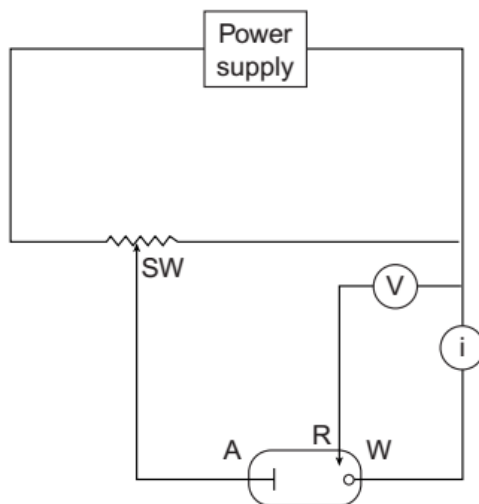
The potential of the working electrode, which changes as the composition of the electrochemical cell changes, is monitored by including a reference electrode and a high-impedance potentiometer.



Schematic diagram of a galvanostat: R = resistor; i = galvanometer; A = auxiliary electrode; W = working electrode; R = reference electrode; V = voltmeter or potentiometer (optional)

Potentiostats

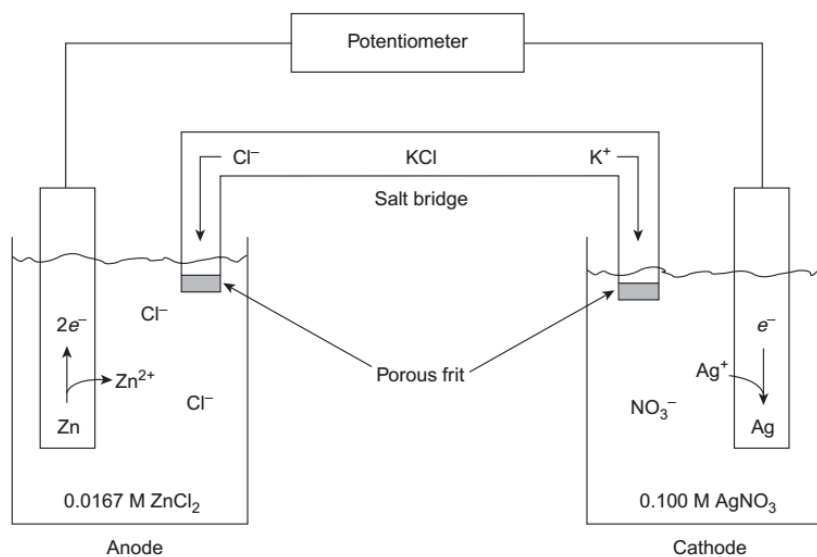
A potentiostat is used for dynamic methods when it is necessary to control the potential of the working electrode. The current flowing between the auxiliary and working electrodes is measured with a galvanostat.



Schematic diagram of a manual potentiostat: SW = slide-wire resistor; A = auxiliary electrode; R = reference electrode; W = working electrode; V = voltmeter or potentiometer; i = galvanometer

Potentiometric Method of Analysis

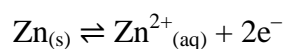
In potentiometry, the potential of an electrochemical cell is measured under static conditions. Because no current, or only a negligible current, flows while measuring a solution's potential, its composition remains unchanged. For this reason, potentiometry is a useful quantitative method.



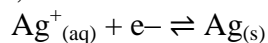
Electrochemical cell for potentiometry

Since no significant current flows in potentiometry, the role of the counter electrode is reduced to that of supplying a reference potential; thus, the counter electrode is usually called the reference electrode.

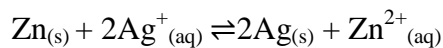
By convention, the electrode on the left is considered to be the anode, where oxidation occurs



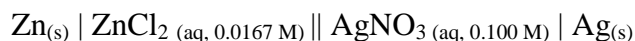
and the electrode on the right is the cathode, where reduction occurs



The electrochemical cell's potential, therefore, is for the reaction



The electrochemical cell is described in shorthand notation as



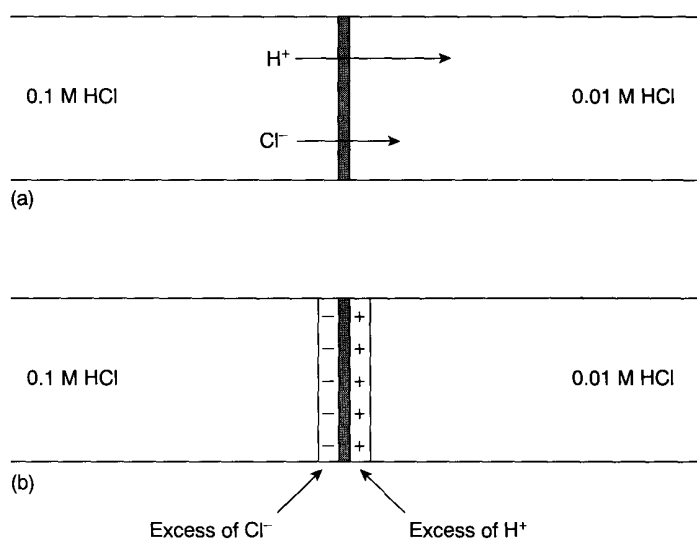
Thus, the potential of a potentiometric electrochemical cell is given as

$$E_{\text{cell}} = E_c - E_a$$

However, at the interface between the salt bridge and the solution in which it is immersed, there is a liquid junction potential.

Liquid junction potential (E_{lj}) is potential that develops at the interface between two ionic solutions that differ in composition, because of a difference in the mobilities of the ions.

For instance, solutions of 0.1 M HCl and 0.01 M separated by a porous membrane will have a net diffusion of H^+ and Cl^- in the direction of the arrows. The mobility of H^+ is greater than that for Cl^- , as shown by the difference in the lengths of their respective arrows. Thus, a potential is produced at the membrane.



The magnitude of the liquid junction potential is determined by the ionic composition of the solutions on the two sides of the interface and may be as large as 30–40 mV.

