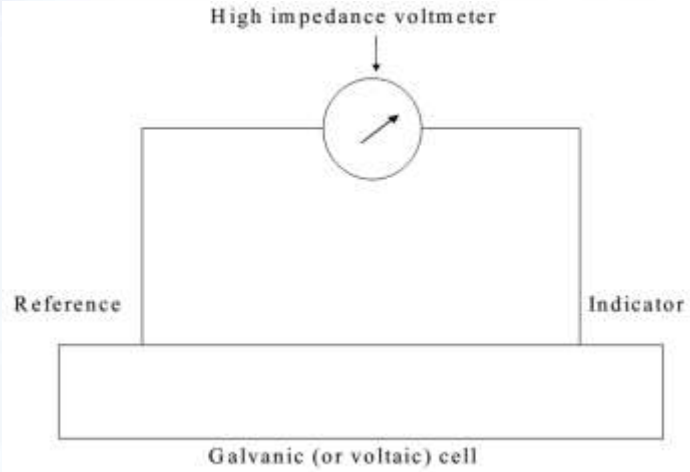
# Analytical chemistry

Lecture №34

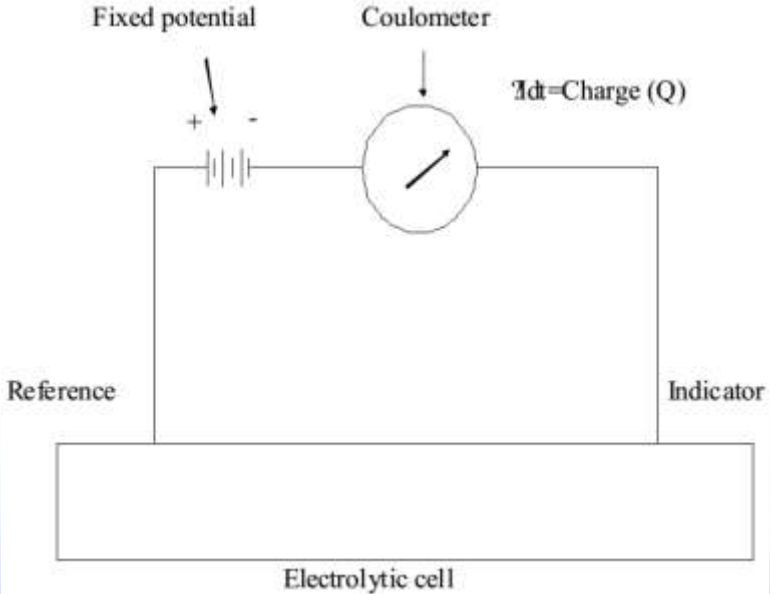
## Electrochemical Methods of Analysis
## Part II

## Common types of electrochemical measurements:

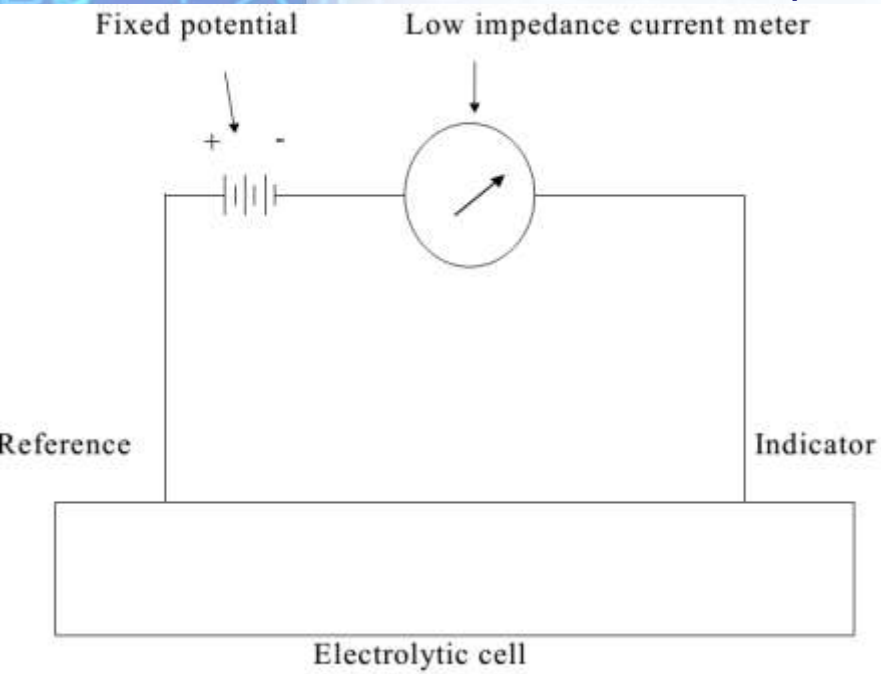
1. ***Potentiometry***: Measurement of a potential (voltage) at an electrode (relative to some reference) in the absence of current flow.



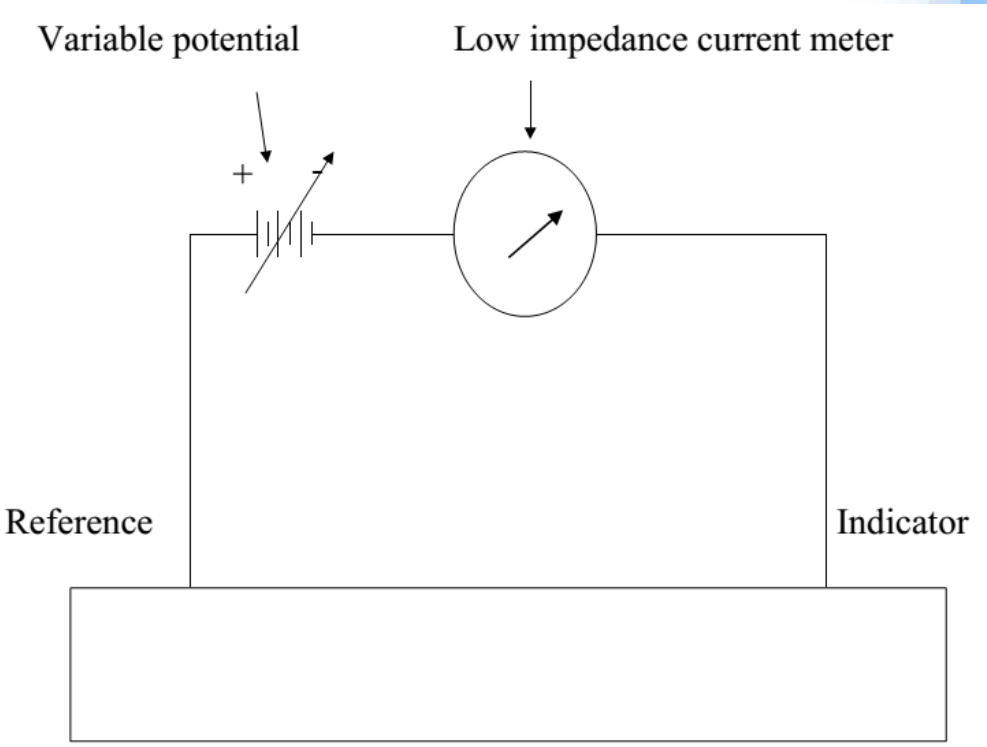

2. ***Coulometry***: Measurement of the quantity of electrical charge needed to convert an analyte from one oxidation state to another.




3. ***Amperometry***: Measurement of a limiting current at a constant potential.




4. ***Voltammetry***: Measurement of current as a function of applied potential.



# Coulometric Methods of Analysis

In potentiometry, the potential of an electrochemical cell under static conditions is used to determine an analyte's concentration. As seen in the preceding section, potentiometry is an important and frequently used quantitative method of analysis. Dynamic electrochemical methods, such as **coulometry, voltammetry, and amperometry,** in which current passes through the electrochemical cell, also are important analytical techniques.

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

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

$$Q = nFN$$

Equation is then used to determine the moles of analyte.

where *n is the number of electrons transferred per mole of analyte, F is Faraday's* constant (96487 C $mol^{-1}$), and *N is the moles of analyte. A coulomb is also equivalent* to an A×s; thus, for a constant current, *i, the charge is given as*

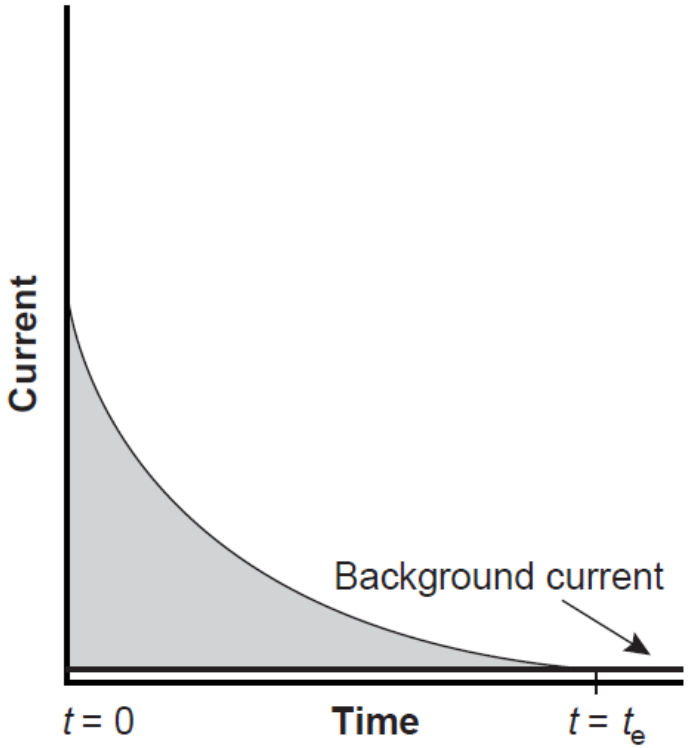
$$Q = it_e$$

where $t_e$ *is the electrolysis time.*

In coulometry, current and time are measured, and 2 equation are used to calculate *Q.*

