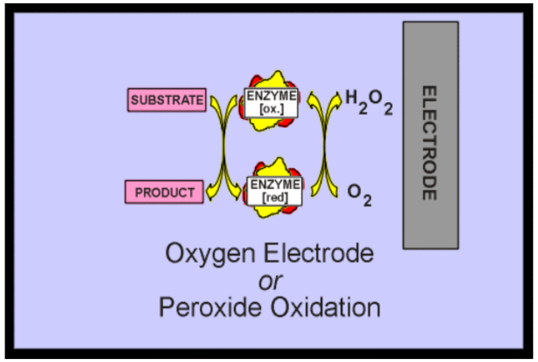
# JS CH3403 Interdisciplinary Chemistry Module 1. 2013/2014.
# Analytical Chemistry: Electrochemical methods of analysis.

## Basic Electroanalytical Chemistry.
## Potentiometric, Voltammetric and Coulometric measurement techniques.





**Professor Mike Lyons**
School of Chemistry TCD
Room 3.2 Main Chemistry Building
melyons@tcd.ie

# Electro-analytical Chemistry.

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

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

Electro-analytical chemists at work !
Beer sampling.
Sao Paulo Brazil 2004.

EU-LA Project MEDIS : Materials Engineering For the design of Intelligent Sensors.

# Outline of Lectures

- Introduction to electroanalytical chemistry: basic ideas
- Potentiometric methods of analysis
- Amperometric methods of analysis
- Coulombic methods of analysis

J. Wang, Analytical Electrochemistry,
3rd edition. Wiley, 2006
R.G. Compton, C.E. Banks, Understanding Voltammetry,
2nd edition, Imperial College Press,2011.
C.M.A. Brett, A.M.Oliveira Brett,
Electrochemistry: Principles, methods and applications,
Oxford Science Publications, 2000.

# Why Electroanalytical Chemistry ?

Electroanalytical methods have certain advantages over other analytical methods. Electrochemical analysis allows for the determination of different oxidation states of an element in a solution, not just the total concentration of the element. Electroanalytical techniques are capable of producing exceptionally low detection limits and an abundance of characterization information including chemical kinetics information. The other important advantage of this method is its low cost.

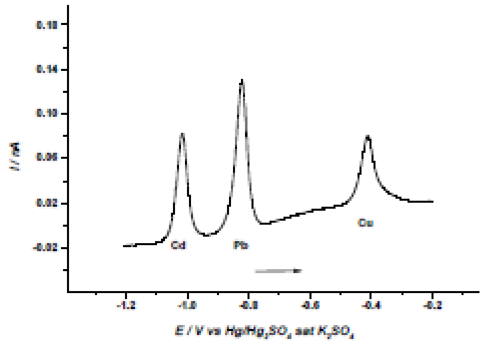



Fig. 3. Anodic stripping voltammogram recorded with a hemispherical Hg microelectrode (25 μm diameter), in a solution containing $2.5\times10^{-7}$ M of both $Cd^{2+}$ and $Pb^{2+}$ and $2\times10^{-7}$ M of $Cu^{2+}$ in 0.1 M $NaClO_4$. $E_d$=−1.2 V, $t_d$=300 s and sweep rate=10 mV $s^{-1}$.

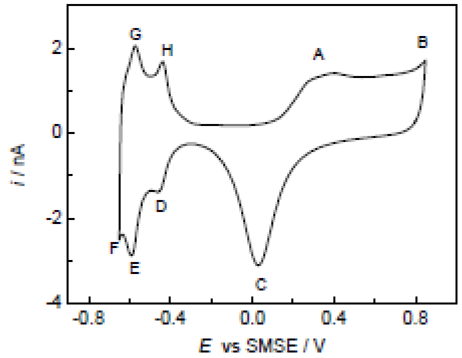
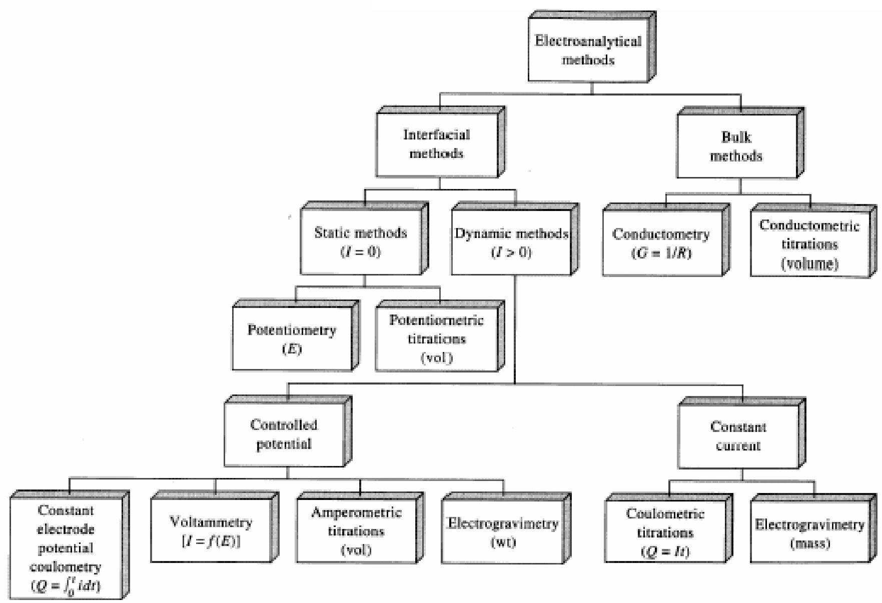



Fig. 1. A typical cyclic voltammogram recorded with a Pt microdisc (25 μm diameter) in 1 M $H_2SO_4$ at 100 mV $s^{-1}$. The letters indicate the redox processes taking place on the Pt surface. (A) Pt oxide formation, (B) oxygen evolution, (C) Pt oxide reduction and stripping, (D) adsorption of strongly bound hydrogen, (E) adsorption of weakly bound hydrogen, (F) hydrogen evolution, (G) desorption of weakly bound hydrogen, (H) desorption of strongly bound hydrogen.

# Electroanalytical methods.

- Electrochemical reactions involve electron transfer (ET) processes at electrode solution interfaces. These ET reactions may be kinetically sluggish or kinetically facile depending on the details of the ET reaction and the nature of the electrode surface.
- Provided an analyte species exhibits electroactivity (can be oxidised or reduced) then it may be detected using the tools of electrochemistry.
- Thus, electrochemical methods may be split up into two major classes : **Potentiometric** and **Amperometric**.
- In potentiometry the ET reaction is kinetically facile and we measure the **potential** of a Galvanic cell under conditions of zero current flow. The cell potential responds to changes in the activity of the analyte species present in the solution in a well defined manner described by the Nernst equation. Indeed the cell potential varies in a **linear** manner with the **logarithm** of the analyte activity.
- In amperometry the kinetics of the ET reaction will have to be driven by an applied potential and so we measure the diffusion controlled current flowing across the electrode/solution interface. This current is **directly proportional** to the bulk concentration of the analyte present in the solution.

# Electrochemical theory and terminology

## Electrical Properties

The are a large number of electrical properties which have been exploited in electroanalytical measurements. The three most important of those from the analytical viewpoint are 'potential', 'current' and 'charge'. The table (9.1) below provides details of these properties along with 'resistance' the other common, but non-specific electrical property of a solution.

| Electrical Property | Symbol | Units | Symbol |
|---|---|---|---|
| Potential | E | Volts | V |
| Current | i | Amperes | A |
| Charge | q | Coulombs | C |
| Resistance | R | Ohms | Ω |

Table 9.1 – analytically useful electrical properties

# Electrochemical Cells – what electroanalytical chemists use

Electrochemical textbooks define two types of electrochemical cell; a **galvanic** (**or voltaic cell**) and an **electrolytic** cell. However for electroanalytical purposes an electrochemical cell can be more broadly defined as the combination of a minimum of two **electrodes** immersed in a solution containing the analyte, with an external connection between the electrodes to complete the electrical circuit. Such a basic cell is illustrated in figure (9.1) below

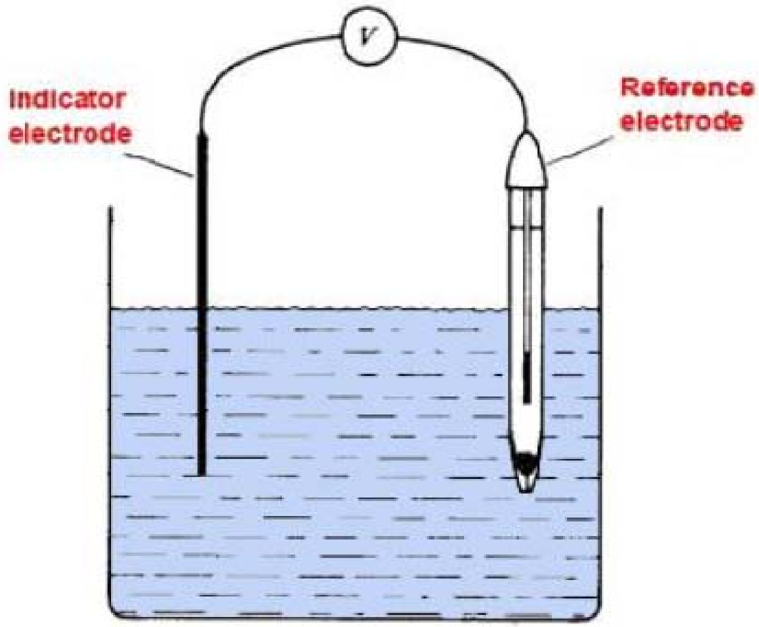
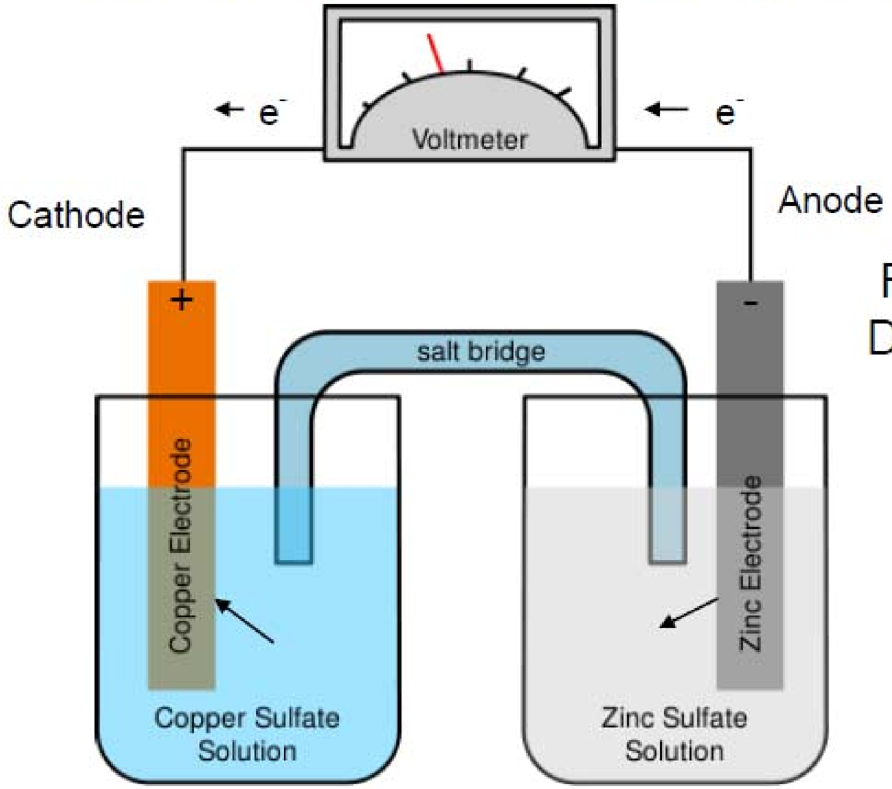