The magnitude of a salt bridge's liquid junction potential is minimized by:

1. using a salt, such as KCl, for which the mobility of the cation and anion are approximately equal.
2. incorporating a high concentration of the salt in the salt bridge. For this reason salt bridges are frequently constructed using solutions that are saturated with KCl

Nevertheless, a small liquid junction potential, generally of unknown magnitude, is always present.

When the potential of an electrochemical cell is measured, the contribution of the liquid junction potential must be included. Thus, potential of a potentiometric electrochemical cell is rewritten as

$$E_{\text{cell}} = E_c - E_a + E_{lj}$$

Reference Electrodes for Potentiometric Method

Potentiometric electrochemical cells are constructed such that one of the half-cells provides a known reference potential, and the potential of the other half-cell indicates the analyte's concentration.

By convention, the reference electrode is taken to be the anode; thus, the shorthand notation for a potentiometric electrochemical cell is



and the cell potential is

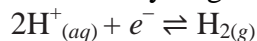
$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}} + E_{\text{ij}}$$

The ideal reference electrode

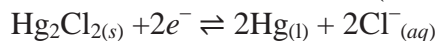
1. must provide a stable potential so that any change in E_{cell} is attributed to the indicator electrode, and, therefore, to a change in the analyte's concentration.
2. should be easy to make and to use.

The reference electrodes commonly used in potentiometric method of analysis are:

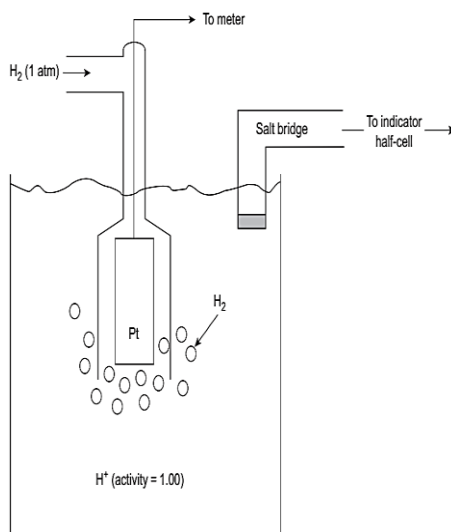
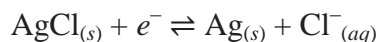
1. Standard hydrogen electrode (SHE)



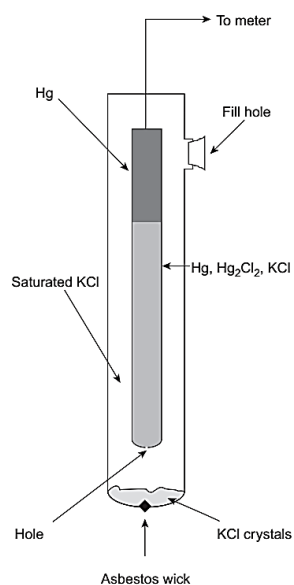
2. Saturated calomel electrode (SCE)



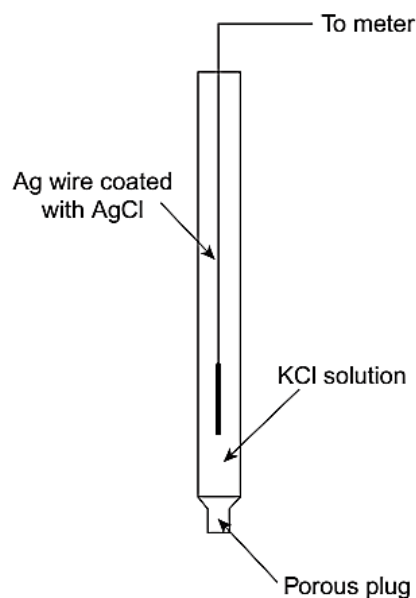
3. Silver–silver chloride electrode (SSCE)



Schematic diagram of SHE



Schematic diagram of SCE



Schematic diagram of SSCE

Indicator Electrode for Potentiometric Method of Analysis

The potential of the indicator electrode in a potentiometric electrochemical cell is proportional to the concentration of analyte.

Two classes of indicator electrodes are used in potentiometry:

1. metallic electrodes and
2. ion-selective electrodes

Metallic Electrodes

The potential of a metallic electrode is determined by the position of a redox reaction at the electrode–solution interface.

Electrodes of the first kind

Metallic indicator electrodes in which a metal is in contact with a solution containing its ion are called electrodes of the first kind.

In general, for a metal M , in a solution of M^{n+} , the cell potential is given as

$$E_{cell} = K - \frac{0.05916}{n} \log \frac{1}{[M^{n+}]} = K + \frac{0.05916}{n} \log [M^{n+}]$$

where, K is a constant that includes the standard-state potential for the M^{n+}/M redox couple, the potential of the reference electrode, and the junction potential.

For a variety of reasons, including slow kinetics for electron transfer, the existence of surface oxides and interfering reactions, electrodes of the first kind are limited to Ag, Bi, Cd, Cu, Hg, Pb, Sn, Tl, and Zn.

Electrodes of the Second Kind

When the potential of an electrode of the first kind responds to the potential of another ion that is in equilibrium with M^{n+} , it is called an electrode of the second kind.

Two common electrodes of the second kind are the calomel and silver/silver chloride reference electrodes. Electrodes of the second kind also can be based on complexation reactions.

For example, an electrode for EDTA is constructed by coupling a Hg^{2+}/Hg electrode of the first kind to EDTA by taking advantage of its formation of a stable complex with Hg^{2+} .

Redox Electrodes

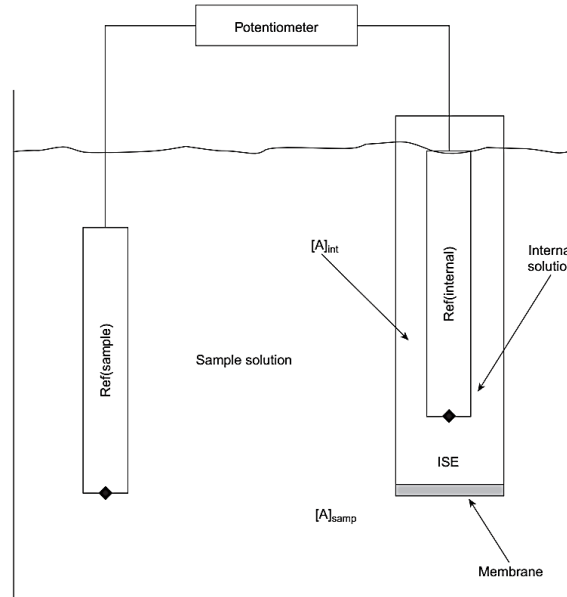
Metallic electrodes that serve simply as a source of, or a sink for, electrons in other redox reactions are called redox electrodes. They are inert electrodes. An example is when platinum is used as a cathode.