# 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. Integrating the area under the curve, from *t = 0 until t = $t_e$, gives the total charge.*

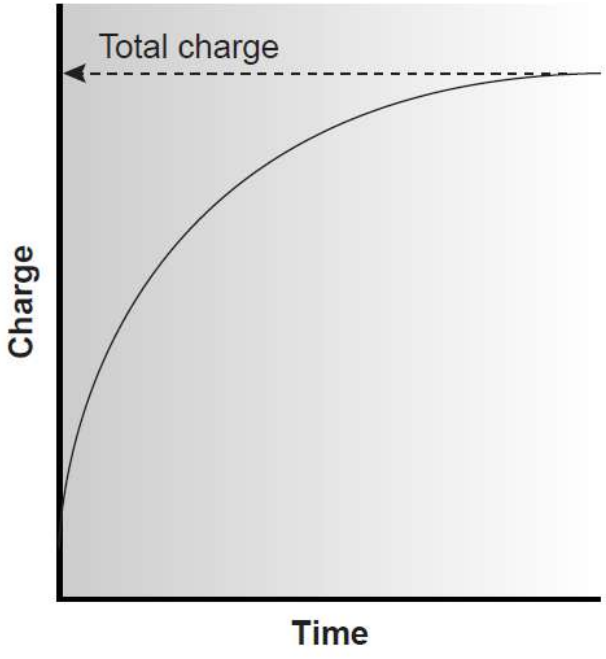



The current-time curve for controlled-potential coulometry in Figure shows that the current decreases continuously throughout electrolysis. An exhaustive electrolysis, therefore, may require a long time. Since time is an important consideration in choosing and designing analytical methods, the factors that determine the analysis time need to be considered. controlled-potential coulometry is carried out in small-volume electrochemical cells, using electrodes with large surface areas and with high stirring rates. A quantitative electrolysis typically requires approximately 30–60 min, although shorter or longer times are possible.

Current–time curve for controlled-potential coulometry.

## Instrumentation

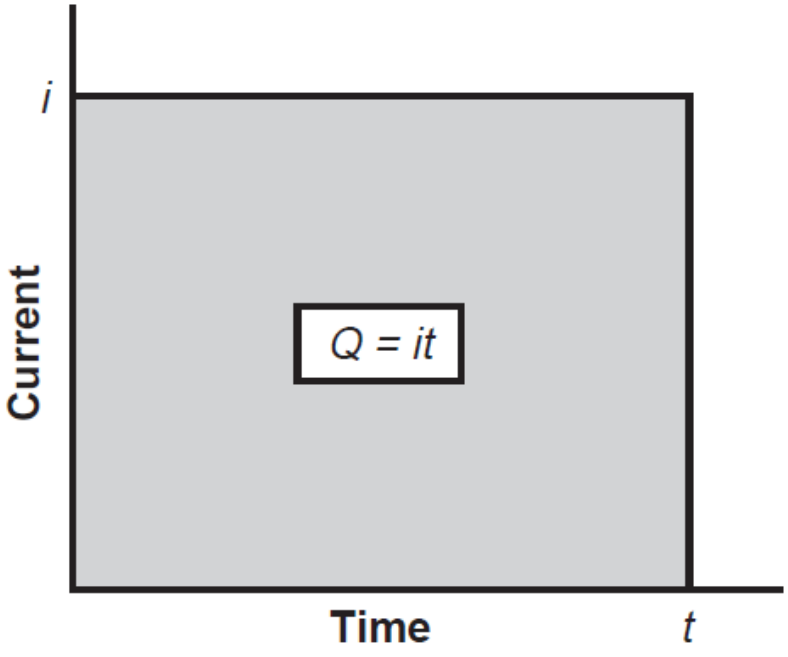
The potential in controlled-potential coulometry is set using a three-electrode ***potentiostat.*** Two types of working electrodes are commonly used: a Pt electrode manufactured from platinum-gauze and fashioned into a cylindrical tube, and an Hg pool electrode. The large overpotential for reducing $H_3O^+$ at mercury makes it the electrode of choice for analytes requiring negative potentials. For example, potentials more negative than –1 V versus the SCE are feasible at an Hg electrode (but not at a Pt electrode), even in very acidic solutions. The ease with which mercury is oxidized, however, prevents its use at potentials that are positive with respect to the SHE. Platinum working electrodes are used when positive potentials are required. The auxiliary electrode, which is often a Pt wire, is separated by a salt bridge from the solution containing the analyte.

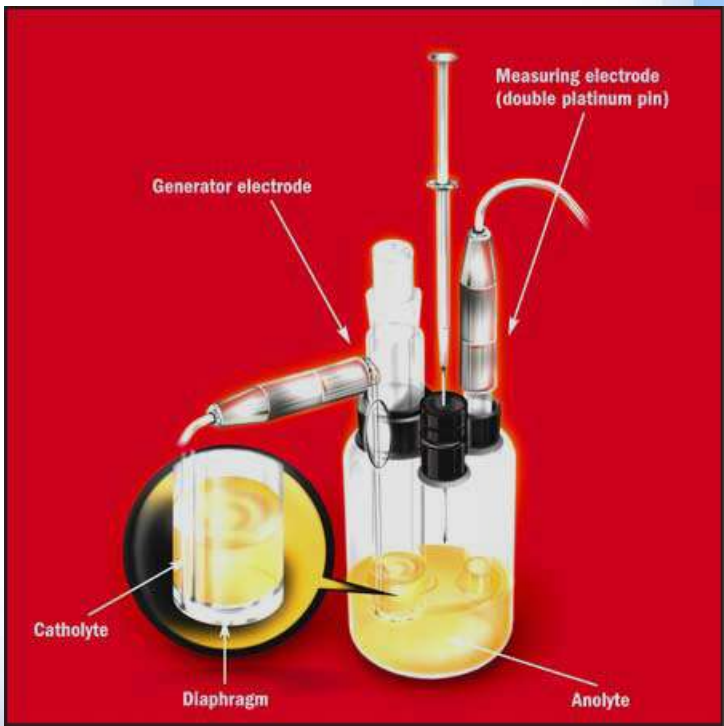



This is necessary to prevent electrolysis products generated at the auxiliary electrode from reacting with the analyte and interfering in the analysis. A saturated calomel or Ag/AgCl electrode serves as the reference electrode. The other essential feature of instrumentation for controlled-potential coulometry is a means of determining the total charge passed during electrolysis. One method is to monitor the current as a function of time and determine the areaunder the curve. Modern instruments, however, use electronic integration to monitor charge as a function of time. The total charge at the end of the electrolysis then can be read directly from a digital readout or from a plot of charge versus time.

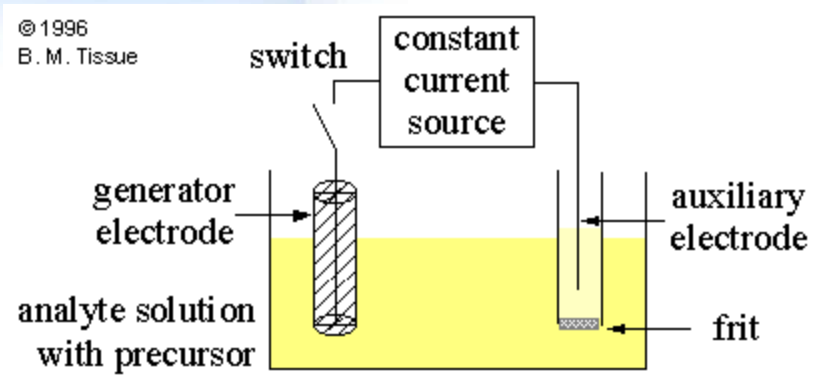
## Controlled-Current Coulometry

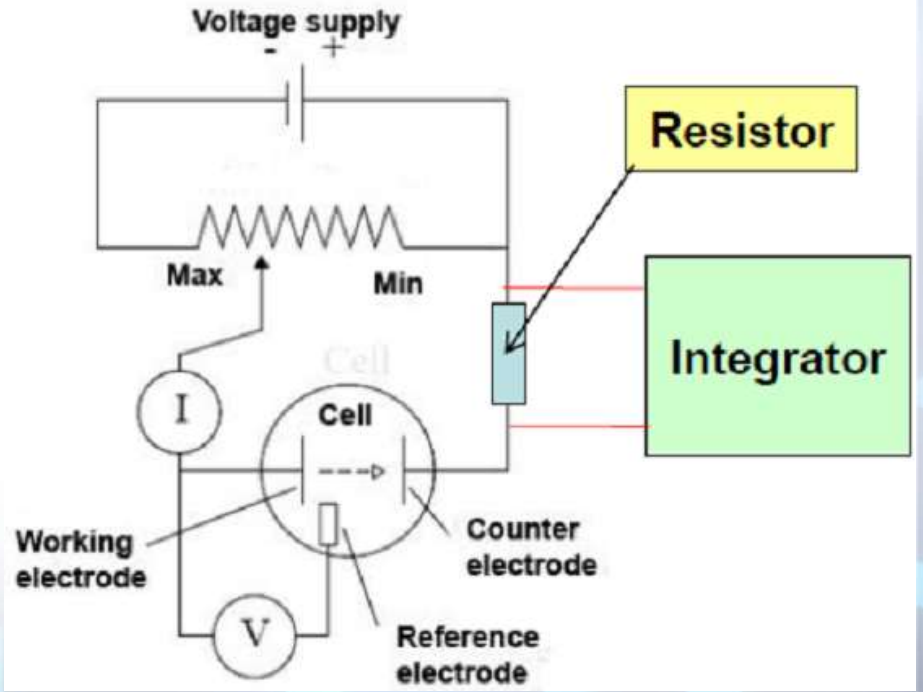
A second approach to coulometry is to use a constant current in place of a constant potential. Controlled-current coulometry, also known as ***amperostatic coulometry*** or ***coulometric titrimetry***, has two advantages over controlled-potential coulometry. First, using a constant current makes for a more rapid analysis since the current does not decrease over time. Thus, a typical analysis time for controlledcurrent coulometry is less than 10 min, as opposed to approximately 30–60 min for controlled-potential coulometry. Second, with a constant current the total charge is simply the product of current and time. A method for integratingthe current–time curve, therefore, is not necessary.