Figure 9.1 – basic electrochemical cell

# Galvanic (or voltaic) Cells

An electrochemical cell which spontaneously produces current when the electrodes are connected. These types of cells are important in potentiometry and as batteries but have limited use in analytical measurement. A typical galvanic cell is the Daniell cell shown in figure (9.2) below:




$Cu^{2+} + 2e^- = Cu_{(s)}$ +0.34V  $Zn_{(s)} = Zn^{2+} + 2e^-$ + 0.76V

Figure 9.2
Daniell Cell

When a zinc half cell (Zn metal in contact with a solution of $Zn^{2+}$) is connected electrically to a copper half cell, there is a spontaneous reaction whereby the Zn metal electrode dissolves with an equivalent quantity of $Cu^{2+}$ being deposited onto the Cu metal electrode. The reaction continues until either all of the Zn has dissolved or all of the $Cu^{2+}$ have been deposited.

# Electrolytic Cells

These are electrochemical cells where a chemical reaction is brought about by applying a voltage from an external power supply in excess to that generated by any natural Galvanic mechanism. The resultant current flow can be measured and used for analytical measurement. These types of cells are important in **voltammetry**, **amperometry** and **coulometry**. A typical cell is illustrated in figure (9.3) which is shown below.

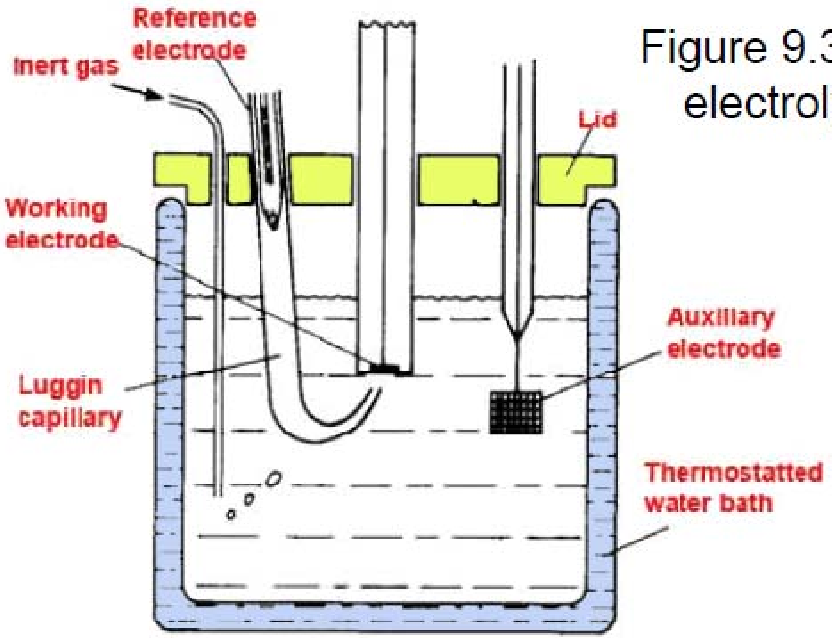



Figure 9.3 – typical electrolytic cell

**Figure (9.3)** shows the cell arrangement for a typical **potentiostatic** arrangement. The current generated by the electrochemical reaction carried out is passed between the working and the auxiliary electrode, whilst the reference electrode is placed close to the working electrode so that the potential at the working electrode can be maintained at a set value.

# Electrodes

In both types of these cells the electrode at which oxidation occurs is the **anode** and that at which reduction occurs is the **cathode**. In the galvanic cell shown in figure (9.2) the cathode reaction is given by:

$Cu^{2+} + 2e^{-} \Rightarrow Cu$ Equation (9.1)

and the anode reaction by:

$Zn \Rightarrow Zn^{2+} + 2e^{-}$ Equation (9.2)

The solutions are contained in separate beakers and connected by a salt bridge (a salt bridge allows charge transfer but prevents mixing of the solutions). If we place a zinc electrode into the zinc solution and a copper electrode in the copper solution and connect the two together we have a voltaic cell. If an ammeter is connected between the two electrodes (in series) it indicates a flow of current from the reduction of copper at the cathode. The released current flows through the wire and oxidises the zinc at the anode. These reactions are referred to as **half cell reactions**.

# Half Cell Reactions – giving and receiving electrons

Equations (9.1 & 2) are examples of half cell reactions. No half cell reaction can occur in isolation. There must always be an **electron donor** (a reducing agent) and an **electron acceptor** (an oxidising agent). In this example $Zn^0$ is the reducing agent and $Cu^{2+}$ is the oxidising agent. Some examples of half cell reactions are shown opposite in figure (9.4)

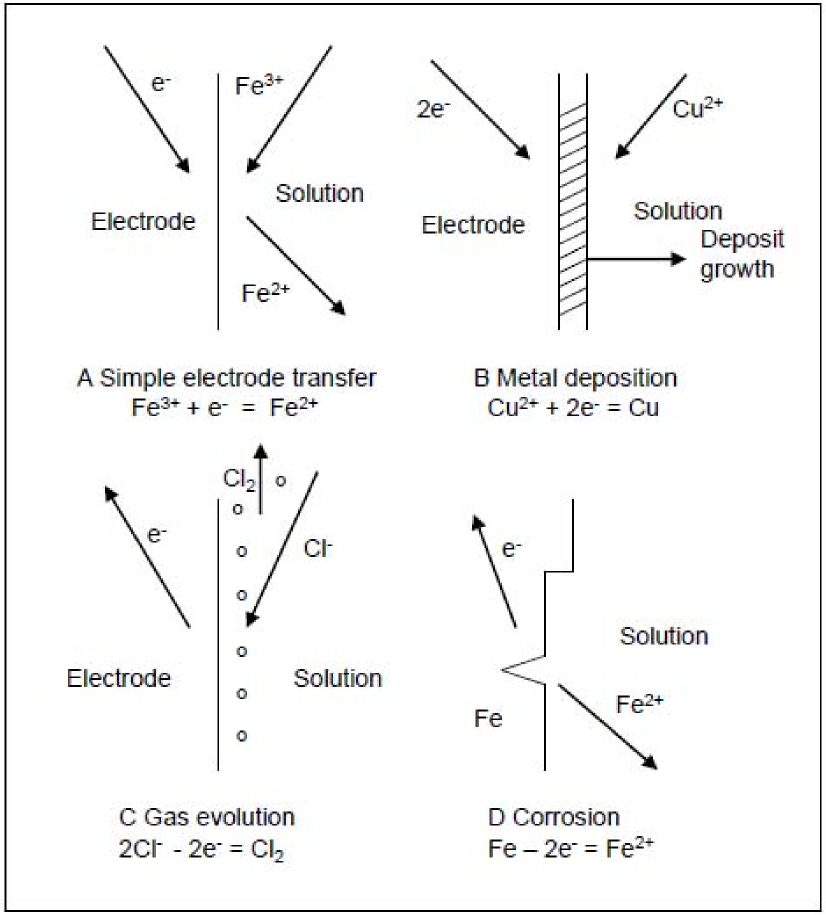
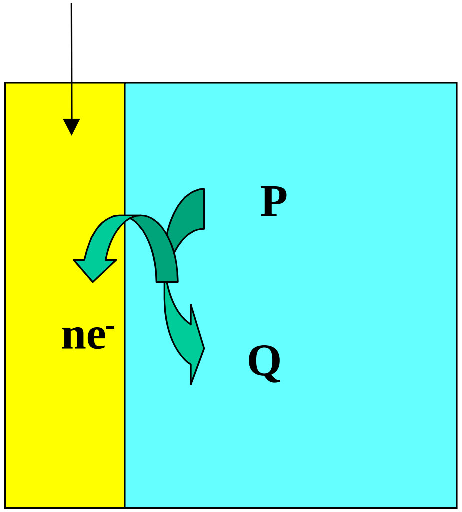
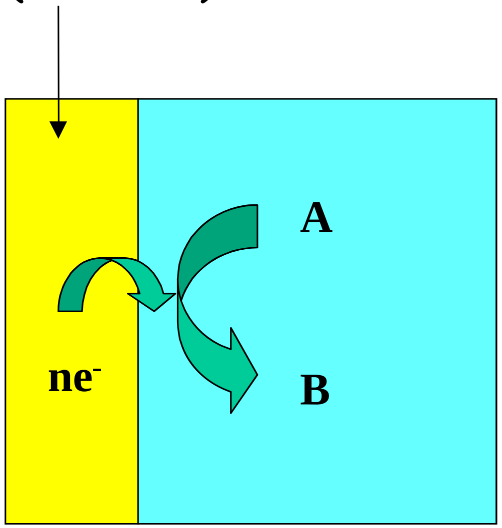



Figure 9.4 – electron donors & acceptors

Electron sink electrode
(Anode).




Electron source electrode
(Cathode).