Ion-Selective Electrodes (ISEs)

ISE is an electrode in which the membrane potential is a function of the concentration of a particular ion in solution. Membrane potential is developed across a conductive membrane whose opposite sides are in contact with solutions of different composition.

ISEs, such as the glass pH electrode, function by using a membrane that reacts selectively with a single ion. Interaction of the analyte with the membrane results in a membrane potential, if there is a difference in the analyte's concentration on opposite sides of the membrane.

One side of the membrane is in contact with an internal solution containing a fixed concentration of analyte, while the other side of the membrane is in contact with the sample.



Electrochemical cell for potentiometry with an ion-selective membrane electrode

Two reference electrodes are used; one positioned within the internal solution, and one in the sample solution. The cell potential, therefore, is

$$E_{\text{cell}} = E_{\text{Ref(int)}} - E_{\text{Ref(samp)}} + E_{\text{mem}} + E_{\text{lj}}$$

where, $E_{\text{ref(int)}}$ = potential of reference electrode within the internal solution, $E_{\text{ref(samp)}}$ = potential of reference electrode within the sample, E_{mem} is the potential across the membrane and E_{lj} = liquid junction potential.

The potential of the membrane is given as

$$E_{\text{mem}} = E_{\text{asy}} - \frac{0.05916}{z} \log \left(\frac{[A]_{\text{int}}}{[A]_{\text{samp}}} \right)$$

where, $[A]_{\text{samp}}$ and $[A]_{\text{int}}$ are the concentrations of analyte in the sample and the internal solution, respectively, and z is the analyte's charge.

Ideally, E_{mem} should be zero when the concentrations of analyte on both sides of the membrane are equal. The term E_{asym} , which is called an **asymmetry potential**, accounts for the fact that the membrane potential is usually not zero under these conditions.

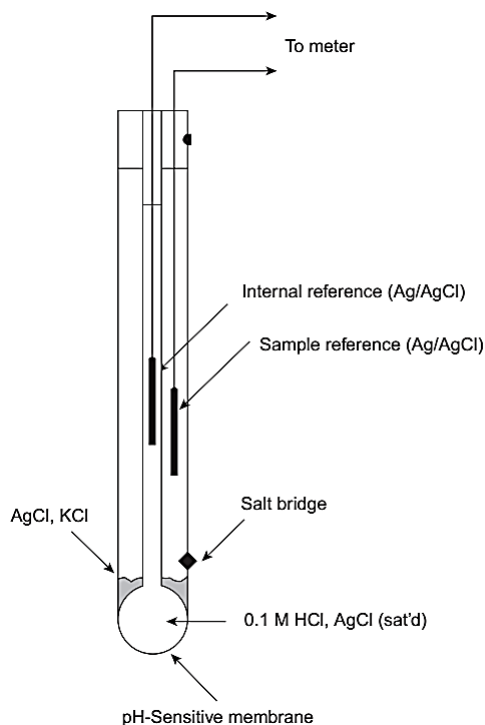
The potential of potentiometer with an ISE is written as

$$E_{\text{cell}} = K + \frac{0.05916}{z} \log [A]_{\text{samp}}$$

Types of ISEs

1. Glass Ion-Selective Electrodes

An ion-selective electrode based on a glass membrane in which the potential develops from an ion-exchange reaction on the membrane's surface. The first commercial **glass electrodes** were manufactured using Corning 015, a glass with a composition of approximately 22% Na_2O , 6% CaO , and 72% SiO_2 .



Schematic diagram of a combination glass electrode for measuring pH

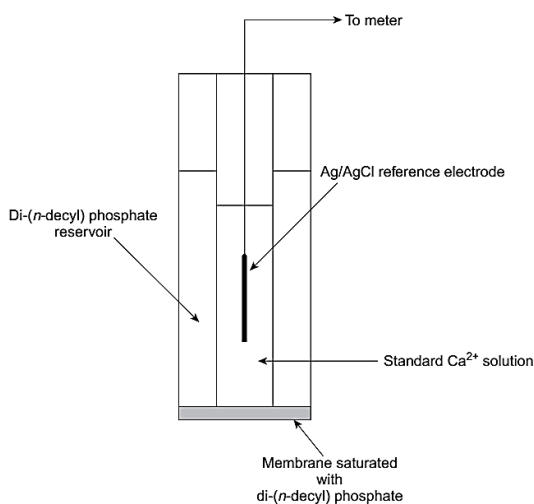
2. *Solid state Ion-Selective Electrode*

An ion-selective electrode based on a sparingly soluble inorganic crystalline material. Polycrystalline ion-selective electrodes are made by forming a thin pellet of Ag_2S , or a mixture of Ag_2S and either a second silver salt or another metal sulphide.

3. *Liquid-Based Ion-Selective Electrodes*

An ion-selective electrode in which a chelating agent is incorporated into a hydrophobic membrane. Three types of organic liquids have been used: cation exchangers, anion exchangers, and neutral **ionophores**. A neutral ligand whose exterior is hydrophobic and whose interior is hydrophilic is called ionophores.

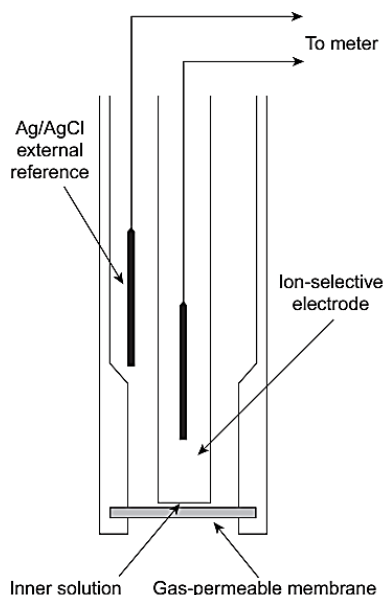
One example of a **liquid-based ion-selective electrode** is that for Ca^{2+} , which uses a porous plastic membrane saturated with di-(*n*-decyl) phosphate.