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%. The second problem 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. In controlled-current coulometry, however, a constant current continues to flow even when the analyte has been completely oxidized or reduced. A suitable means of determining the end-point of the reaction, $t_e$, is needed.



## Instrumentation

Controlled-current coulometry normally is carried out using a galvanostat and an electrochemical cell consisting of a working electrode and a counter electrode. 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. The counter electrode is isolated from the analytical solution by a salt bridge or porous frit to prevent its electrolysis products from reacting with the analyte. Alternatively, oxidizing or reducing the mediator can be carried out externally, and the appropriate products flushed into the analytical solution.

Mediator - A species that transfers electrons from the electrode to the analyte.

Controlled-current coulometric methods commonly are called coulometric titrations because of their similarity to conventional titrations.

***coulometric titrations*** **-** A titration in which the equivalence point is the time required for a constant current to completely oxidize or reduce the analyte.

# Coulometric Methods

*A.) Introduction:*

*1.) Coulometry:* electrochemical method based on the quantitative oxidation or reduction of analyte

- measure amount of analyte by measuring amount of current and time required to complete reaction

  - charge = current (i) x time in coulombs

- electrolytic method → external power added to system

*2.) Example:*

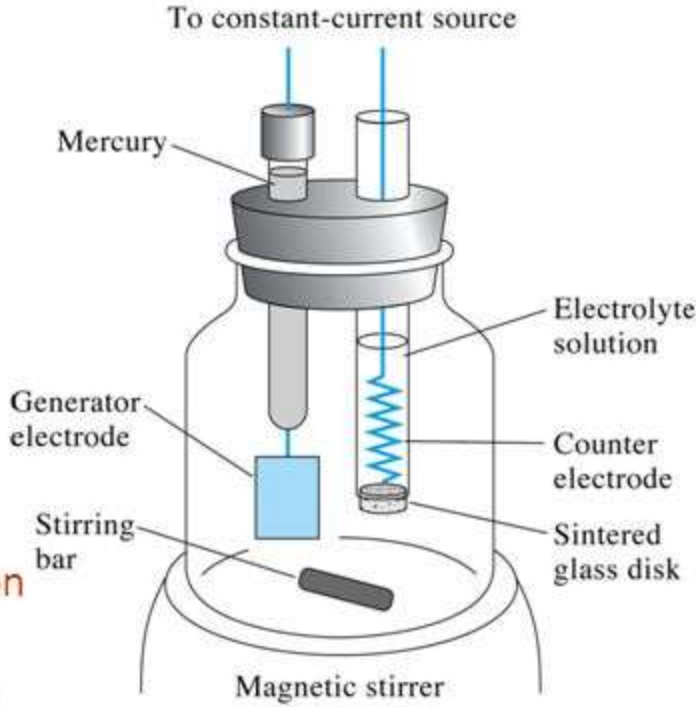
- Coulometric Titration of $Cl^-$

- use Ag electrode to produce $Ag^+$

$$Ag\ (s) \leftrightarrow Ag^+ + e^-$$

$$Ag^+ + Cl^- \leftrightarrow AgCl\ (ppt.)$$

- measure $Ag^+$ in solution by 2nd electrode
- only get complete circuit when $Ag^+$ exists in solution
- only occurs after all $Cl^-$ is consumed
- by measuring amount of current and time required to complete reaction can determine amount of $Cl^-$



## Quantitative Applications

Coulometry may be used for the quantitative analysis of both inorganic and organic compounds. The majority of controlled-potential coulometric analyses involve the determination of inorganic cations and anions, including trace metals and halides.

The use of a mediator makes controlled-current coulometry a more versatile analytical method than controlled-potential coulometry. For example, the direct oxidation or reduction of a protein at the working electrode in controlled-potential coulometry is difficult if the protein's active redox site lies deep within its structure. The controlled-current coulometric analysis of the protein is made possible, however, by coupling its oxidation or reduction to a mediator that is reduced or oxidized at the working electrode. Controlled-current coulometric methods have been developed for many of the same analytes that may be determined by conventional redox titrimetry.

The absolute amount of analyte in a coulometric analysis is determined by applying Faraday's law.

## Evaluation

### *Scale of Operation*

Coulometric methods of analysis can be used to analyze small absolute amounts of analyte. In controlled-current coulometry, for example, the moles of analyte consumed during an exhaustive electrolysis carried out with a constant current of 100 μA for 100 s, therefore, consumes only $1 \times 10^{-7}$ mol of analyte if n = 1.

### *Accuracy*

These measurement errors suggest that accuracies of 0.1–0.3% are feasible. The limiting factor in many analyses, therefore, is current efficiency.

### *Precision*

Precision is determined by the uncertainties of measuring current, time, and the end point in controlled-current coulometry and of measuring charge in controlled-potential coulometry. Precisions of ±0.1–0.3% are routinely obtained for coulometric titrations, and precisions of ±0.5% are typical for controlled-potential coulometry.

### *Time, Cost, and Equipment*

Controlled-potential coulometry is a relatively time consuming analysis, with a typical analysis requiring 30–60 min. Coulometric titrations, require only a few minutes and are easily adapted for automated analysis. Commercial instrumentation for both controlled-potential and controlled-current coulometry is available and is relatively inexpensive. Low-cost potentiostats and constant-current sources are available for less than $1000.

Advantages of coulometric titration versus volumetric titration:

1. No need to prepare, standardize, store standard sol'n.
2. Can prepare unstable reagents, since they react almost as soon as they are generated – e.g., $Cl_2$, $Br_2$
3. Straightforward to generate tiny quantities of reagent with good accuracy since it is easy to control current and time electronically.
4. A single coulometric titration apparatus can be used for redox, acid/base, precipitation, complexometric, etc., titrations

advantage of volumetric titrations - simple

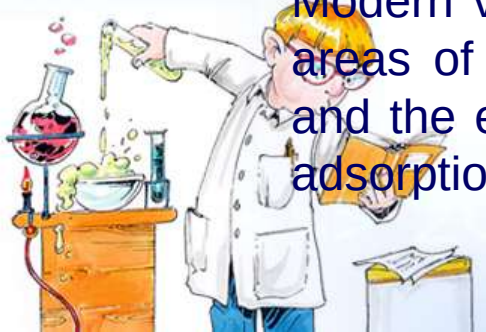
The main advantage is that the analyses can be termed as ***absolute*** and thus require no prior calibration, the accurate quantitative measurement being based upon accepted physical constant.

The term **voltammetry** refers to a group of electroanalytical methods in which we acquire information about the analyte by measuring current in an electrochemical cell as a function of applied potential. We obtain this information under conditions that promote polarization of a small indicator, or working, electrode. When current proportional to analyte concentration is monitored at a fixed potential, the technique is called **amperometry.** To enhance polarization, working electrodes in voltammetry and amperometry have surface areas of a few square millimeters at the most and in some applications, a few square micrometers or less. Voltammetry is widely used by inorganic, physical, and biological chemists for fundamental studies of oxidation and reduction processes in various media, adsorption processes on surfaces, and electron transfer mechanisms at chemically modified electrode surfaces.

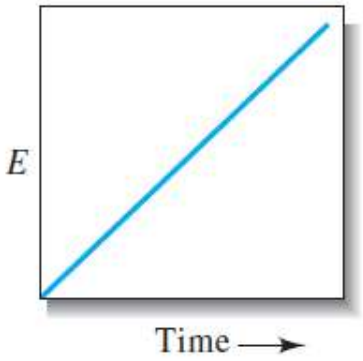
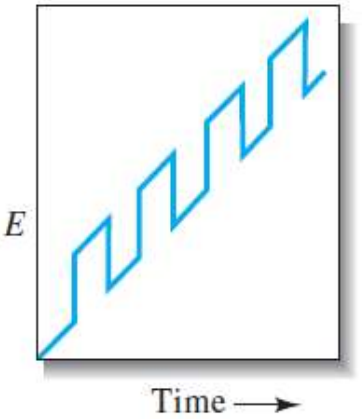
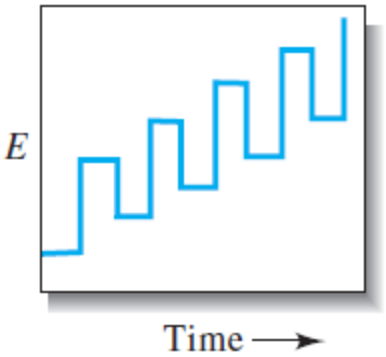
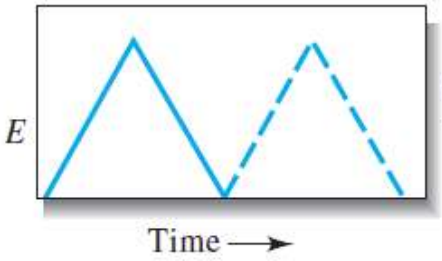
**Voltammetry**

- Methods based on an electrolytic cell
- Apply potential or current to electrochemical cell & concentrations change at electrode surface due to oxidation & reduction reactions
- Can have 2 or 3 electrodes
- Stirred or unstirred solution
- Measure current or voltage

Historically, the field of voltammetry developed from ***polarography,*** which is a particular type of voltammetry that was invented by the Czechoslovakian chemist Jaroslav Heyrovsky in the early 1920s. Polarography differs from other types of voltammetry in that the working electrode is the unique ***dropping mercury electrode***. At one time, polarography was an important tool used by chemists for the determination of inorganic ions and certain organic species in aqueous solutions. In recent years, the number of applications of polarography in the analytical laboratory has declined dramatically. This decline has been largely a result of concerns about the use of mercury in the laboratory and possible contamination of the environment, the somewhat cumbersome nature of the apparatus, and the broad availability of faster and more convenient (mainly spectroscopic) methods. While polarography has declined in importance, voltammetry and amperometry at working electrodes other than the dropping mercury electrode have grown at an astonishing pace. Furthermore, voltammetry and amperometry coupled with liquid chromatography have become powerful tools for the analysis of complex mixtures. Modern voltammetry also continues to be an excellent tool in diverse areas of chemistry, biochemistry, materials science and engineering, and the environmental sciences for studying oxidation, reduction, and adsorption processes.