Oxidation or de-electronation.
P = reductant (electron donor)
Q = Product

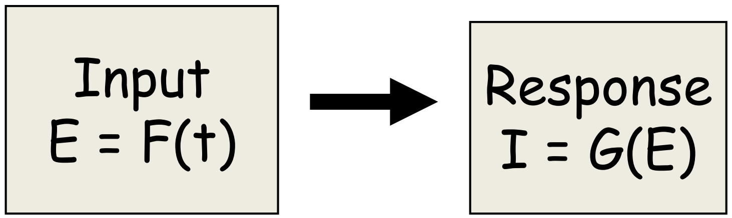
Reduction or electronation.
A = oxidant (electron acceptor)
B = Product

In potentiometry an interfacial ET reaction is in equilibrium and the interfacial potential is governed by the Nernst equation. In voltammetry an analyte species is oxidised or reduced at an indicator electrode giving rise to a current flow which is directly proportional to the bulk analyte concentration.

| Device Type | Potentiometric | Amperometric |
|---|---|---|
| Method of operation | Measure potential at Zero current | Measure transport limited current |
| Electrode kinetics | Must be fast | Electrode potential can drive reaction |
| Response | Concentration depends exponentially on potential via Nernst equation | Concentration is a linear function of current |
| Mass transport | Unimportant | Must be controlled |
| Sensitivity | Ca. $10^{-6}$ M but can be less (ca. $10^{-8}$M). | Ca. $10^{-9}$ M |

# Voltammetry.

- Voltammetry is an electroanalytical method in which the controlled parameter, the potential of the indicator electrode varies in a definite manner with time, and in which the current flowing through the indicator electrode is the measured parameter.
- The voltammetry method relies on the fact that the current measured reflects rate determining diffusion of the analyte species from the bulk solution to the surface of the indicator electrode where it is readily oxidised or reduced. Under such conditions of diffusion control the measured current is linearly proportional to the bulk concentration of the analyte species.
- Voltammetric techniques are classified according to the type of voltage perturbation applied to the indicator electrode, i.e. the way that the voltage signal input varies with time. The form of the input V(t) function will determine the form of the resulting current response.
- The current/potential response curve is called a voltammogram.




Linear potential sweep voltammetry

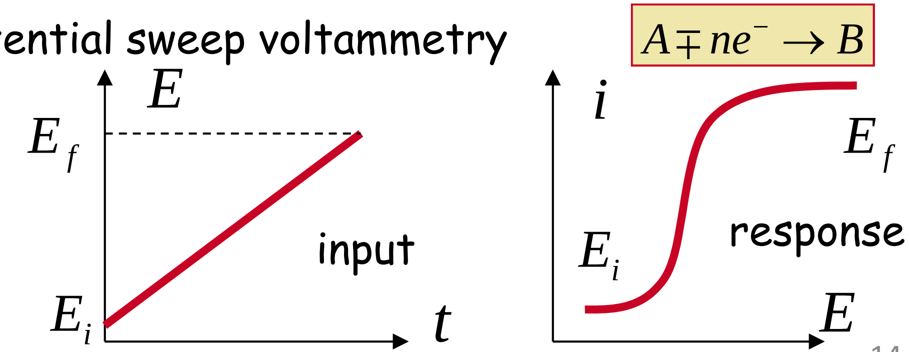


**TABLE 1.1**

General classification of electrochemical dynamic methods

<table>
<tr><td rowspan="10">Controlled Potential</td><td rowspan="3">Potential Step</td><td>Amperometry</td><td colspan="2">Chronoamperometry; Double Potential Step Chronoamperometry</td></tr>
<tr><td colspan="3">Chronocoulometry; Double Potential Step Chronocoulometry</td></tr>
<tr><td colspan="3">Sampled Current Voltammetry; Differential Pulse Voltammetry; Square Wave Voltammetry</td></tr>
<tr><td rowspan="5">Potential Sweep</td><td rowspan="5">Voltammetry</td><td rowspan="2">Stationary</td><td>Linear Scan Voltammetry</td></tr>
<tr><td>Cyclic Voltammetry</td></tr>
<tr><td rowspan="2">Hydro-dynamic</td><td>Stirred Solution/ Flow Cell</td></tr>
<tr><td>Rotating Disk Electrode; Rotating Ring-Disk Electrode</td></tr>
<tr><td colspan="2">Anodic Stripping Voltammetry (Stationary/Hydrodynamic)</td></tr>
<tr><td rowspan="2">Constant Potential</td><td rowspan="2">Bulk Electrolysis</td><td colspan="2">Stirred Solution</td></tr>
<tr><td colspan="2">Flow Electrolysis</td></tr>
<tr><td rowspan="6">Controlled Current</td><td colspan="2" rowspan="4">Chronopotentiometry</td><td colspan="2">Constant-Current</td></tr>
<tr><td colspan="2">Linearly Increasing Current</td></tr>
<tr><td colspan="2">Current Reversal</td></tr>
<tr><td colspan="2">Cyclic</td></tr>
<tr><td colspan="2">Coulometry</td><td colspan="2">Coulometric Titrations</td></tr>
<tr><td colspan="4">Electrolysis</td></tr>
<tr><td>Controlled Charge</td><td>Charge Step</td><td colspan="3">Coulostatic Methods</td></tr>
<tr><td rowspan="2">Impedance Techniques</td><td colspan="4">ac Voltammetry (ac Polarography)</td></tr>
<tr><td colspan="4">Electrochemical Impedance Spectroscopy</td></tr>
</table>

# Measuring Current

Many electroanalytical measurements are based on the measurement of a current generated at an electrode due to the application of a voltage. Hence they can be considered to be mini electrolysis reactions and are sometimes referred to as dynamic electroanalysis as a reflection of the fact that the absolute concentration of the analyte changes over time as a result of undergoing electrolysis due to the applied potential.

There are generally two types of measurement possible:

- Measurement of the current generated at a fixed potential (**Amperometry**);
- Measurement of the varying current generated as the potential is scanned between two fixed values (**Voltammetry**).

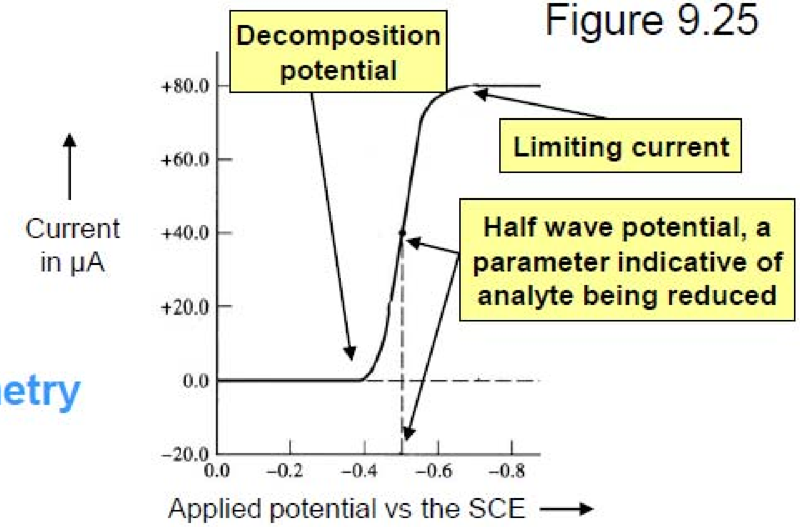
The techniques can offer very high levels of sensitivity ($10^{-10} - 10^{-12}$ mol $dm^{-3}$ have been reported), however require great care with the experimentation and are not readily adaptable to automation. However the cost of the equipment is relatively low and are increasingly available in portable versions allowing on site measurements for example in environmental analysis.