Schematic diagram of a Ca^{2+} liquid-based ion-selective electrode

4. *Gas-Sensing Electrodes*

A number of membrane electrodes have been developed that respond to the concentration of dissolved gases. The membrane is permeable to the gaseous analyte, but is not permeable to non-volatile components in the sample matrix.

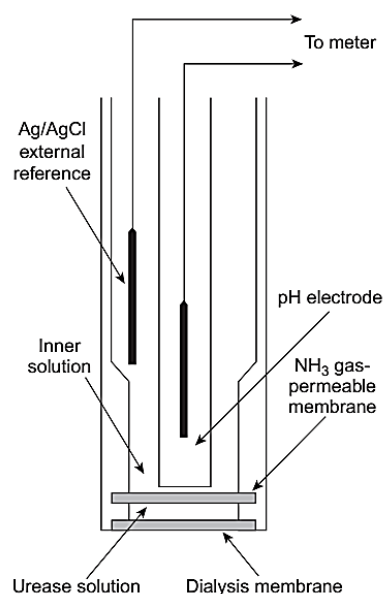


Schematic diagram of a gas-sensing membrane electrode

5. Potentiometric Biosensors

Potentiometric electrodes for the analysis of molecules of biochemical importance can be constructed in a fashion similar to that used for gas-sensing electrodes. The most common class of potentiometric biosensors are the so-called **enzyme electrodes**, in which an enzyme is trapped or immobilized at the surface of an ion-selective electrode.

Potentiometric biosensors have also been designed around other biologically active species, including antibodies, bacterial particles, tissue, and hormone receptors.



Schematic diagram of an enzyme-based potentiometric biosensor for urea in which urease is trapped between two membranes

Applications of Potentiometry

1. Measurement of pH

With the availability of inexpensive glass pH electrodes and pH meters, the determination of pH has become one of the most frequent quantitative analytical measurements.

2. Clinical Applications

For extracellular fluids, such as blood and urine, the analysis can be made in vitro with conventional electrodes, provided that sufficient sample is available.

3. Environmental Applications

Standard methods have been developed for the analysis of CN^- , F^- , NH_3 , and NO_3^- in water and wastewater.

4. Potentiometric Titrations

The potentiometric determination of equivalence points is feasible for acid–base, complexation, redox, and precipitation titrations, as well as for titrations in aqueous and non-aqueous solvents.

Coulometric Method of Analysis

Coulometric methods of analysis are based on an exhaustive electrolysis of the analyte. By exhaustive we mean that the analyte is quantitatively oxidized or reduced at the working electrode or reacts quantitatively with a reagent generated at the working electrode.

There are two forms of coulometry namely:

1. controlled-potential coulometry, in which a constant potential is applied to the electrochemical cell, and
2. controlled-current coulometry, in which a constant current is passed through the electrochemical cell.

The total charge, Q , in coulombs, passed during electrolysis is related to the absolute amount of analyte by **Faraday's law**

$$Q = nFN$$

where, n = number of electrons transferred per mole of analyte, F = Faraday's constant (96487 C mol⁻¹), and N = moles of analyte.

$$Q = it_e = nFN$$

where, t_e = electrolysis time and i = current.

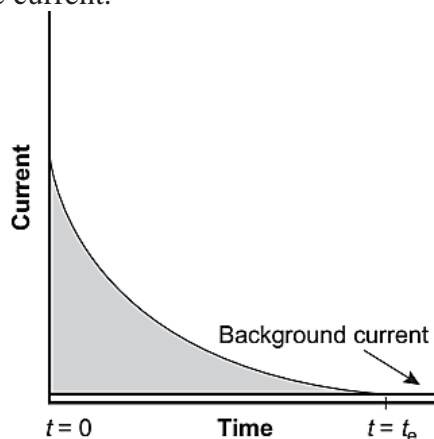
If current varies with time, as it does in controlled-potential coulometry, then the total charge is given by

$$Q = \int_{t=0}^{t=t_e} i(t) dt$$

To obtain an accurate value for N , therefore, all the current must result in the analyte's oxidation or reduction. In other words, coulometry requires 100% **current efficiency**, which is percentage of current that actually leads to the analyte's oxidation or reduction.

Controlled-Potential Coulometry

The easiest method for ensuring 100% current efficiency is to maintain the working electrode at a constant potential that allows for the analyte's quantitative oxidation or reduction, without simultaneously oxidizing or reducing an interfering species. The current flowing through an electrochemical cell under a constant potential is proportional to the analyte's concentration. As electrolysis progresses the analyte's concentration decreases, as does the current.



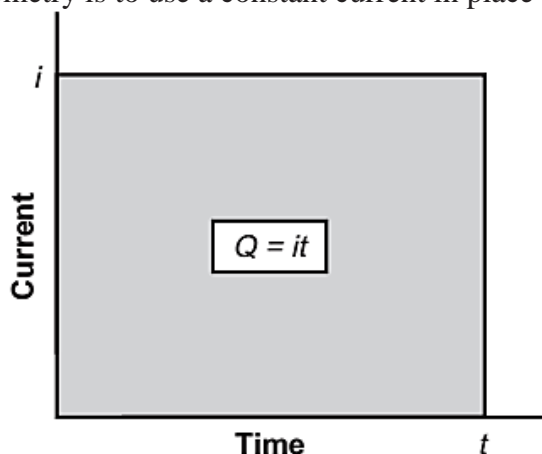
Current–time curve for controlled-potential coulometry

The potential in controlled-potential coulometry is set using a three-electrode potentiostat. Two types of working electrodes are commonly used: a Pt electrode manufactured from platinum-gauze and fashioned into a cylindrical tube, and an Hg pool electrode.

The auxiliary electrode, which is often a Pt wire, is separated by a salt bridge from the solution containing the analyte. This is necessary to prevent electrolysis products generated at the auxiliary electrode from reacting with the analyte and interfering in the analysis. A saturated calomel or Ag/AgCl electrode serves as the reference electrode.