In voltammetry, a variable potential excitation signal is impressed on a working electrode in an electrochemical cell. This excitation signal produces a characteristic current response, which is the measurable quantity.

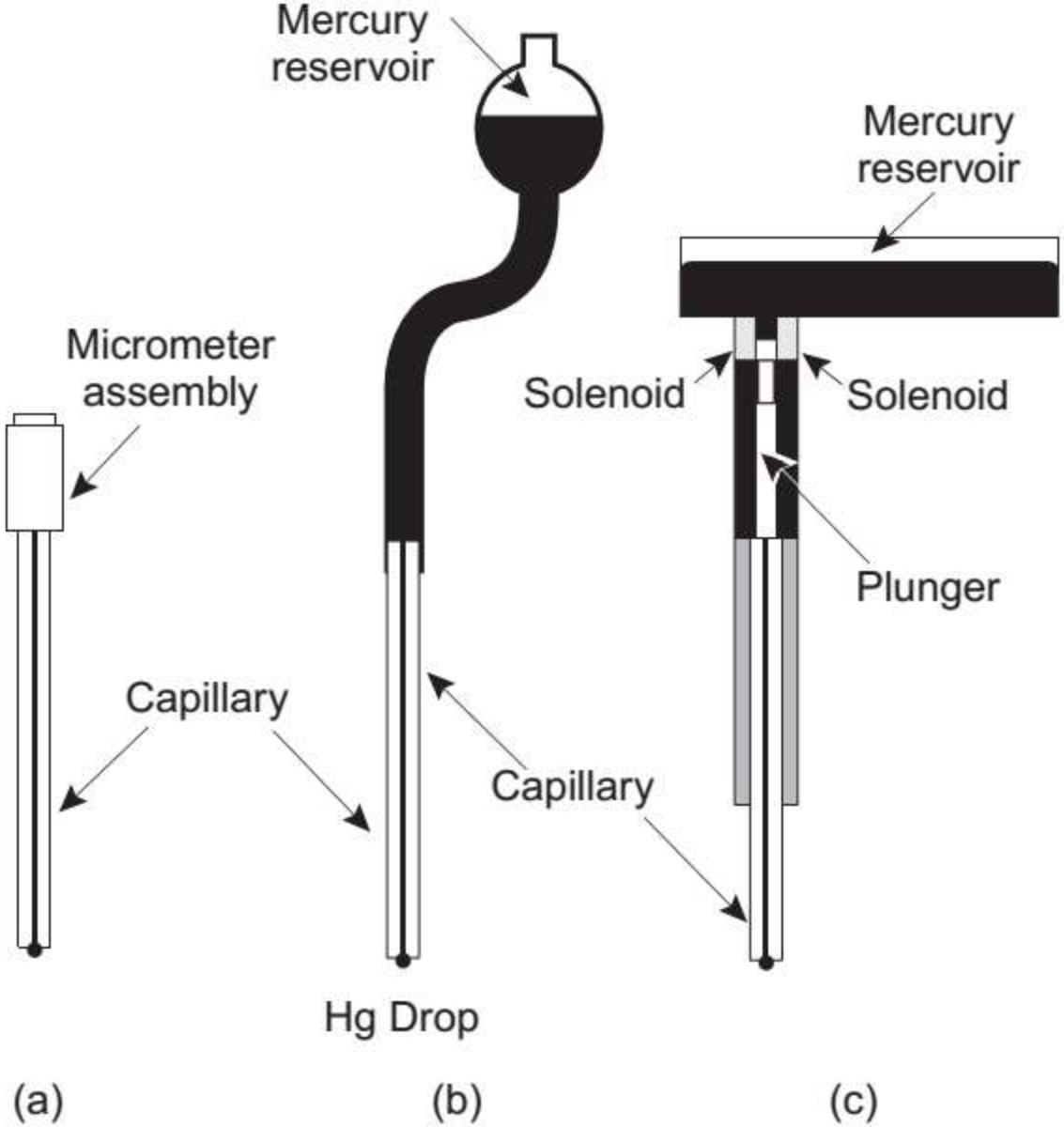
| Name | Waveform | Type voltammetry |
|---|---|---|
| (a) Linear scan |   | Polarography<br>Hydrodynamic voltammetry |
| (b) Differential pulse |   | Differential-pulse polarography |
| (c) Square wave |   | Square-wave voltammetry |
| (d) Triangular |   | Cyclic voltammetry |

Voltage versus time excitation signals used in voltammetry.

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. 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.

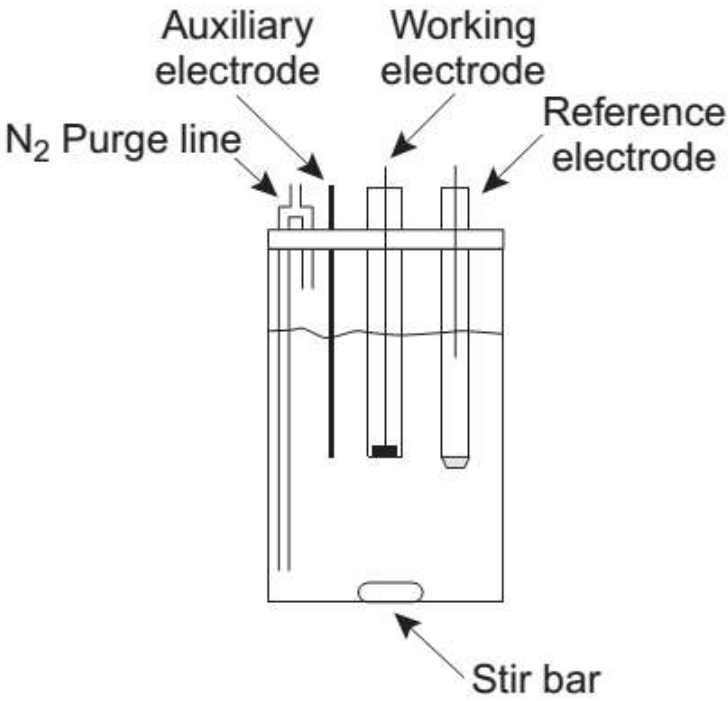
Although early voltammetric methods relied on the use of only two electrodes, modern voltammetry makes use of a three-electrode potentiostat. A time-dependent potential excitation signal is applied to the working electrode, changing its potential relative to the fixed potential of the referenceelectrode. The resulting current between the working and auxiliary electrodes is measured. The auxiliary electrode is generally a platinum wire, and the SCE and Ag/AgCl electrode are common reference electrodes.

Several different materials have been used as working electrodes, including mercury, platinum, gold, silver, and carbon. The earliest voltammetric techniques, including polarography, used mercury for the working electrode. Since mercury is a liquid, the working electrode often consists of a drop suspended from the end of a capillary tube (Figure). In the hanging mercury drop electrode, or 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. In the dropping mercury electrode, or 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. The static mercury drop electrode, or 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.



## Current 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.*** Since the reaction of interest occurs at the working electrode, the classification of current is based on this reaction. A current due to the analyte's reduction is called a ***cathodic current*** and, by convention, is considered positive. ***Anodic currents*** are due to oxidation reactions and carry a negative value.

Although the applied potential at the working electrode determines if a faradaic current flows, the magnitude of the current is determined by the rate of the resulting oxidation or reduction reaction at the electrode surface. Two factors contribute to the rate of the electrochemical reaction: the rate at which the reactants and products are transported to and from the surface of the electrode, and the rate at which electrons pass between the electrode and the reactants and products in solution.