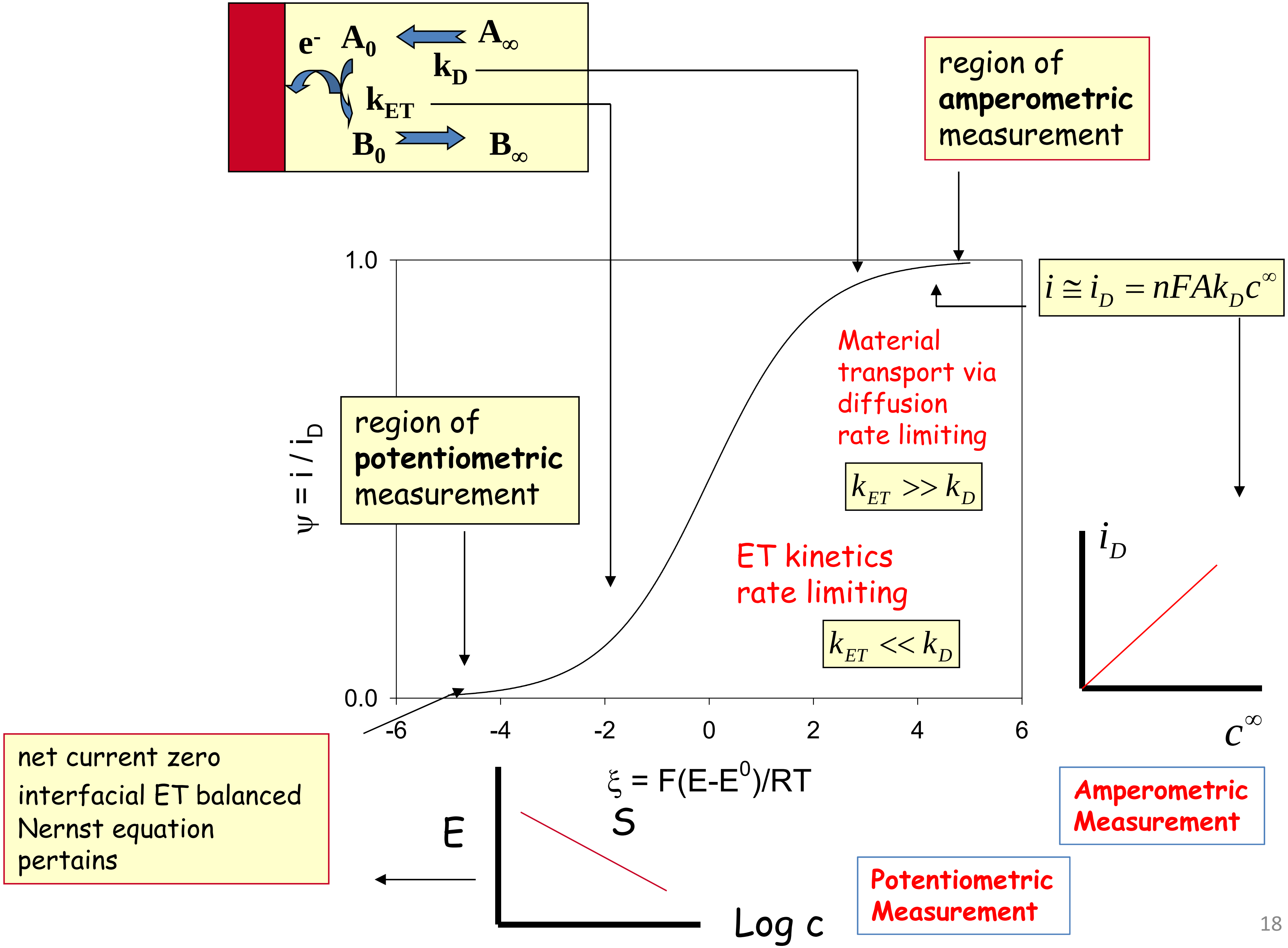
# Voltammetry

This is an electrolytic technique performed on a micro scale, using inert micro electrodes. Platinum, gold and a range of carbon based electrodes are now used for this purpose, mercury (in the form of a dropping mercury electrode) having now been largely superseded. **Voltammetry** is a current *versus* voltage technique, whereby the potential of the micro working electrode is varied (scanned slowly) between two set values and the resulting current flow is recorded as a function of the applied potential. This recording is termed a **voltammogram**. When an analyte is present that can be electrochemically oxidised or reduced, a current will be recorded when the applied potential becomes sufficiently negative (for reductions) or positive (for oxidations)

Provided the analyte concentration in the solution is sufficiently dilute, the current will reach a limiting value which can be shown to be proportional to the analyte concentration. A typical current/voltage graph is shown In figure (9.25). When measurements are made at a selected, constant potential on the limiting current plateau, the technique is termed **Amperometry**

Figure 9.25





e⁻ A0 A∞
kD
kET
B0 B∞
region of **amperometric** measurement
$i \cong i_D = nFAk_Dc^\infty$
1.0
0.0
ψ = i / iD
region of **potentiometric** measurement
Material transport via diffusion rate limiting
$k_{ET} >> k_D$
ET kinetics rate limiting
$k_{ET} << k_D$
-6 -4 -2 0 2 4 6
ξ = F(E-E0)/RT
$i_D$
$c^\infty$
net current zero
interfacial ET balanced
Nernst equation pertains
E
S
Log c
Potentiometric Measurement
Amperometric Measurement

**Table 1.** Overview of typical electrode configurations found in electrochemical systems: WE=Working electrode, CE= Counter electrode, RE=reference electrode, CE/RE=counter electrode also acting as a reference electrode. WE/CE=working electrode alternatively acting as a counter electrode.

| Technique | Number of electrodes | Electrode configurations |
|---|---|---|
| Potentiometry | 2 | Indicator electrode+RE |
| | 3 | Indicator electrode+RE +common electrode |
| Amperometry or voltammetry | 2 | WE+CE/RE |
| | 3 | WE+CE+RE |
| | 4 | 2 WE+1 CE+1 RE |
| | Arrays | n WE+1 CE+1 RE |
| Impedimetry | 2 | WE+CE or 2 WE/CE |
| | 3 | WE+CE+RE |
| | 4 | 2 WE+2 indicator electrodes |

**Table 2.** Overview of electrochemical techniques. $E$ is the electrode potential, $i$ the current flowing between electrodes, $Q$ the charge passed (the integral of the current over time), $Z$ the electrical impedance of the electrochemical circuit. $f$ and $t$ are respectively the frequency and time of the potential perturbation. $c$ and $a$ are respectively the concentration and activity of the analyte of interest.

| Method | Control parameter | Signal measured | Relation to analyte | Driving circuitry required |
|---|---|---|---|---|
| Amperometry or voltammetry | $E$ =fixed, stepped, ramped | $i$ | $i \propto c$ | Yes |
| Coulometry | $E$ | $Q$ | $Q \propto c$ | Yes |
| Impedimetry – Conductimetric sensing – Capacitive sensing | $i$ or $E = \sin(2\pi \ f t)$ | $Z$ | $Z \propto (\sum c)^{-1}$ | Yes |
| Potentiometry | $i = 0$ | $E$ | $E \propto \ln(a)$ | No |
| Self-powered electrochemical cells | Chemistry, electrode material | $i$ | $i \propto c$ | No |

G. Denault, Ocean Sci., 5 (2009) 697-710.

The electrochemical reaction only takes place at the electrode surface. As the electrolysis proceeds, the analyte in the vicinity of the electrode is depleted creating a concentration gradient between surface of the electrode and the bulk of the solution as illustrated in figure (9.26). So long as the applied potential is close to the decomposition potential, analyte can diffuse rapidly from the bulk of the solution to the electrode surface to maintain the electrolytic reaction. However as the potential is increased, the increased current flow, causes the analyte to diffuse at ever increasing rates in order to maintain the current. Eventually the maximum rate at which the analyte can diffuse is reached, leading to a steady-state situation whereby all analyte reaching the electrode is immediately reacted. This results in the establishment of a current plateau as indicated in figure (9.25) on the previous slide. In the absence of the solution being stirred, the thickness of the diffusion layer will gradually extend further into the bulk of the solution leading to a distortion of the plateau wave. By stirring the solution however, the thickness of the diffusion layer remains constant.

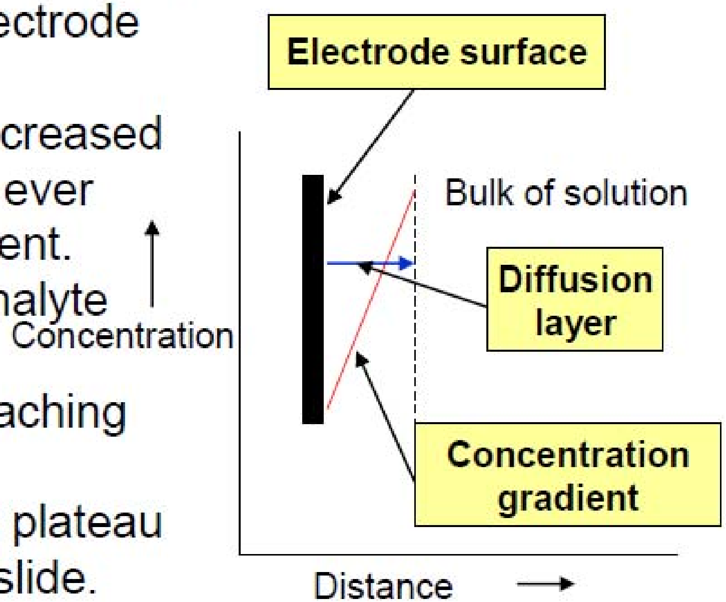
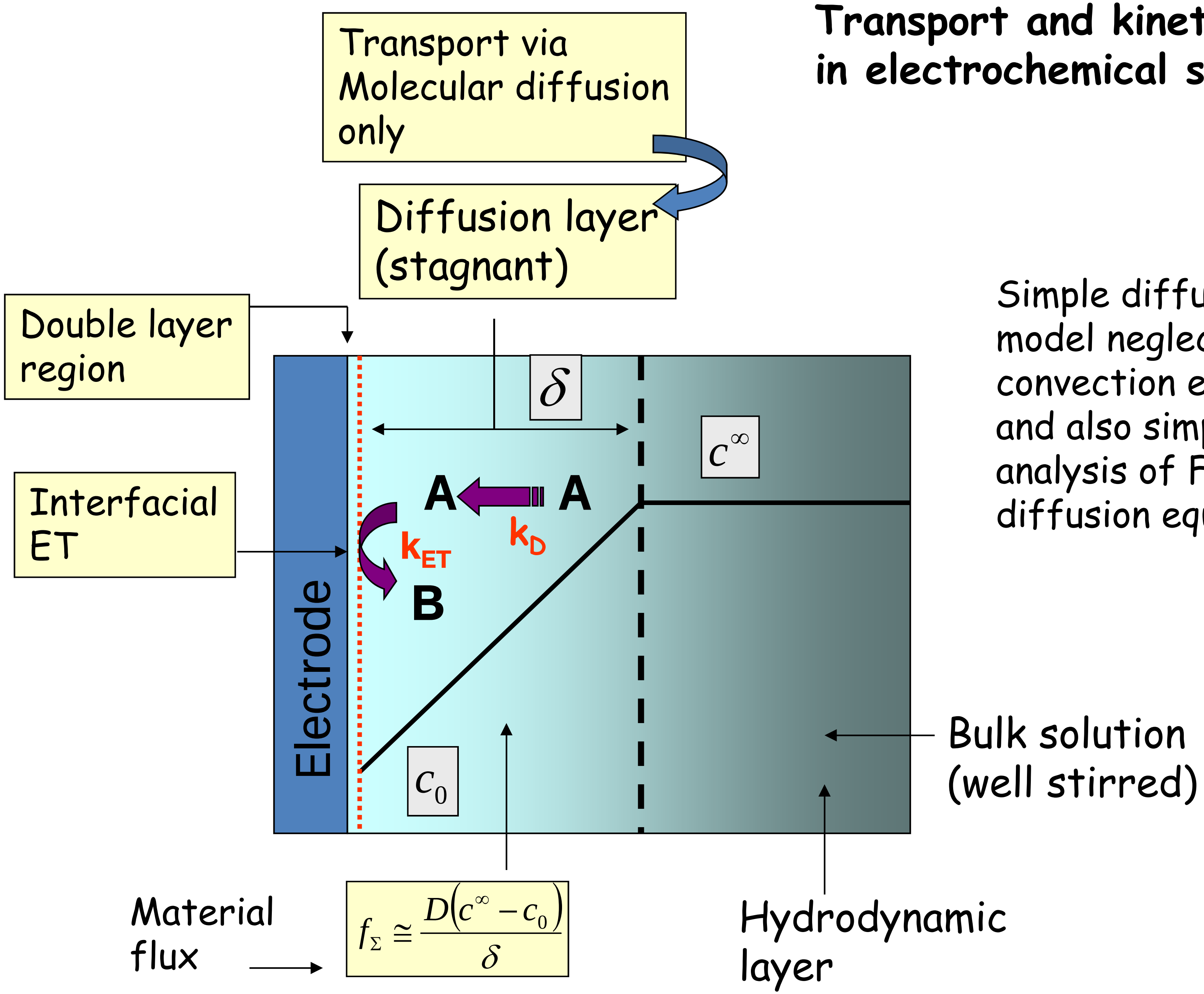



Figure 9.26 – establishment of a concentration gradient

**Transport and kinetics in electrochemical systems.**




Simple diffusion layer model neglects convection effects and also simplifies analysis of Fick diffusion equations.