Controlled-Current Coulometry

A second approach to coulometry is to use a constant current in place of a constant potential.



Current–time curve for controlled-current coulometry

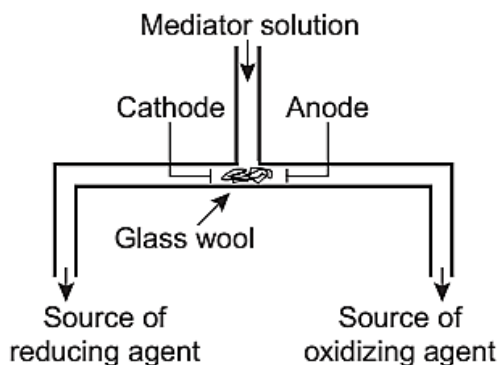
Controlled-current coulometry, also known as amperostatic coulometry or coulometric titrimetry, has two advantages over controlled-potential coulometry:

1. more rapid analysis since the current does not decrease over time. Thus, a typical analysis time for controlled-current coulometry is less than 10 min, as opposed to approximately 30–60 min for controlled-potential coulometry.
2. the total charge is simply the product of current and time. A method for integrating the current–time curve, therefore, is not necessary.

There are two important experimental problems that must be solved if accurate results are to be obtained:

1. First, as electrolysis occurs the analyte's concentration and, therefore, the current due to its oxidation or reduction steadily decreases. To maintain a constant current the cell potential must change until another oxidation or reduction reaction can occur at the working electrode. Unless the system is carefully designed, these secondary reactions will produce a current efficiency of less than 100%.
2. There is the need for a method of determining when the analyte has been exhaustively electrolyzed. In controlled-potential coulometry this is signaled by a decrease in the current to a constant background or residual current.

Controlled-current coulometry normally is carried out using a galvanostat and an electrochemical cell consisting of a working electrode and a counterelectrode. The working electrode, which often is constructed from Pt, is also called the generator electrode since it is where the mediator reacts to generate the species reacting with the analyte. A species, such as Ce^{3+} , which is used to maintain 100% current efficiency, is called a **mediator**.



Method for the external generation of oxidizing and reducing agents in coulometric titrations

Applications of Coulometry

1. **Quantitative analysis**

Coulometry may be used for the quantitative analysis of both inorganic and organic compounds.

2. **Coulometric titrations**

This is advantageous over conventional titrimetry, because electrochemical generation of a “titrant” that reacts immediately with the analyte allows the use of reagents whose instability prevents their preparation and storage as a standard solution.

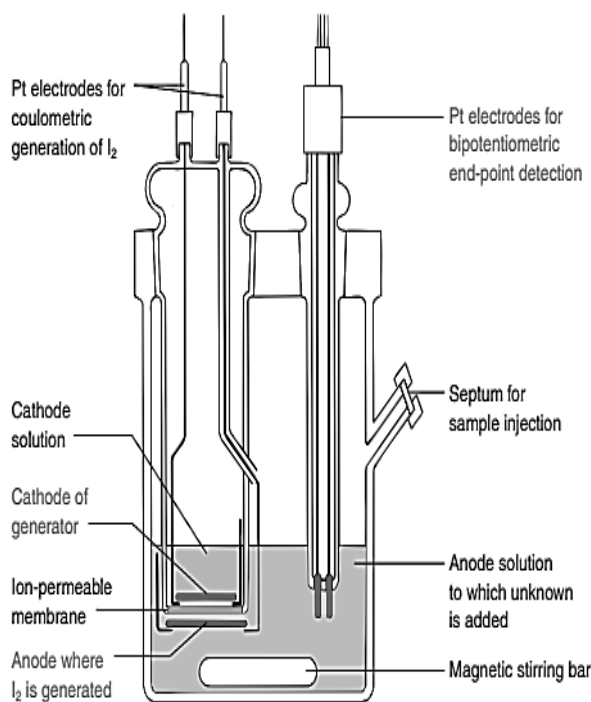
3. **Characterization Applications**

Studies aimed at characterizing the mechanisms of electrode reactions often make use of coulometry for determining the number of electrons involved in the reaction.

Karl Fischer Titration of Water

The Karl Fischer titration, which measures traces of water in transformer oil, solvents, foods, polymers, and other substances, is performed half a million times each day.

The titration is usually performed by delivering titrant from an automated burette or by coulometric generation of titrant. The volumetric procedure tends to be appropriate for larger amounts of water (but can go as low as) and the coulometric procedure tends to be appropriate for smaller amounts of water.



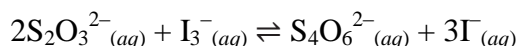
Apparatus for coulometric Karl Fischer titration

Worked Example

The purity of a sample of $\text{Na}_2\text{S}_2\text{O}_3$ was determined by a coulometric redox titration using Γ^- as a mediator, and I_3^- as the “titrant.” A sample weighing 0.1342 g is transferred to a 100-mL volumetric flask and

diluted to volume with distilled water. A 10.00-mL portion is transferred to an electrochemical cell along with 25 mL of 1 M KI, 75 mL of a pH 7.0 phosphate buffer, and several drops of a starch indicator solution. Electrolysis at a constant current of 36.45 mA required 221.8 s to reach the starch indicator end point. Determine the purity of the sample. [Na = 23, S = 32, O = 16, I = 127, F = 96,487 C]

Solution



Using

$$Q = it_e = nFN$$

where, $i = 36.45 \text{ mA} = 3.645 \times 10^{-2} \text{ A}$, $t_e = 221.8 \text{ s}$, $n = 1$ and $N = \frac{\text{Mass of substance}}{\text{Molar mass of the substance}}$

Hence,

$$\frac{\text{Mass of Na}_2\text{S}_2\text{O}_3}{\text{Molar mass of Na}_2\text{S}_2\text{O}_3} = \frac{it_e}{nF}$$

$$\text{Mass of Na}_2\text{S}_2\text{O}_3 = \frac{\text{Molar mass of Na}_2\text{S}_2\text{O}_3 \times it_e}{nF}$$

$$\text{Mass of Na}_2\text{S}_2\text{O}_3 = \frac{\text{Molar mass of Na}_2\text{S}_2\text{O}_3 \times it_e}{nF}$$

$$\text{Mass of Na}_2\text{S}_2\text{O}_3 = \frac{158 \times 0.03645 \times 221.8}{1 \times 96487} = 0.01324 \text{ g Na}_2\text{S}_2\text{O}_3$$

This represents the amount of Na₂S₂O₃ in a 10.00 ml portion of a 100.00 ml sample. Thus, 0.1325 g of Na₂S₂O₃ is present in the original sample.