## Influence of Mass Transport on the Faradaic Current

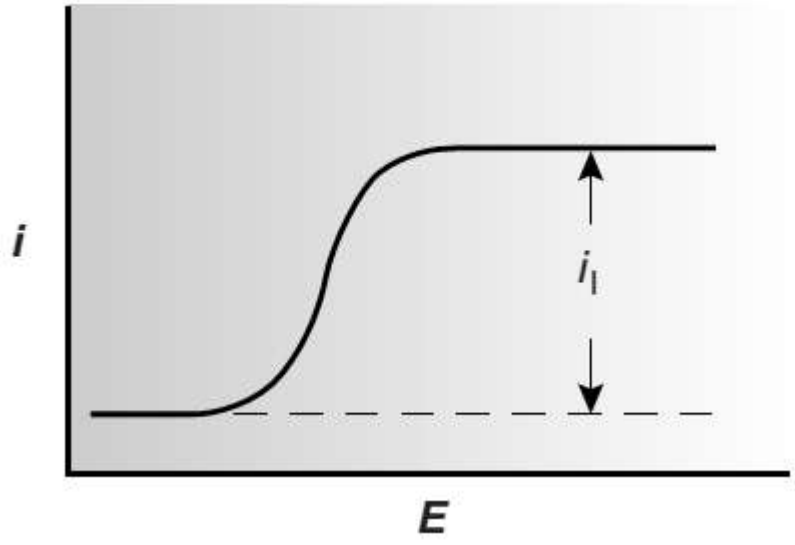
There are three modes of ***mass transport*** that influence the rate at which reactants and products are transported to and from the electrode surface: diffusion, migration, and convection. ***Diffusion*** from a region of high concentration to a region of low concentration occurs whenever the concentration of an ion or molecule at the surface of the electrode is different from that in bulk solution. When the potential applied to the working electrode is sufficient to reduce or oxidize the analyte at the electrode surface, a concentration gradient is established. The volume

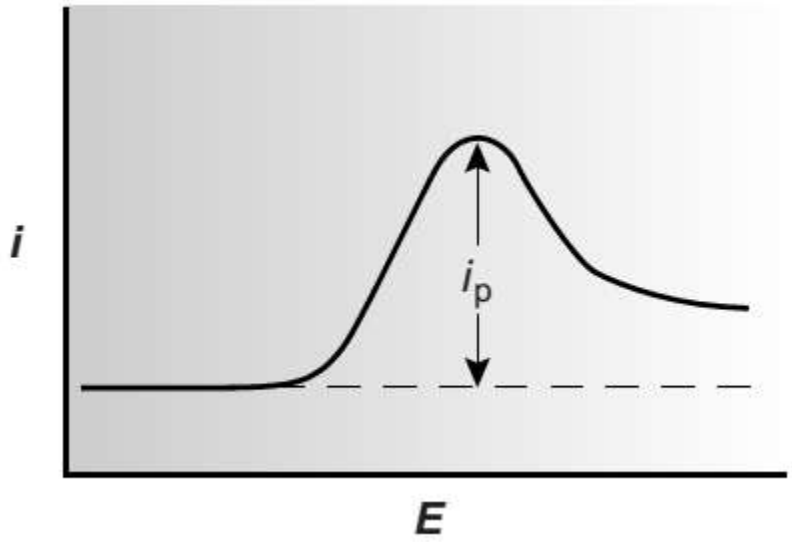
of solution in which the concentration gradient exists is called the ***diffusion layer***. Without other modes of mass transport, the width of the diffusion layer, δ, increases with time as the concentration of reactants near the electrode surface decreases. The contribution of diffusion to the rate of mass transport, therefore, is time-dependent.

***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. Other methods include rotating the electrode and incorporating the electrode into a flow cell. The final mode of mass transport is ***migration***, which 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.

# Shape of Voltammograms

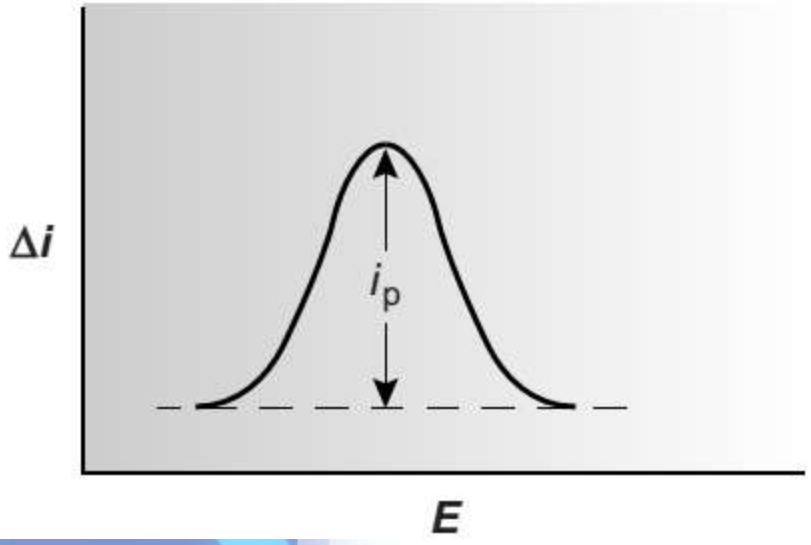
The shape of a voltammogram is determined by several experimental factors, the most important of which are how the current is measured and whether convection is included as a means of mass transport.




The voltammogram is characterized by a current that increases from the background residual current to a limiting current at potentials at which the analyte is oxidized or reduced. A limiting current implies that the thickness of the diffusion layer remains constant. The simplest method for obtaining a limiting current is to stir the solution, which can be accomplished with a magnetic stir bar, or by rotating the electrode. Voltammetric techniques that include convection by stirring are called ***hydrodynamic voltammetry***. When convection is absent, the thickness of the diffusion layer increases with time, resulting in a peak current in place of a limiting current.

In both voltammograms, the current is monitored as a function of the applied potential.



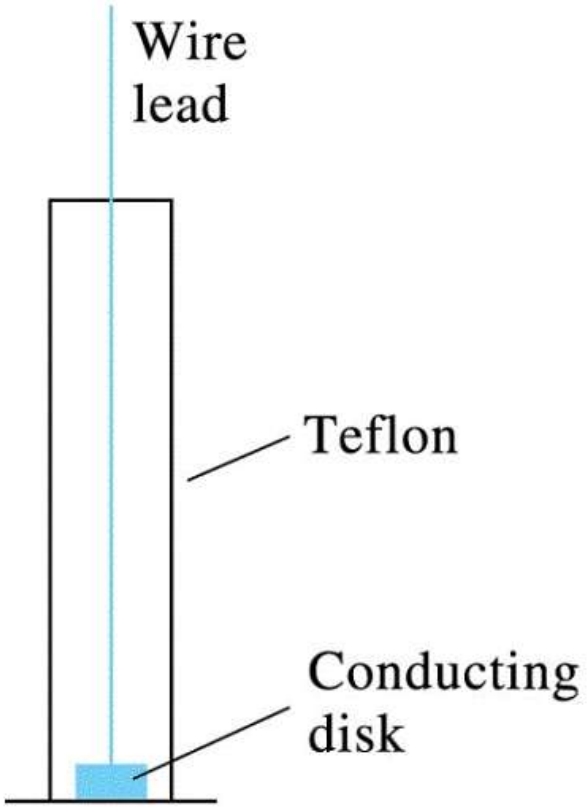

the change in current followinga change in potential may be measured. The resulting voltammogram, also is characterized by a peak current.

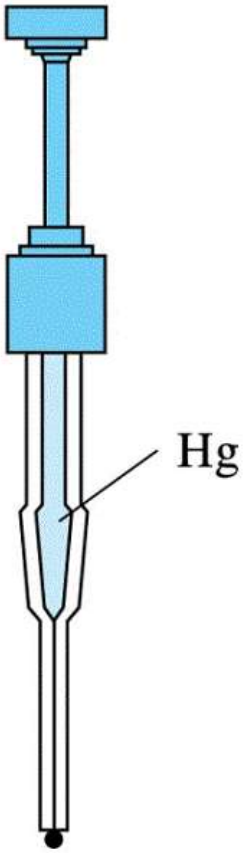
Quantitative information is obtained by relating current to the concentration of analyte in the bulk solution.

Qualitative information is obtained from the voltammogram by extracting the standard-state potential for the redox reaction.

## Linear sweep voltammetry:

- Potential of working electrode changed at a rate of mV/s
- Excess of nonreactive supporting electrolyte to minimize migration (motion of analyte ions due to external field).
- Reference electrode connected via a high impedance voltmeter. Current flows primarily between working electrode and counter electrode.



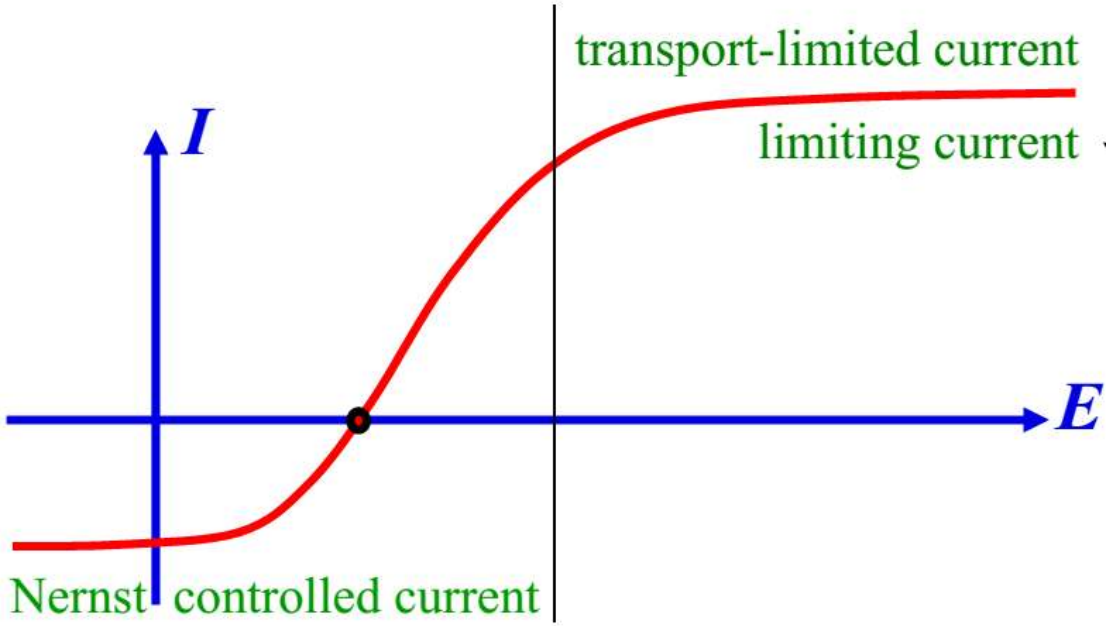




Typical working electrodes are a disk electrode (left) and a mercury electrode (right).