# Transport and kinetics at electrodes.

Current density

$$f_\Sigma = \frac{i}{nFA} = \frac{j}{nF}$$

Net flux

$$k_D = \frac{D}{\delta}$$

$$f_\Sigma = D\left(\frac{dc}{dx}\right)_0 = \frac{D}{\delta}\left\{c^\infty - c_0\right\} = k_D\left\{c^\infty - c_0\right\}$$

$$c_0 = \frac{c^\infty}{1 + \dfrac{k_{ET}\delta}{D}}$$

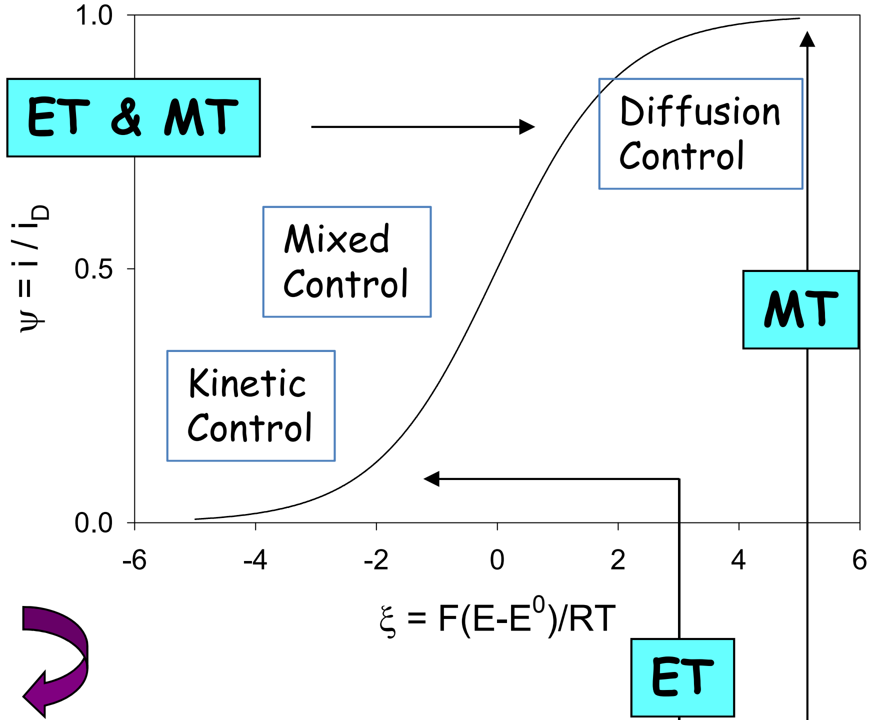
$$f_\Sigma = \frac{k_{ET}k_D c^\infty}{k_D + k_{ET}}$$

$$\frac{1}{f_\Sigma} = \frac{1}{k_{ET}c^\infty} + \frac{1}{k_D c^\infty}$$

$$f_\Sigma = k_{ET}c_0$$

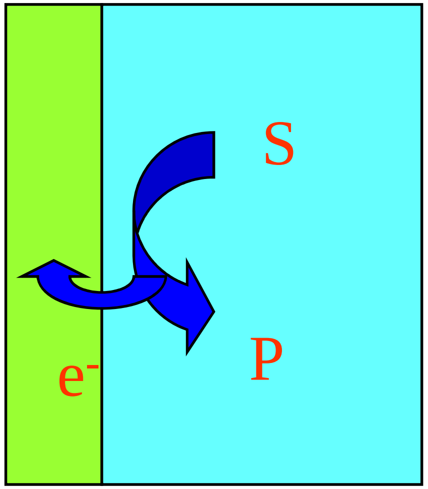
$$k_{ET} = k^0 \exp[\pm \beta \xi]$$

Normalised potential



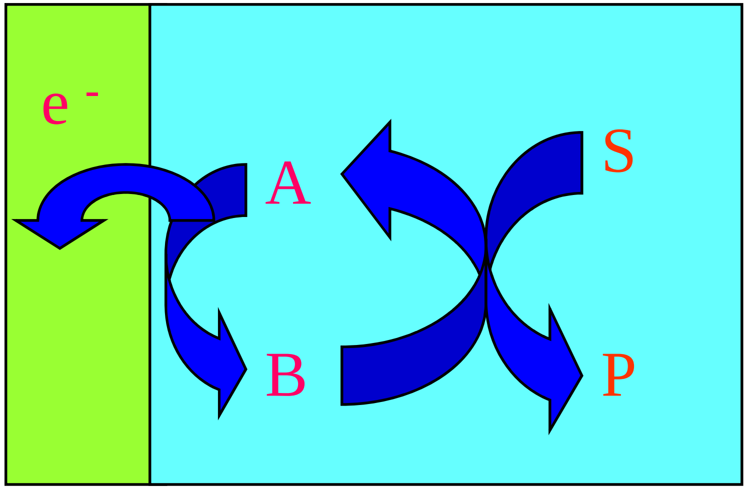
# Mediated vs unmediated ET at electrodes .

- Redox groups bound to support surface as 2D monolayer or as 3D multilayer .




Direct unmediated ET .

$$S \xrightarrow{\mp ne^-} P$$

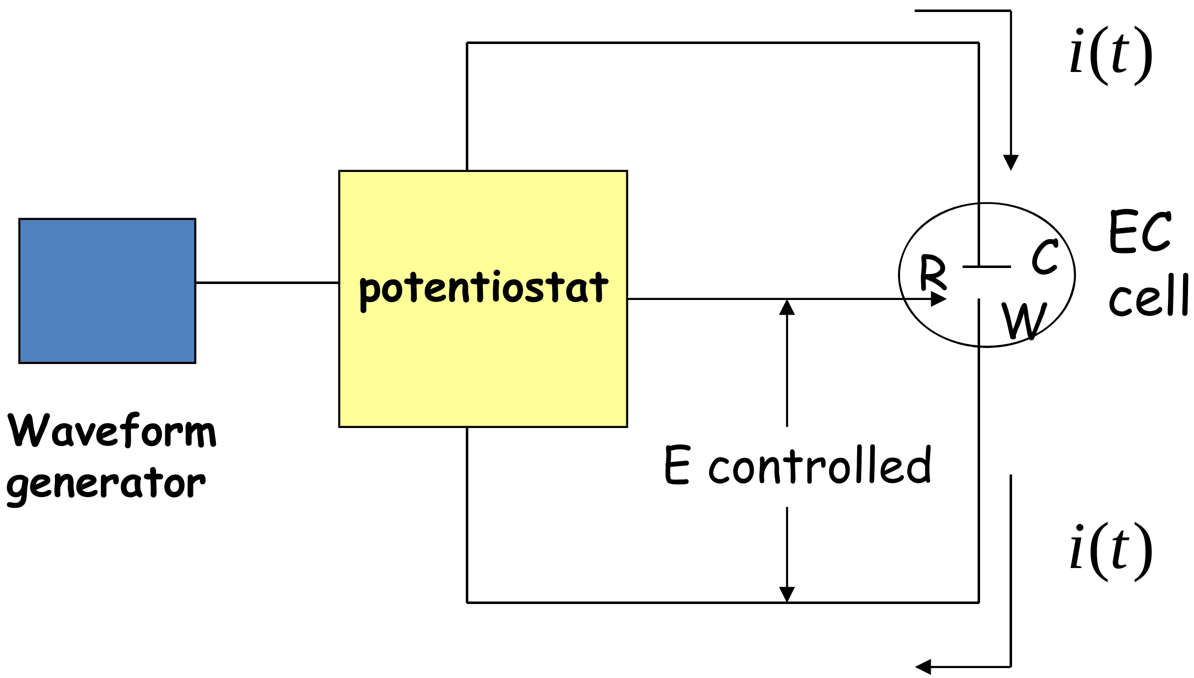



Heterogeneous redox catalysis : mediated ET via surface bound redox groups .

$$A \xrightarrow{\mp ne^-} B$$

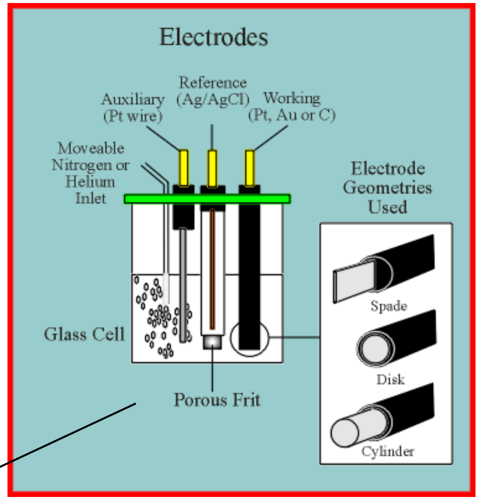
$$B + S \rightarrow A + P$$

A schematic experimental arrangement for controlled potential measurement is outlined across.
W denotes the working or indicator electrode,
R represents the reference electrode,
and C is the counter or auxiliary electrode.




The potentiostat controls the voltage between the working electrode and the counter electrode according to a pre-selected voltage time programme supplied by a waveform generator or computer. The potential difference between the working and reference electrodes is measured by a high impedance feedback loop based on operational amplifiers. Current flow is measured between the counter and the working electrodes.