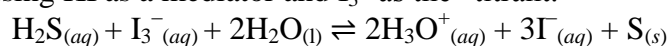
Then,

$$\% \text{ Purity} = \frac{0.1325 \text{ g of Na}_2\text{S}_2\text{O}_3}{0.1342 \text{ g of sample}} \times 100$$

$$\% \text{ Purity} = 98.73\% \text{ Na}_2\text{S}_2\text{O}_3$$

Try these

1. A 0.3619 g sample of tetrachloropicolinic acid, C₆HNO₂Cl₄, is dissolved in distilled water, transferred to a 100 mL volumetric flask, and diluted to volume. An exhaustive controlled-potential electrolysis of a 10.00 mL portion of this solution at a spongy silver cathode requires 5.374 C of charge. What is the value of n for this reduction reaction? (Ans ≈ 4 to the nearest whole number)
2. The concentration of H₂S in the drainage from an abandoned mine can be determined by a coulometric titration using KI as a mediator and I₃⁻ as the “titrant.”



A 50.00-mL sample of water is placed in a coulometric cell, along with an excess of KI and a small amount of starch as an indicator. Electrolysis is carried out at a constant current of 84.6 mA, requiring 386 s to reach the starch end point. Report the concentration of H₂S in the sample in parts per million. (Ans = 115 ppm H₂S)

Voltammetric Methods of Analysis

In **voltammetry** a time-dependent potential is applied to an electrochemical cell, and the current flowing through the cell is measured as a function of that potential.

Although early voltammetric methods relied on the use of only two electrodes, modern voltammetry makes use of a three-electrode potentiostat. The working electrode is commonly mercury electrode, the auxiliary electrode, which is a platinum wire, and the SCE and Ag/AgCl electrode are common reference electrodes.

Since mercury is a liquid, the working electrode often consists of a drop suspended from the end of a capillary tube, which exists as:

1. *Hanging mercury drop electrode (HMDE)*

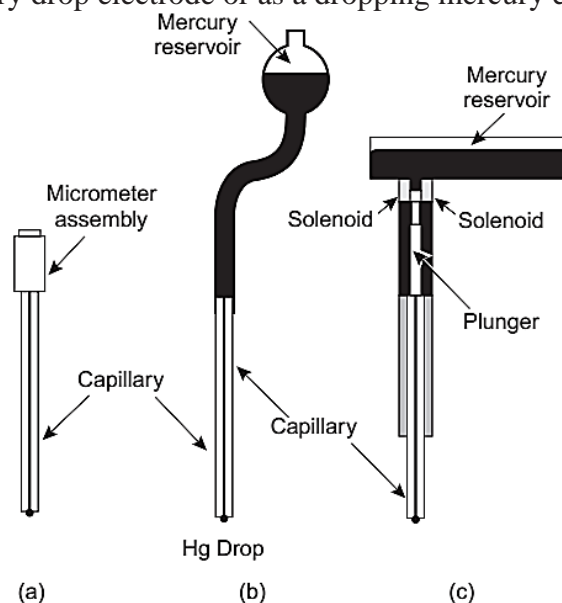
In HMDE, a drop of the desired size is formed by the action of a micrometer screw that pushes the mercury through a narrow capillary tube.

2. *Dropping mercury electrode (DME)*

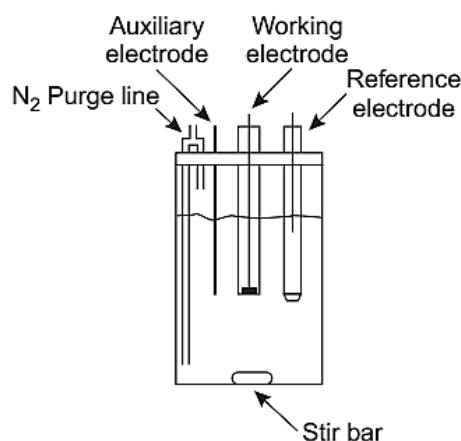
In DME, mercury drops form at the end of the capillary tube as a result of gravity. Unlike the HMDE, the mercury drop of a DME grows continuously and has a finite lifetime of several seconds. At the end of its lifetime the mercury drop is dislodged, either manually or by gravity, and replaced by a new drop.

3. *Static mercury drop electrode (SMDE)*

SMDE uses a solenoid-driven plunger to control the flow of mercury. The SMDE can be used as either a hanging mercury drop electrode or as a dropping mercury electrode.



Mercury electrodes: (a) hanging mercury drop electrode; (b) dropping mercury electrode; (c) static mercury drop electrode



Typical electrochemical cell for use in voltammetry

When an analyte is oxidized at the working electrode, a current passes electrons through the external electric circuitry to the auxiliary electrode, where reduction of the solvent or other components of the solution matrix occurs. Reducing an analyte at the working electrode requires a source of electrons, generating a current that flows from the auxiliary electrode to the cathode. In either case, a current resulting from redox reactions at the working and auxiliary electrodes is called a **faradaic current**.

There are three modes of **mass transport** that influence the rate at which reactants and products are transported to and from the electrode surface:

1. **Diffusion**

Diffusion from a region of high concentration to a region of low concentration occurs whenever the concentration of an ion or molecule at the surface of the electrode is different from that in bulk solution

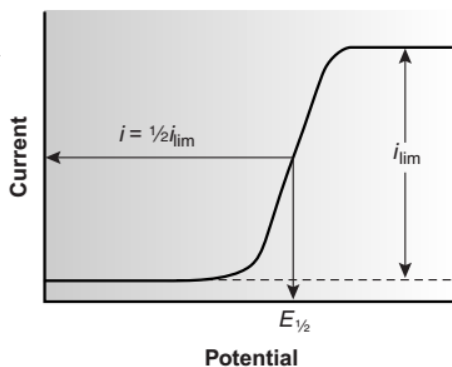
2. **Migration**

Migration occurs when charged particles in solution are attracted or repelled from an electrode that has a positive or negative surface charge. Thus, when the electrode is positively charged, negatively charged particles move toward the electrode, while positively charged particles move toward the bulk solution. Unlike diffusion and convection, migration only affects the mass transport of charged particles.