## Theory

assume Ox + n e- $\rightarrow$Red

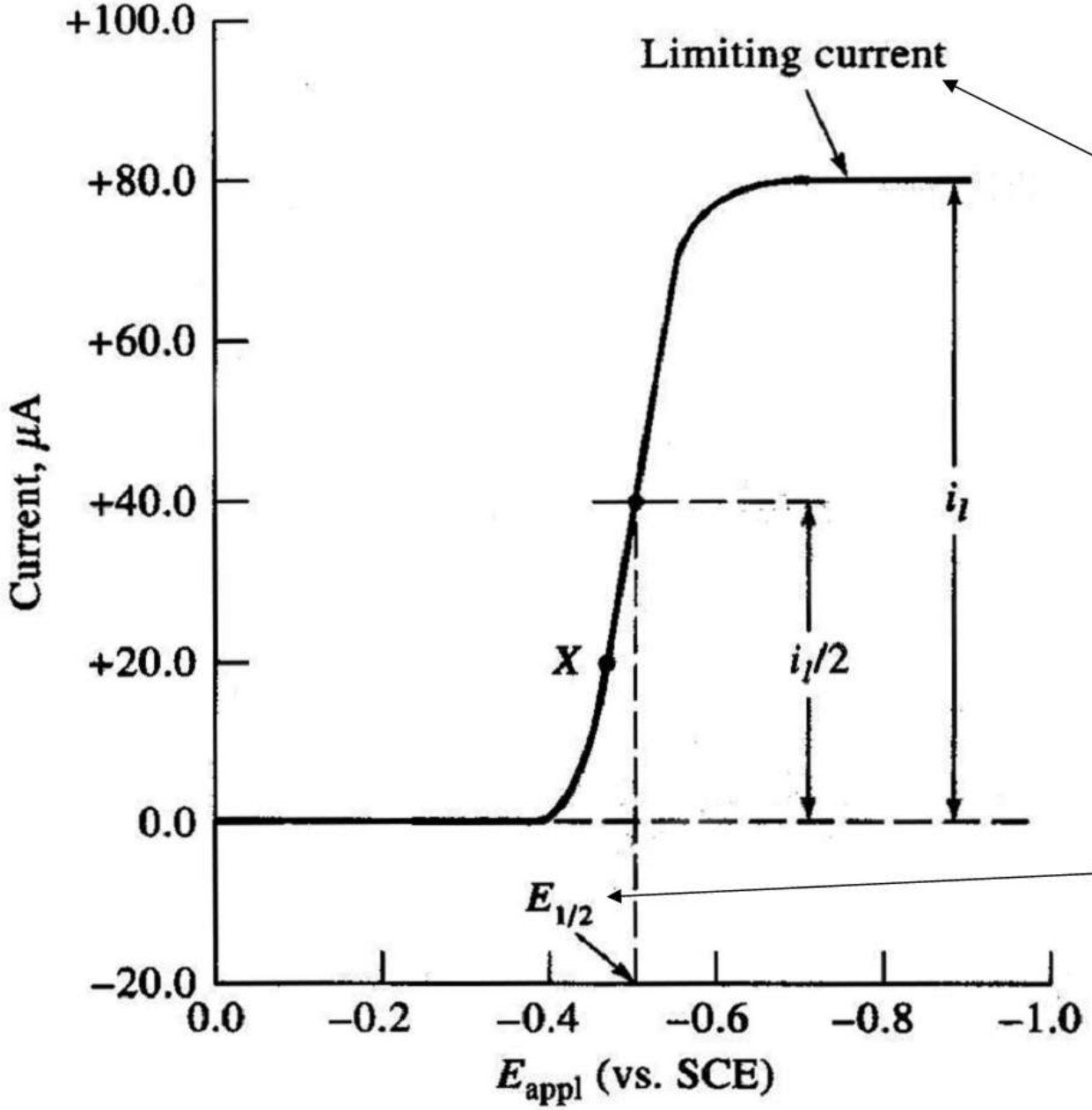
- both Ox and Red are soluble
- reversible reaction (electrochemically)
- potential varies
- Define - Limiting Current as steady state current when [Ox] = 0 at electrode surface i.e., applied potential is sufficiently cathodic such that all Ox is reduced at electrode




$$I = \frac{nFADC_{bulk}}{\delta}$$

Gives quantitative information

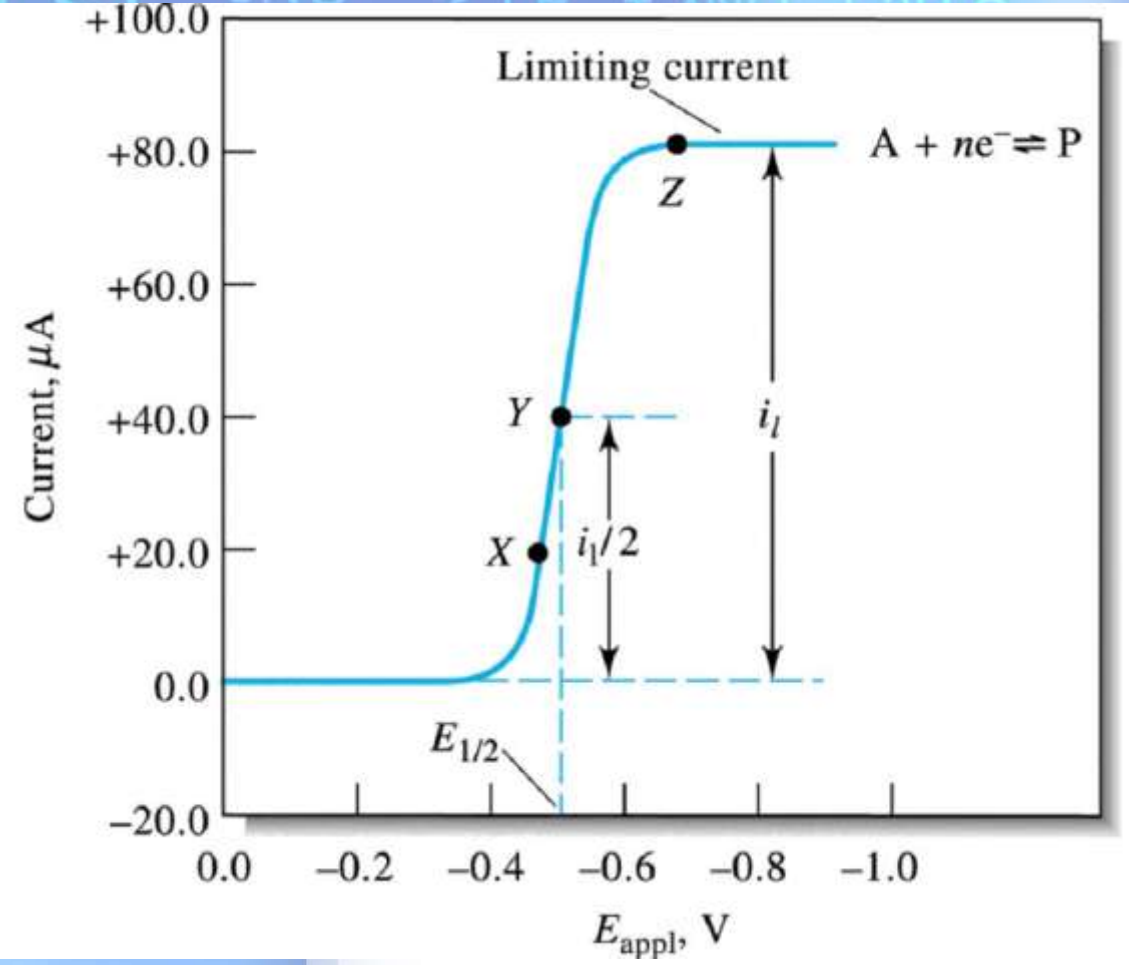
$$E = E^{o} - \frac{RT}{nF} \ln \frac{[Red]}{[Ox]}$$




quantitative information

qualitative information

Linear-scan voltammogram → for stirred solution




∫-shaped curve is referred to as a voltammetric wave.
Point Z – limiting current,
il – current limited by polarization
il = kc, k is a constant, c = analyte concentration

The point at which i = il/2, E1/2, is referred to as the ***half-wave potential*** and it is approximately equal to the standard potential for the half-reaction. This value can be used for identification purposes. Hence linear sweep voltammetry can be both a qualitative and quantitative technique.