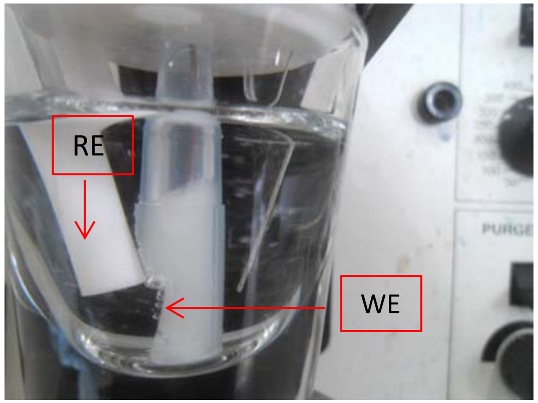
Electrochemical Cell

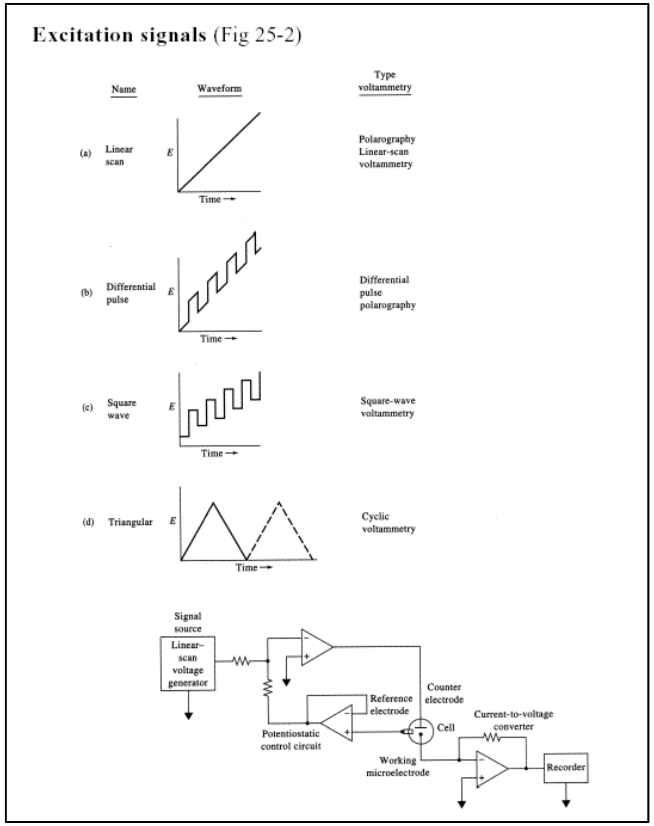

Large variety of digital waveforms can be generated via computer software.

Potentiostat

Electrochemical Cell stand




Electrochemical water Splitting in electrolyte Filled cell (OER)



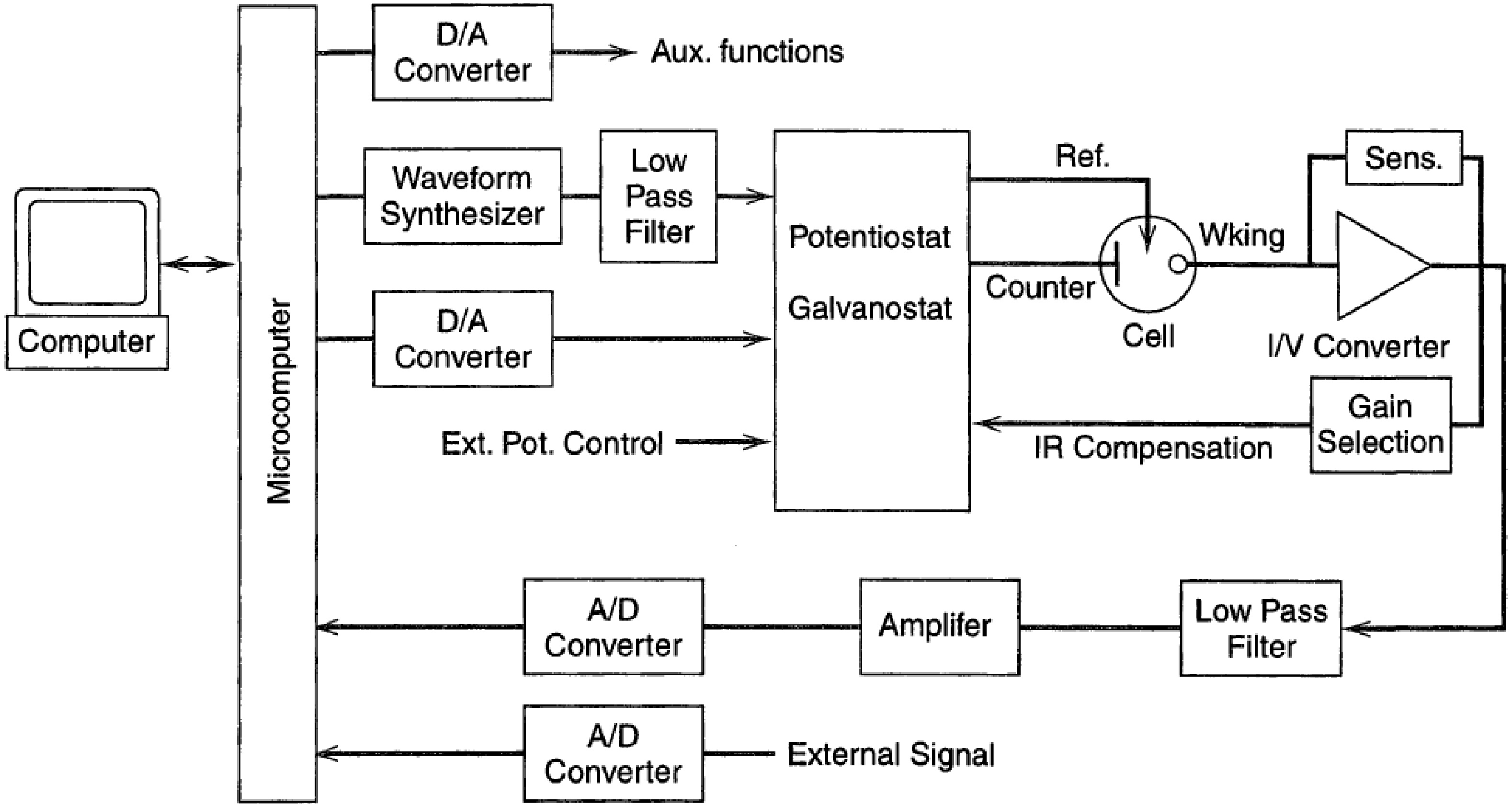

D/A Converter
Aux. functions
Waveform Synthesizer
Low Pass Filter
Potentiostat
Galvanostat
Ref.
Counter
Cell
Wking
Sens.
I/V Converter
Gain Selection
IR Compensation
Computer
Microcomputer
D/A Converter
Ext. Pot. Control
A/D Converter
Amplifer
Low Pass Filter
A/D Converter
External Signal

**Table 4.** Common voltammetric techniques based on analog potential ramps shown with the corresponding amperometric responses typical of diffusion controlled processes.

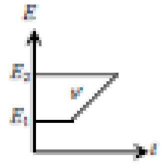
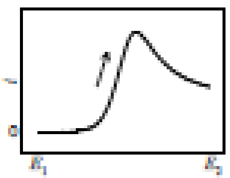
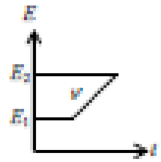
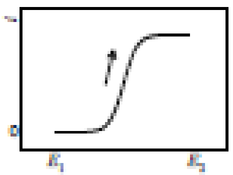
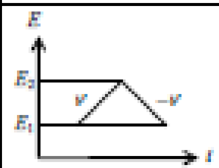
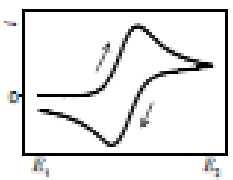
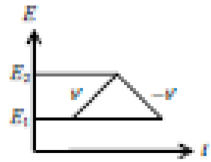
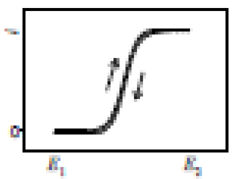
| Technique | Driving waveform | Response |
|---|---|---|
| Linear sweep voltammetry<br><br>transient response |  |  |
| Linear sweep voltammetry<br><br>steady state response |  |  |
| Cyclic voltammetry<br><br>transient response |  |  |
| Cyclic voltammetry<br><br>steady state response |  |  |

**Table 3.** Common chronoamperometric techniques with the potential waveforms and corresponding amperometric responses typical of diffusion controlled processes.

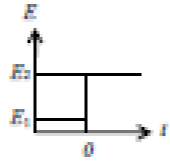
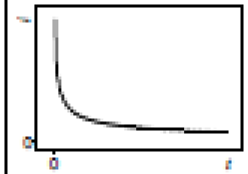
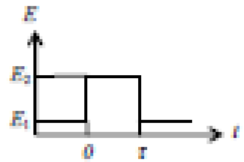
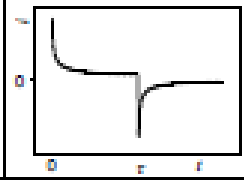
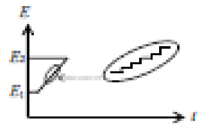
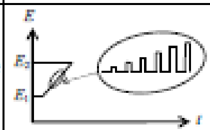
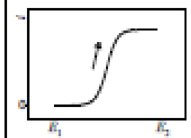
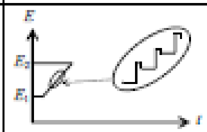
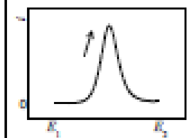
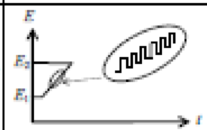
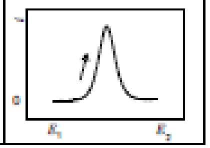
| Technique | Driving waveform | Response |
|---|---|---|
| Single pulse chrono-amperometry |  |  |
| Double pulse chrono-amperometry |  |  |

**Table 5.** Common voltammetric techniques based on digital potential waveforms shown with the corresponding amperometric responses typical of diffusion controlled processes.