3. **Convection**

Convection occurs when a mechanical means is used to carry reactants toward the electrode and to remove products from the electrode. The most common means of convection is to stir the solution using a stir bar. Voltammetry that involves convection by stirring is called hydrodynamic voltammetry.

A plot of current as a function of applied potential is called a **voltammogram** and is the electrochemical equivalent of a spectrum in spectroscopy, providing quantitative and qualitative information about the species involved in the oxidation or reduction reaction.

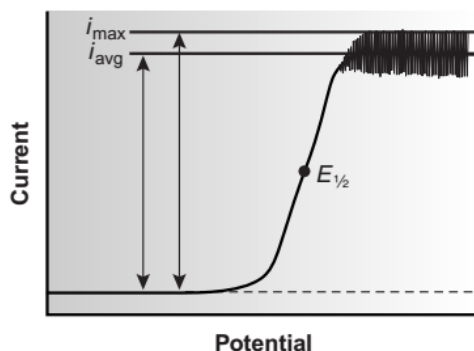


Typical voltammogram

Types of Voltammetric Techniques

1. Polarography

The earliest voltammetric experiment was normal **polarography** at a dropping mercury electrode. Although polarography takes place in an unstirred solution, a limiting current is obtained because the falling Hg drops mix the solution. Each new Hg drop, therefore, grows in a solution whose composition is identical to that of the initial bulk solution.



Voltammogram for normal polarography

Oscillations in the current are due to the growth of the Hg drop, which leads to a time-dependent change in the area of the working electrode. The limiting current, which is also called the diffusion current, may be measured from the maximum current, i_{max} , or from the average current, i_{avg} . The half-wave potential, $E_{1/2}$, provides qualitative information about the redox reaction

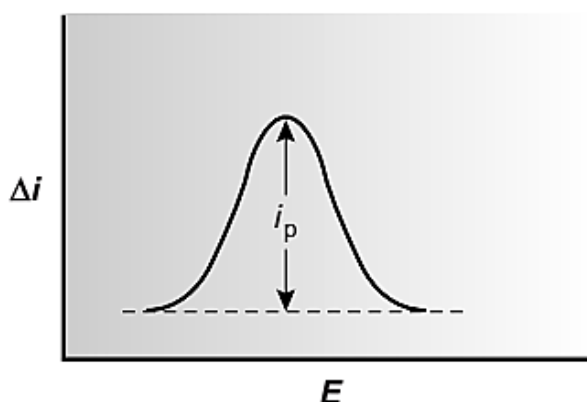
The relationship between the concentration of analyte, C_A , and the limiting current is given by the Ilkovic equation:

$$(i_{lim})_{max} = 706nD^{1/2}m^{2/3}t^{1/6}C_A$$

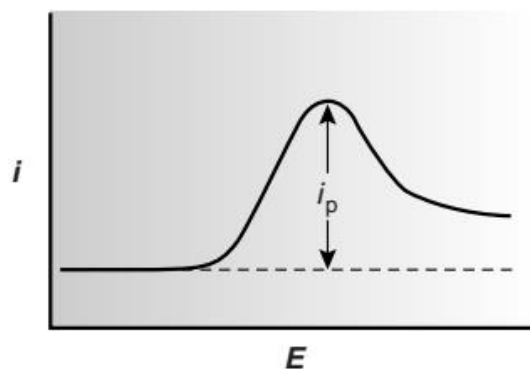
$$(i_{lim})_{avg} = 607nD^{1/2}m^{2/3}t^{1/6}C_A$$

where, n = number of electrons transferred in the redox reaction, D = analyte's diffusion coefficient, m = flow rate of the Hg, and t = drop time.

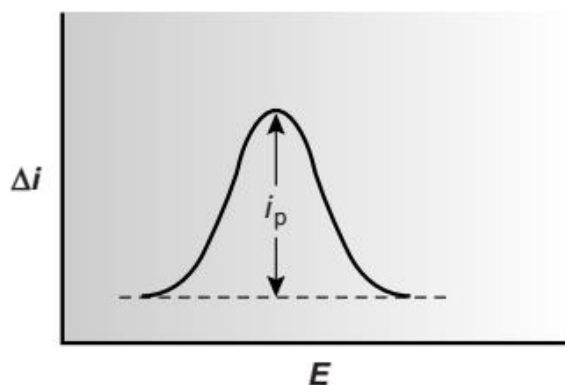
There are other forms of polarography, in addition to normal, which include differential pulse polarography, staircase polarography and square-wave polarography



Voltammogram for differential pulse polarography



Voltammogram for staircase polarography



Voltammogram for square-wave polarography

2. Hydrodynamic Voltammetry

In hydrodynamic voltammetry, current is measured as a function of the potential applied to a solid working electrode. The same potential profiles used for polarography, such as a linear scan or a differential pulse, are used in hydrodynamic voltammetry.

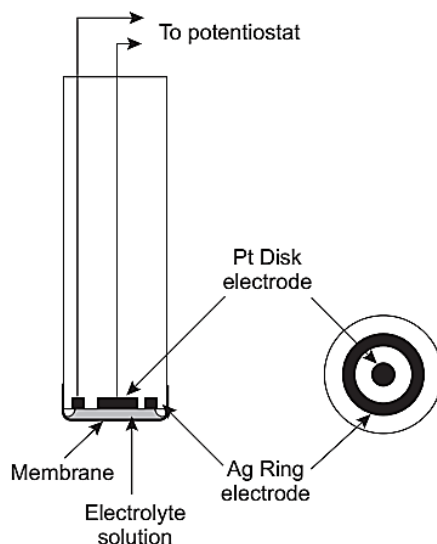
3. Stripping Voltammetry

One of the most important quantitative voltammetric techniques is **stripping voltammetry**, which is composed of three related techniques: anodic, cathodic, and adsorptive stripping voltammetry.