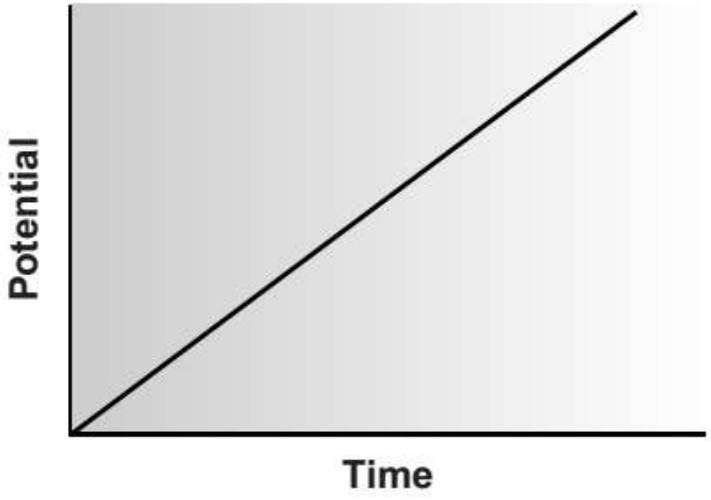
## Uses of linear sweep hydrodynamic voltammetry:

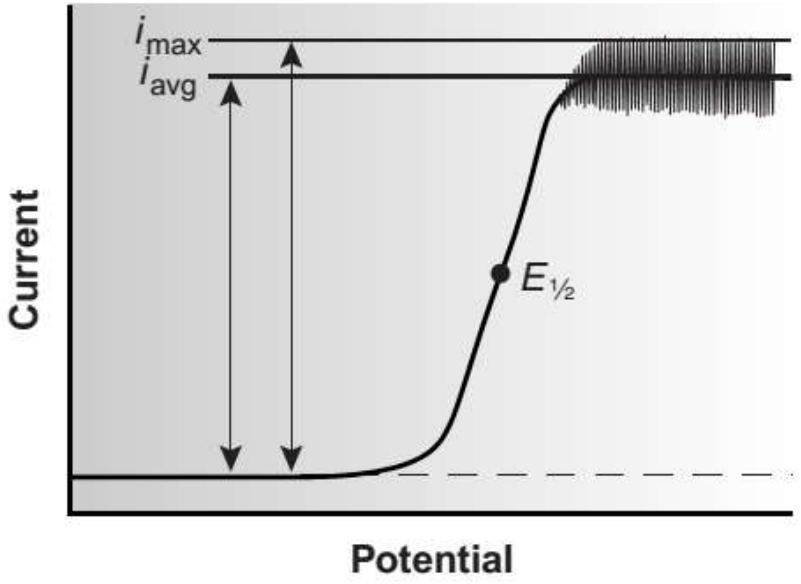
1.) For oxidizable or reducible species in flowing streams, as in the outlet of a liquid chromatograph

2.) Sensors – cells established to be selective for particular species (e.g., oxygen, glucose) usually a fixed V msmt (amperometry)

## Polarography

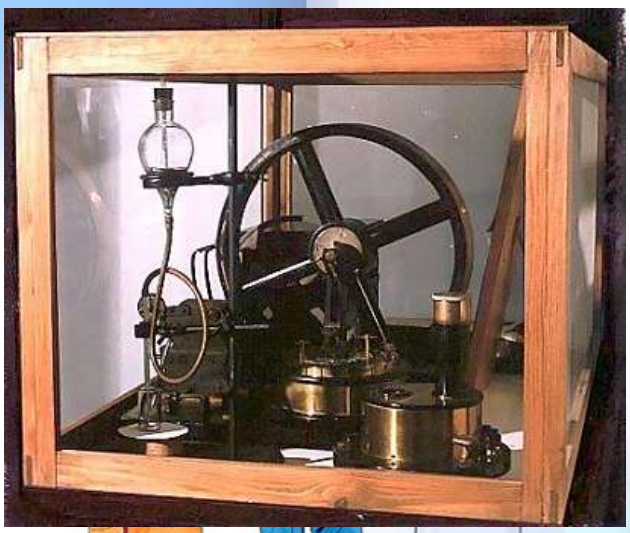
The earliest voltammetric experiment was normal polarography at a dropping mercury electrode. In normal polarography the potential is linearly scanned, producing voltammograms such as that shown in Figure. Although polarography takes place in an unstirred solution, a limiting current is obtained because 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.



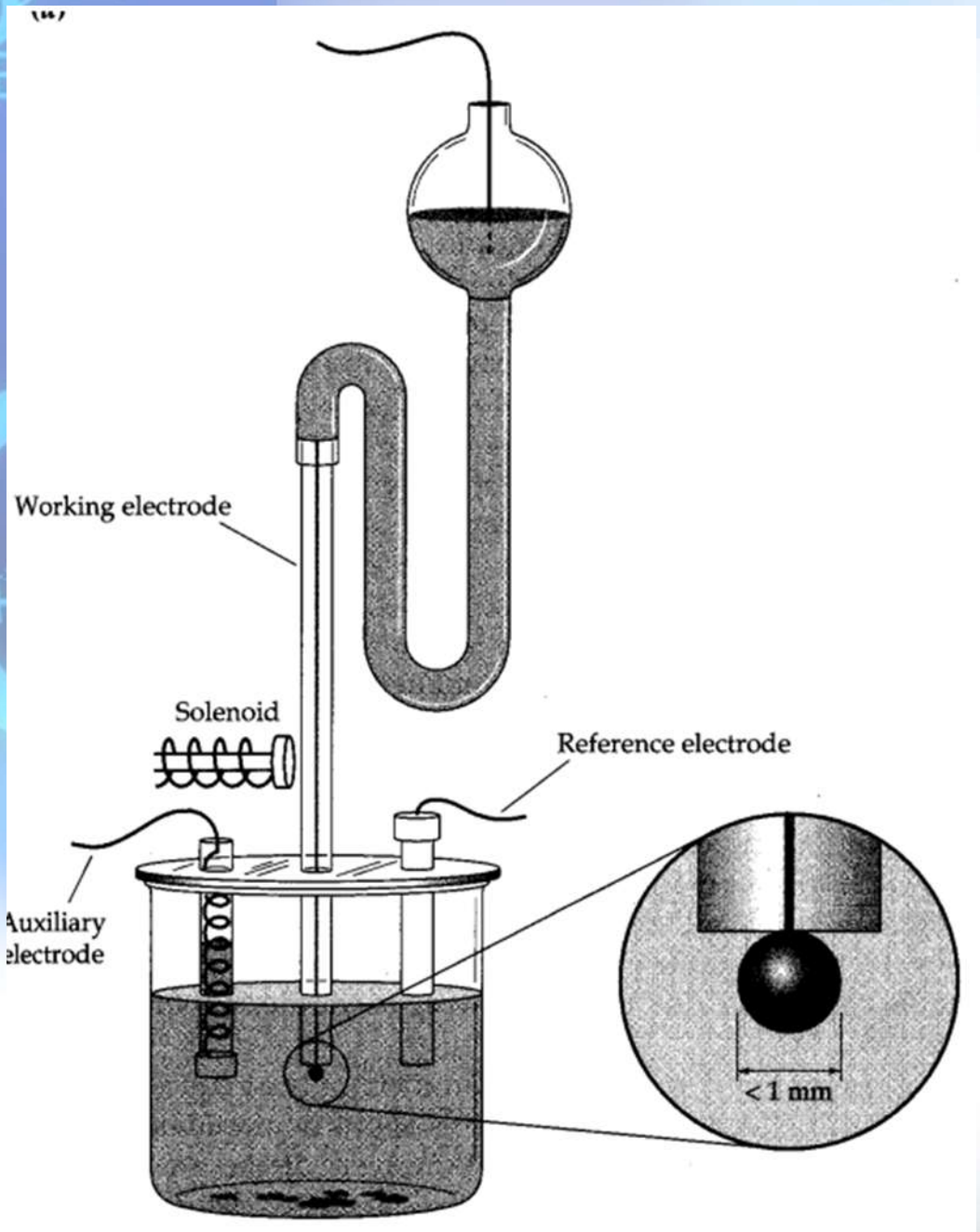



Jaroslav Heyrovský was the inventor of the polarographic method, and the father of electroanalytical chemistry, for which he was the recipient of the Nobel Prize. His contribution to electroanalytical chemistry can not be overestimated. All modern voltammetric methods used now in electroanalytical chemistry originate from polarography.

**Polarography** uses mercury droplet electrode that is regularly renewed during analysis.
Applications: Metal ions (especially heavy metal pollutants) - high sensitivity. Organic species able to be oxidized or reduced at electrodes: quinones, reducing sugars and derivatives, thiol and disulphide compounds, oxidation cofactors (coenzymes etc), vitamins, pharmaceuticals. Alternative when spectroscopic methods fail.



On February 10, 1922, the "polarograph" was born as Heyrovský recorded the current-voltage curve for a solution of 1 M NaOH.
Heyrovský correctly interpreted the current increase between -1.9 and -2.0 V as being due to deposition of Na+ ions, forming an amalgam.




Spherical Hg drop formed at the end of a glass capillary.

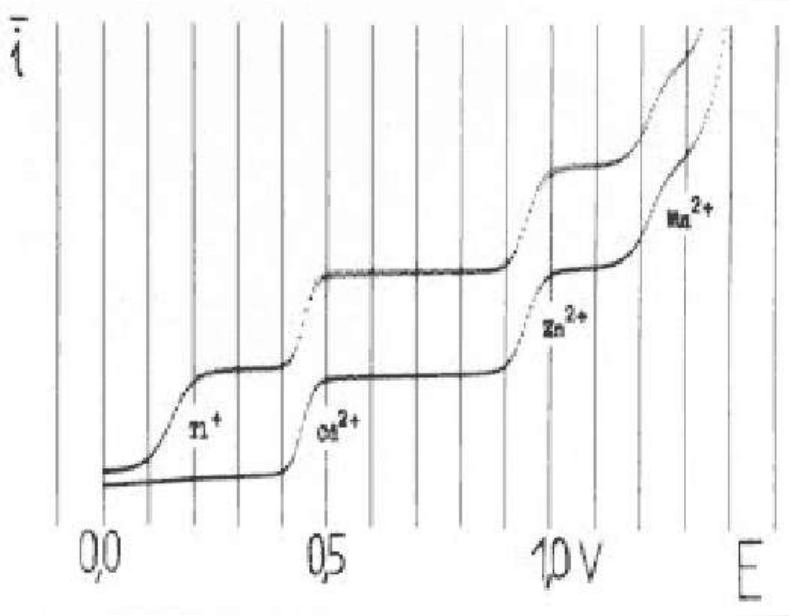
This is used as a working electrode. Linear potential ramp used as perturbation. Resulting current response examined as function of potential.

Using the dropping mercury electrode (DME) or the static mercury drop electrode (SMDE)

the drop size and drop lifetime can be accurately controlled. Each data point measured at a new Hg drop ensuring constant surface renewal.