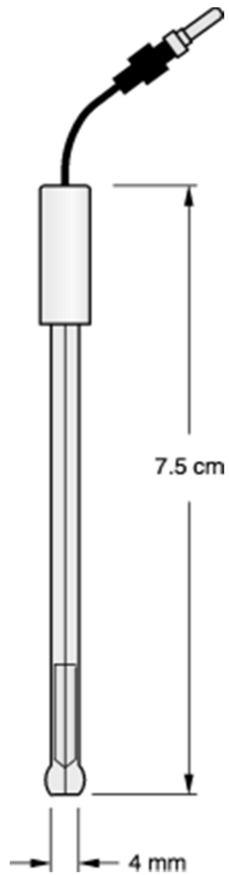
| Technique | Driving waveform | Response |
|---|---|---|
| Staircase voltammetry |  |  |
| Normal pulse voltammetry |  |  |
| Differential pulse voltammetry |  |  |
| Square wave voltammetry |  |  |

# Working electrode

- Most common is a small sphere, small disc or a short wire, but it could also be metal foil, a single crystal of metal or semiconductor or evaporated thin film.
- Has to have useful working potential range.
- Can be large or small – usually < 0.25 $cm^2$
- Smooth with well defined geometry for even current and potential distribution.
- Mercury and amalgam electrodes.
  - reproducible homogeneous surface.
  - large hydrogen overvoltage.
- Wide range of solid materials – most common are “inert” solid electrodes like gold, platinum, glassy carbon.
  - Reproducible pretreatment procedure.
  - Well defined geometry.
  - Proper mounting.

# Working Electrodes

- Size
  - Analytical macro
    - 1.6 - 3 mm diameter
  - Micro
    - 10-100 μm diameter



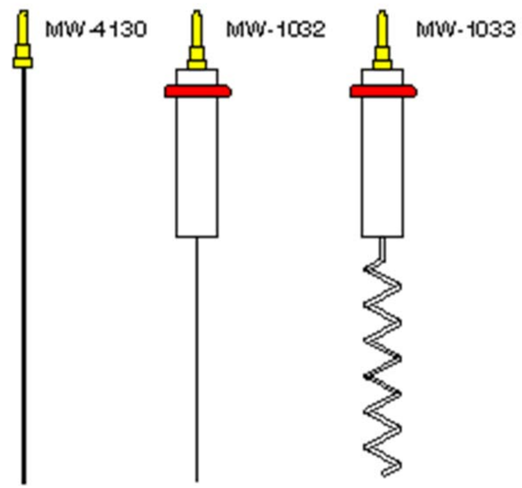


From BAS www-site:
http://www.bioanalytical.com/

# Counter (Auxiliary) Electrode

- Serve to supply the current required by the W.E. without limiting the measured response.
- Current should flow readily without the need for a large overpotential.
- Products of the C.E. reaction should not interfere with the reaction being studied.
- It should have a large area compared to the W.E. and should ensure equipotentiality of the W.E.

- Area must be greater than that of working
- Usually long Pt wire (straight or coiled) or Pt mesh (large surface area)
- No special care required for counter




**From BAS www-site: http://www.bioanalytical.com/**

# Reference Electrode (RE)

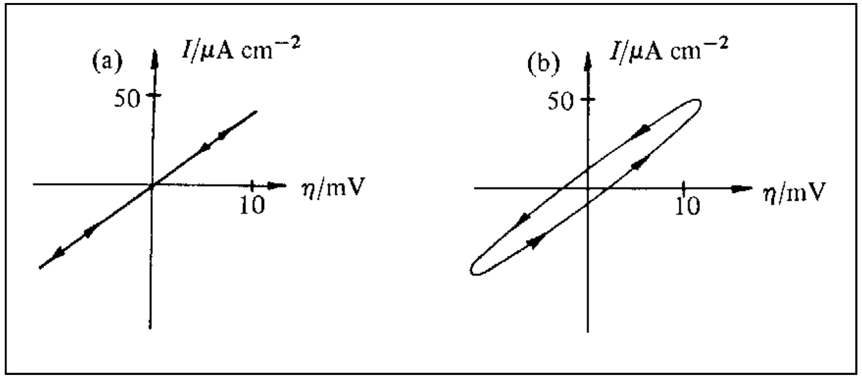
- The role of the R.E. is to provide a fixed potential which does not vary during the experiment.
- A good R.E. should be able to maintain a constant potential even if a few micro-amps are passed through its surface.

**Aqueous**

- SCE
- Ag/AgCl
- Hg/HgO
- RHE

**Nonaqueous**

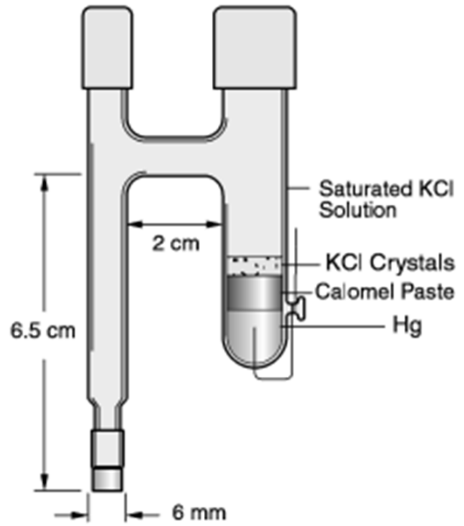
- $Ag^+/Ag$
- Pseudoreferences
  - Pt, Ag wires
- Ferrocene/ferricinium couple




Micropolarization test. (a) response of a good and (b) bad reference electrode.

# Saturated calomel electrode SCE

- $Cl^-(aq)/Hg_2Cl_2/Hg(l)$
- $Hg_2^{2+} + 2e^- = 2Hg(l)$
- $E^0 = 0.24$ V vs. SHE @ $25^0C$




**Advantages**

- Most polarographic data referred to SCE


From BAS web site: http://www.bioanalytical.com

# Silver/silver chloride reference electrode Ag/AgCl

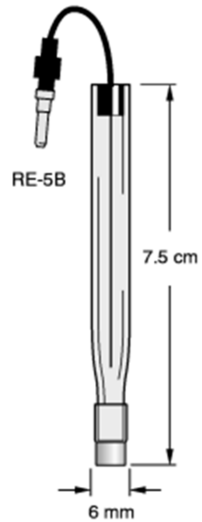
- Ag wire coated with AgCl(s), immersed in NaCl or KCl solution
- $Ag^+ + e^- = Ag(s)$
- $E^0 = 0.22$ V vs. SHE @ $25^0C$


**Advantages**

- chemical processing industry has standardized on this electrode
- convenient
- rugged/durable

**Disadvantages**

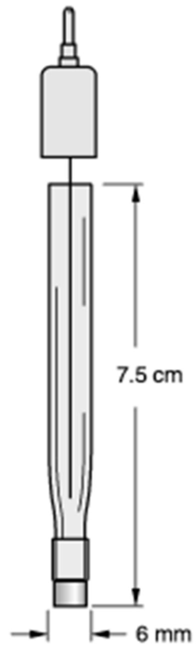
- solubility of KCl/NaCl temperature dependent
  $dE/dT = -0.73$ mV/K
  (must quote temperature)




From BAS site
http://www.bioanalytical.com/

# Silver/silver ion reference electrode $Ag^{+}/Ag$

- $Ag^{+} + e^{-} = Ag(s)$
- Requires use of internal potential standard




**Advantages**

- Most widely used
- Easily prepared
- Works well in all aprotic solvents:
  - THF, AN, DMSO, DMF

**Disadvantages**

- Potential depends on
  - solvent
  - electrolyte (LiCl, $TBAClO_4$, $TBAPF_6$, $TBABF_4$
- Care must be taken to minimize junction potentials

From BAS site:
http://www.bioanalytical.com/

# Mercury-Mercuric oxide reference electrode Hg/HgO

Metal/metal oxide reference electrode.

$$HgO(s) + H_2O + 2e^- \rightleftharpoons Hg + 2OH^-$$

$$E = E^0\left(Hg, HgO, OH^-\right) - 0.059\log a_{OH^-}$$

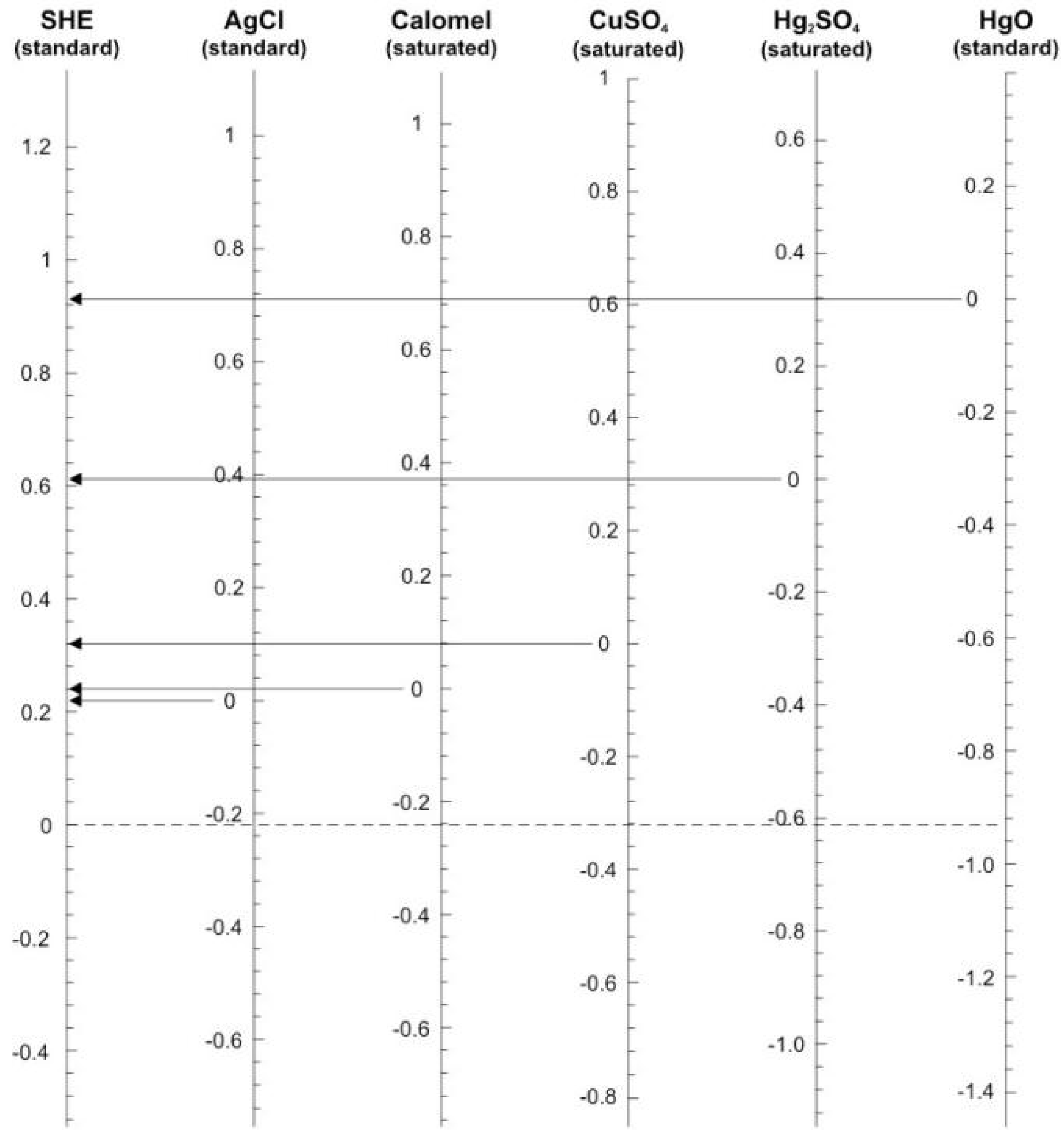
$$E^0\left(Hg, HgO, OH^-\right) = 0.0984\,V\left(vs\,SHE\right)$$

$$\begin{aligned} E &= 0.0984 - 0.059\log a_{OH^-} \\ &= 0.0984 + 0.059\,pOH \\ &= 0.924 - 0.059\,pH \end{aligned}$$