4. Amperometry

The final voltammetric technique to be considered is **amperometry**, in which a constant potential is applied to the working electrode, and current is measured as a function of time. Since the potential is not scanned, amperometry does not lead to a voltammogram.

One important application of amperometry is in the construction of chemical sensors. One of the first amperometric sensors to be developed was for dissolved O_2 in blood, which was developed in 1956 by L. C. Clark.



Clark amperometric sensor for the determination of dissolved O_2

A gas-permeable membrane is stretched across the end of the sensor and is separated from the working and counter electrodes by a thin solution of KCl. The working electrode is a Pt disk cathode, and an Ag ring anode is the counter electrode.

Applications of Voltammetric Method of Analysis

1. Multicomponent Analysis

One advantage of voltammetry as a quantitative method of analysis is its capability for analyzing two or more analytes in a single sample.

2. Environmental Samples

One area in which quantitative voltammetry has had a significant effect is in the analysis of trace metals in environmental samples. The most common samples are natural waters, including groundwater, lakes, rivers and streams, sea water, rain, and snow. Concentrations of trace metals at the parts-per billion (ppb) level can be determined using differential pulse polarography, whereas with anodic stripping voltammetry the determination of trace metals at the parts per-trillion (ppt) level is possible.

3. Clinical Samples

Differential pulse polarography and stripping voltammetry have been used to determine the concentration of trace metals in a variety of matrices, including blood, urine, and tissue samples.

4. Miscellaneous Samples

Besides environmental and clinical samples, differential pulse polarography and stripping voltammetry have been used for the analysis of trace metals in other samples, including food, steels and other alloys, gasoline, gunpowder residues, and pharmaceuticals.

5. Characterization Applications

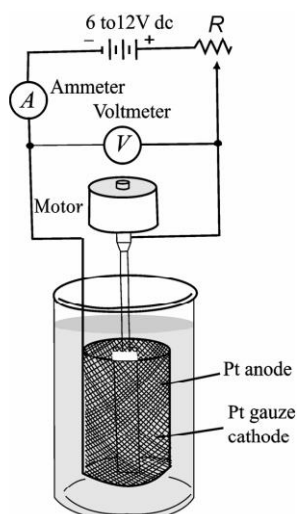
Voltammetry also can be used to obtain additional information, including verifying electrochemical reversibility, determining the number of electrons transferred in a redox reaction, and determining equilibrium constants for coupled chemical reactions.

Electrogravimetric Method of Analysis

Electrolytic precipitation or electrodeposition has been widely used for the determination of metals. In most applications, the metal is deposited on a weighed platinum cathode and the increase in mass is determined.

There are two types of electrogravimetric methods:

1. Constant current electrolysis
2. Constant potential electrolysis



Apparatus for constant current electrolysis

Constant Current Electrolysis

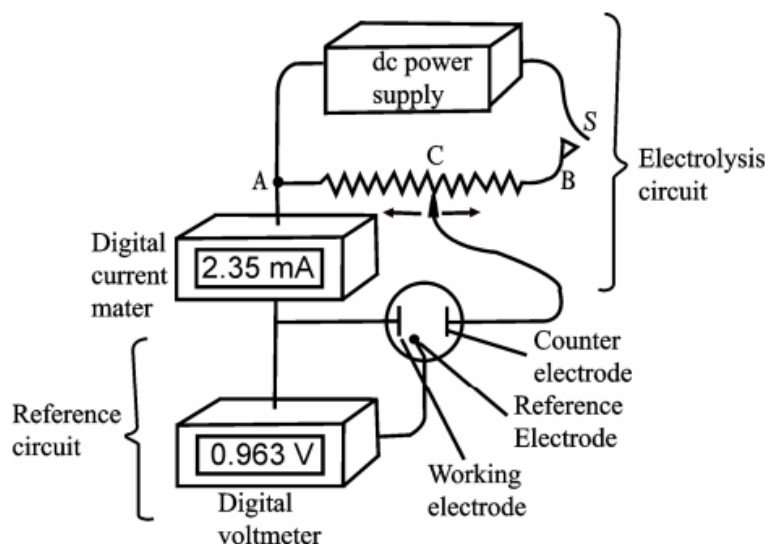
It is important that the deposits produced by electrolysis is pure, strongly adherent, dense and smooth so that it can be washed, dried and weighed without any mechanical loss. Spongy, powdery or flaky deposits are likely to be less pure and less adherent.

Current density, temperature and the presence of complexing agents are the factors influencing the physical characteristics of the deposits. Ordinarily, the best deposits are formed at current densities that are less than $0.1\text{A}/\text{cm}^2$.

Stirring generally improves the quality of a deposit. The time of deposition is reduced when the solution is stirred vigorously or if the electrode is rotated at a uniform speed. This type of stirring lowers the concentration overpotential and enables a higher current density without any adverse effect.

Constant Potential Electrolysis

By controlled potential electrolysis, it is possible to separate two elements whose deposition potentials differ sufficiently (by a few tenths of a volt). The potential of the cathode is controlled so that it never becomes sufficiently negative to allow the deposition of the next element.



Apparatus for controlled-potential electrolysis

Applications of Electrogravimetric Method of Analysis

1. Successive deposition of the metals

A mixture of copper, bismuth, lead, cadmium, zinc and tin can be determined by successive deposition of the metals on a platinum cathode.

2. Simultaneous depositions

A mixture of copper and lead can be determined by the deposition of copper in the presence of nitrate ions at the cathode. Lead is deposited as lead dioxide at the anode.

3. Preparative organic chemistry

If an organic compound can undergo a series of reductions (or oxidations) each at a definite potential, it is then possible to reduce the starting material to the desired product by controlling the potential of the cathode during reduction.

Further Reading

1. Conductometry and its applications

References

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2. Bagotsky, V.S. (2005). Fundamentals of Electrochemistry (2nd Ed.), John Wiley and Sons Inc., New Jersey.
3. Jeffery, G.H., Bassett, J., Mendham, J. and Denny, R.C. (1978). Vogel's Textbook of Quantitative Chemical Analysis (5th Ed.), Longman Scientific and Technical, New York.