## Ilkovich equation

Typical polarographic curves (dependence of current I on the voltage E applied to the electrodes. The small oscillations indicate the slow dropping of mercury): lower curve - the supporting solution of ammonium chloride and hydroxide containing small amounts of cadmium, zinc and manganese, upper curve - the same after addition of small amount of thallium.




Ilkovich equation

Drop time

$$i_D = 607 n D^{1/2} m^{2/3} t^{1/6} c^{\infty}$$

Mass flow rate ($gs^{-1}$)

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

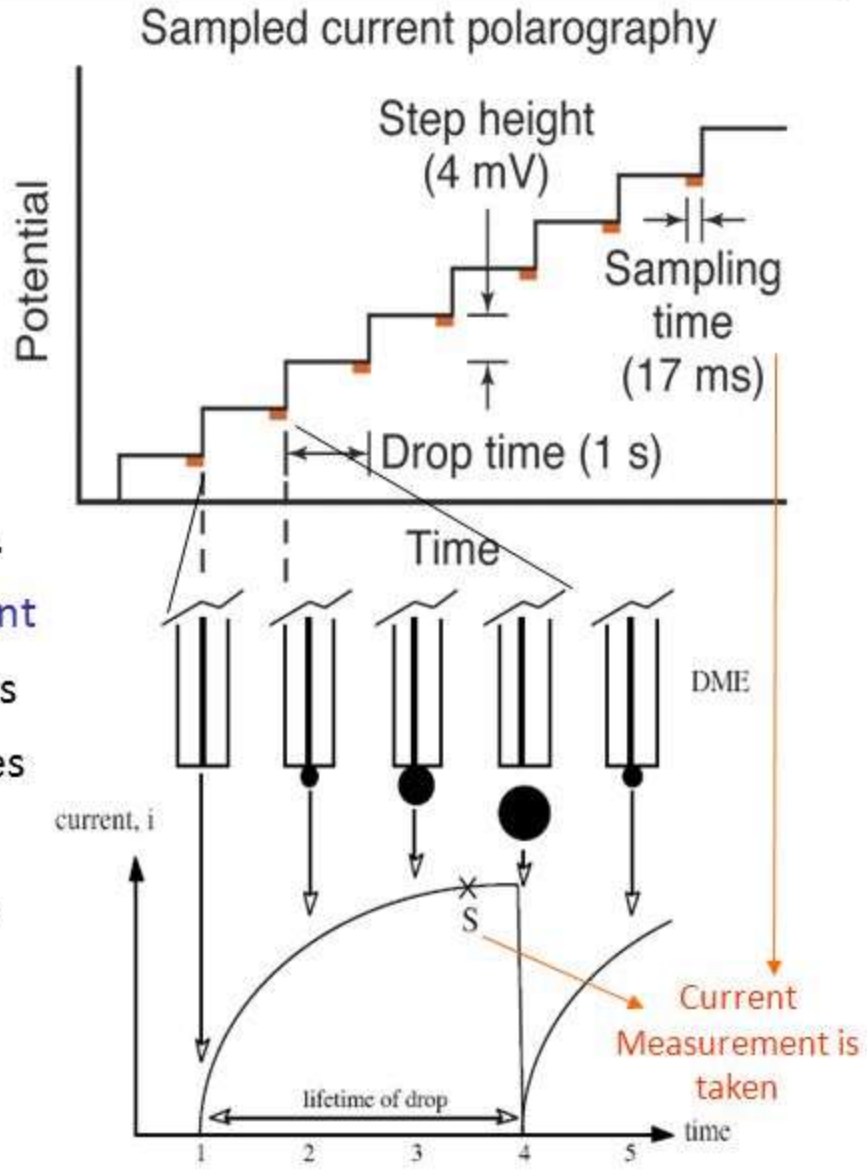
# 3. The Polarographic experiment

## Voltage Scan

- ✓ Potential is varied with time.
- ✓ After each new drop of Hg is dispensed, the voltage is made more negative by 4 mV (Staircase voltage ramp).

## Current during the life time of the drop

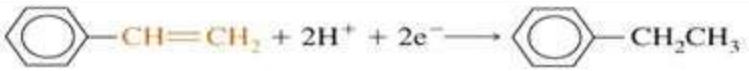
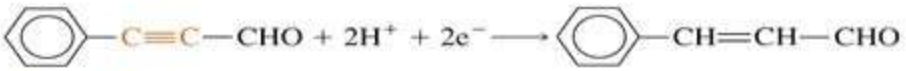
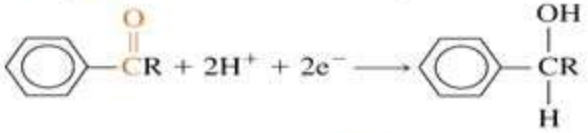
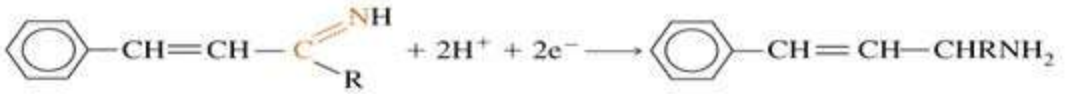
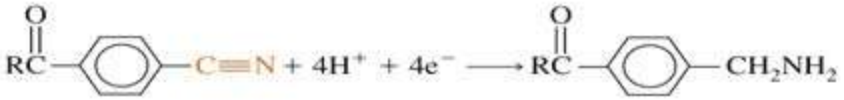
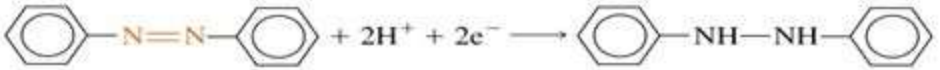
- ✓ The current oscillates permanently between a minimum and maximum value.
- ✓ This behavior is caused by the non-constant electrode surface area. The current rises as the drop surface area grows, and decreases as the drop falls and then rises again.
- ✓ Current is measured during the last 17 ms of the life of each Hg drop (sampled current).



# 10. Applications of polarography

Polarography can be used for the determination of many inorganic ions than can be reduced in the range of +0.4 and -1.2 V. Mainly most of the **transition metals**, **lanthanides and actinides** can be determined by polarography. It can be also used for quantitative analysis of a wide variety of **electroactive organic functional groups**. It is possible to analyze simultaneously a mixture of 3 or 4 electroactive ions.

**Table 17-2** Polarographic behavior of various functional groups

| Group | Reaction |
|---|---|
| C=C |  |
| C≡C |  |
| C—X | $RCH_2{-}Br + H^+ + 2e^- \rightarrow RCH_3 + Br^-$ |
| C=O |  |
| C=N |  |
| C≡N |  |
| N=N |  |
| N=O | $R{-}NO + 2H^+ + 2e^- \rightarrow RNHOH$ |
| $NO_2$ | $RNO_2 + 4H^+ + 4e^- \rightarrow RNHOH + H_2O$ |

## 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.

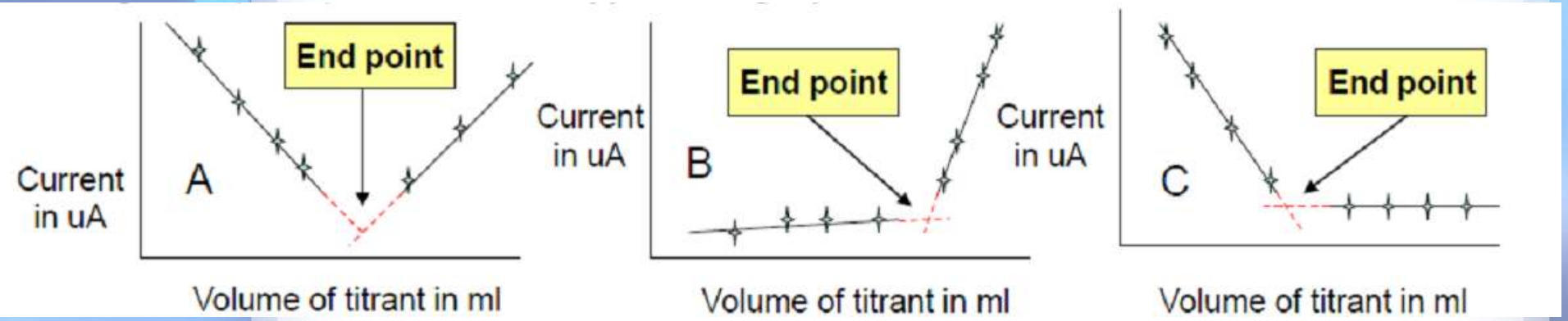



**Figure (9.31A) shows the situation where both the analyte and the titrant are electroactive at the chosen potential;**
**Figure (9.31B) shows only the titrant to be electroactive;**
**Figure (9.31C) shows only the analyte to be electroactive.**

# Evaluation

## Accuracy

The accuracy of a voltammetric analysis often is limited by the ability to correct for residual currents, particularly those due to charging. For analytes at the parts-per-million level, accuracies of ±1–3% are easily obtained.

## Precision

Precision is generally limited by the uncertainty in measuring the limiting or peak current. Under most experimental conditions, precisions of ±1–3% can be reasonably expected.

Selectivity Selectivity in voltammetry is determined by the difference between half-wave potentials or peak potentials, with minimum differences of ±0.2–0.3 V required for a linear potential scan, and ±0.04–0.05 V for differential pulse voltammetry.

## Time, Cost, and Equipment

Commercial instrumentation for voltammetry ranges from less than $1000 for simple instruments to as much as $20,000 for more sophisticated instruments. In general, less expensive instrumentation is limited to linear potential scans, and the more expensive instruments allow for more complex potential-excitation signals using potential pulses. Except for stripping voltammetry, which uses long deposition times, voltammetric analyses are relatively rapid.

# THANK YOU

Good luck