Used in particular for electrochemical studies in aqueous alkaline solution.
1.0 M NaOH usually used in inner electrolyte compartment which is separated from Test electrolyte solution via porous polymeric frit. Hence reference electrode in like SHE system in that it is pH independent.

Comparing various Reference Electrode potential scales to SHE scale.

E (vs SHE) = E (vs REF) + $E_{REF}$ (vs SHE)



# Electrolyte Solution

- Consists of solvent and a high concentration of an ionized salt and electroactive species
- Functions to increase the conductivity of the solution, and to reduce the resistance between
  - W.E. and C.E. (to help maintain a uniform current and potential distribution)
  - and between W.E. and R.E. to minimize the potential error due to the uncompensated solution resistance $iR_u$

# Nernst Equation – Effects of concentrations on potentials

The standard potentials ($E^0$ values) listed in table 9.2 were determined under the special conditions where all the species present in the cell were at **unit activity**. The first empirical $E^0$ tables were produced by Volta and the values were obtained under very controlled and defined conditions. Nernst demonstrated that the potential was dependent upon the concentration of the species and varies from the standard potential. This potential dependence is described by the **Nernst equation**.

$$aOx + ne^- \Rightarrow bRed \qquad \text{Equation (9.7)}$$

$$E = E^0 - \frac{2.3026RT}{nF} \log \frac{[Red]^b}{[Ox]^a} \qquad \text{Equation (9.8)}$$

where E is the reduction potential at the specific concentrations, n is the number of electrons involved in the half cell reaction, R is the gas constant (8.3143 V coul $deg^{-1}$ $mol^{-1}$), T is the absolute temperature and F is the Faraday constant (96,485 coul $eq^{-1}$).

# Measurement of Potential

To measure a potential we need to create a voltaic cell containing two electrodes, one of which is the **indicator electrode** and one of which is the **reference electrode**. We measure the voltage of the cell which is giving a reading of the potential of the indicator electrode relative to the reference electrode. This potential can be related to the analyte activity or concentration via the Nernst equation.

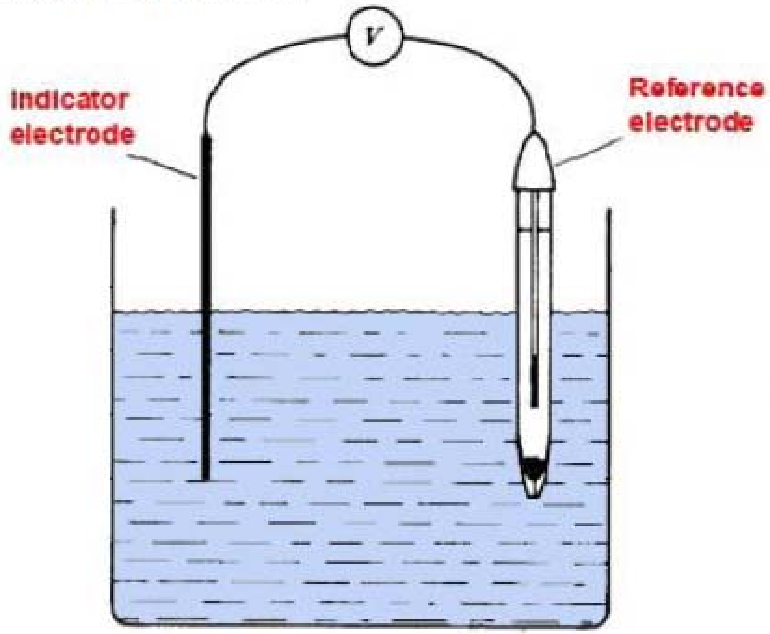



Figure 9.9 – basic potentiometric cell

A typical example of such a cell is:

$Hg \mid Hg_2Cl_2(s) \mid KCl(saturated) \parallel HCl(solution), H_2(g) \mid Pt$ Equation (9.10)

The double line represents the **liquid junction** between two dissimilar solutions and is often in the form of a salt bridge. The purpose of this is to prevent mixing of the two solutions. In this way the potential of one of the electrodes is constant, independent of the composition of the test solution and determined by the solution in which it dips. The electrode on the left of the cell is the saturated calomel electrode, a common reference electrode (see slide 14). The cell is set up using the hydrogen electrode as the indicating electrode to measure pH.

The disadvantage of this type of cell is that there is a potential associated with the liquid junction called the **liquid junction potential**.

# Liquid Junction Potentials

The potential of the cell in equation 9.10 is:

$$E_{cell} = (E_{right} - E_{left}) + E_j \qquad \text{Equation (9.11)}$$

where $E_j$ is the liquid junction potential and can be positive or negative. This potential results from the unequal migration of ions on either side of the boundary. Unequal migration occurs when there is a concentration difference across the junction and the species involved migrate at different rates, for example hydrogen ions migrate about five times faster than chloride ions.

A typical junction might be a fine-porosity frit separating two solutions of differing concentration of the same electrolyte, for example HCl (0.1 M || HCl (0.01 M). The net migration will be from high to low concentrations (although ions will move in both directions), with the concentration gradient being the driving force for the migration. Since the hydrogen ions migrate five times faster than the chloride ions, there is a net build up of positive charge on the right hand side of the boundary leaving a net negative charge on the left hand side. This charge separation represents a potential.

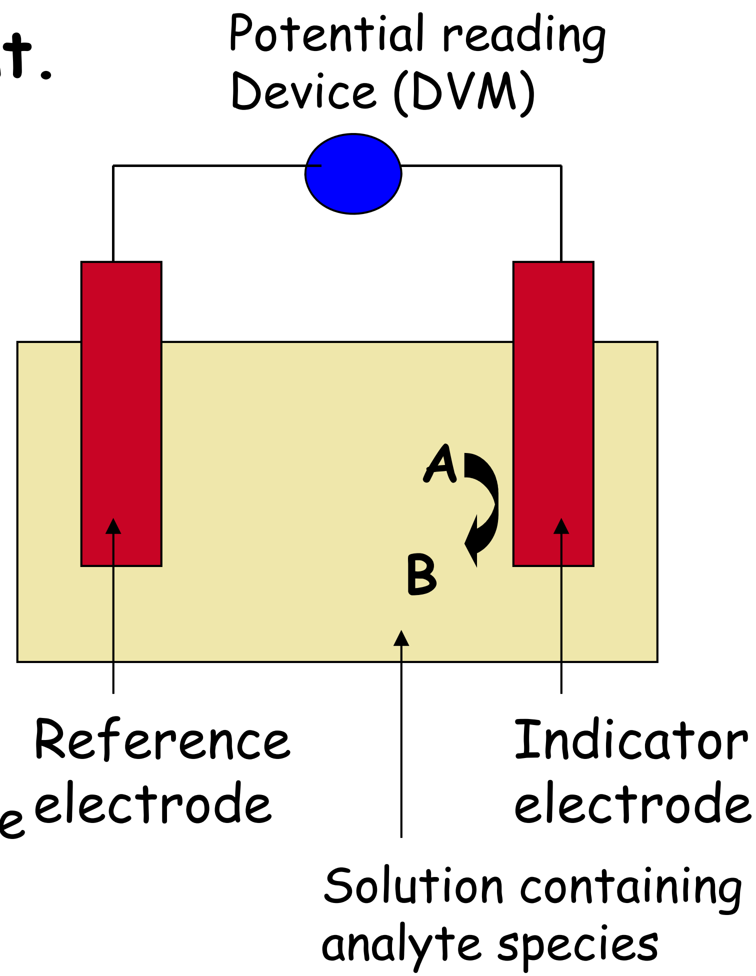
Table 9.4 illustrates some typical liquid junction potentials illustrating both the effect of concentration and ionic mobility on those values.

A careful choice of salt bridge or reference electrode containing a suitable electrolyte can minimise the liquid junction potential and make it reasonably constant and therefore in many practical cases suitable calibration can account for this. Note that the potentials are quoted in mV.

| **Boundary** | **$E_j$ (mV)** |
|---|---|
| 0.1 M KCl \|\| 0.1 M NaCl | +6.4 |
| 3.5 M KCl \|\| 0.1 M NaCl | +0.2 |
| 3.5 M KCl \|\| 1.0 M NaCl | +1.9 |
| 0.1 M KCl \|\| 0.1 M HCl | -27.0 |
| 3.5 M KCl \|\| 0.1 M HCl | +3.1 |

Table 9.4 – some liquid junction potentials at 25°C

## The potentiometric measurement.




In a potentiometric measurement two electrodes are used. These consist of the **indicator** or sensing electrode, and a **reference** electrode. Electroanalytical measurements relating potential to analyte concentration rely on the response of one electrode only (the indicator electrode). The other electrode, the reference electrode is independent of the solution composition and provides A stable constant potential. The open circuit cell potential is measured using a potential measuring device such as a potentiometer, a high impedance voltameter or an electrometer.

# The Potentiometer and pH Meter

There are two commonly used instruments for making potentiometric measurements.

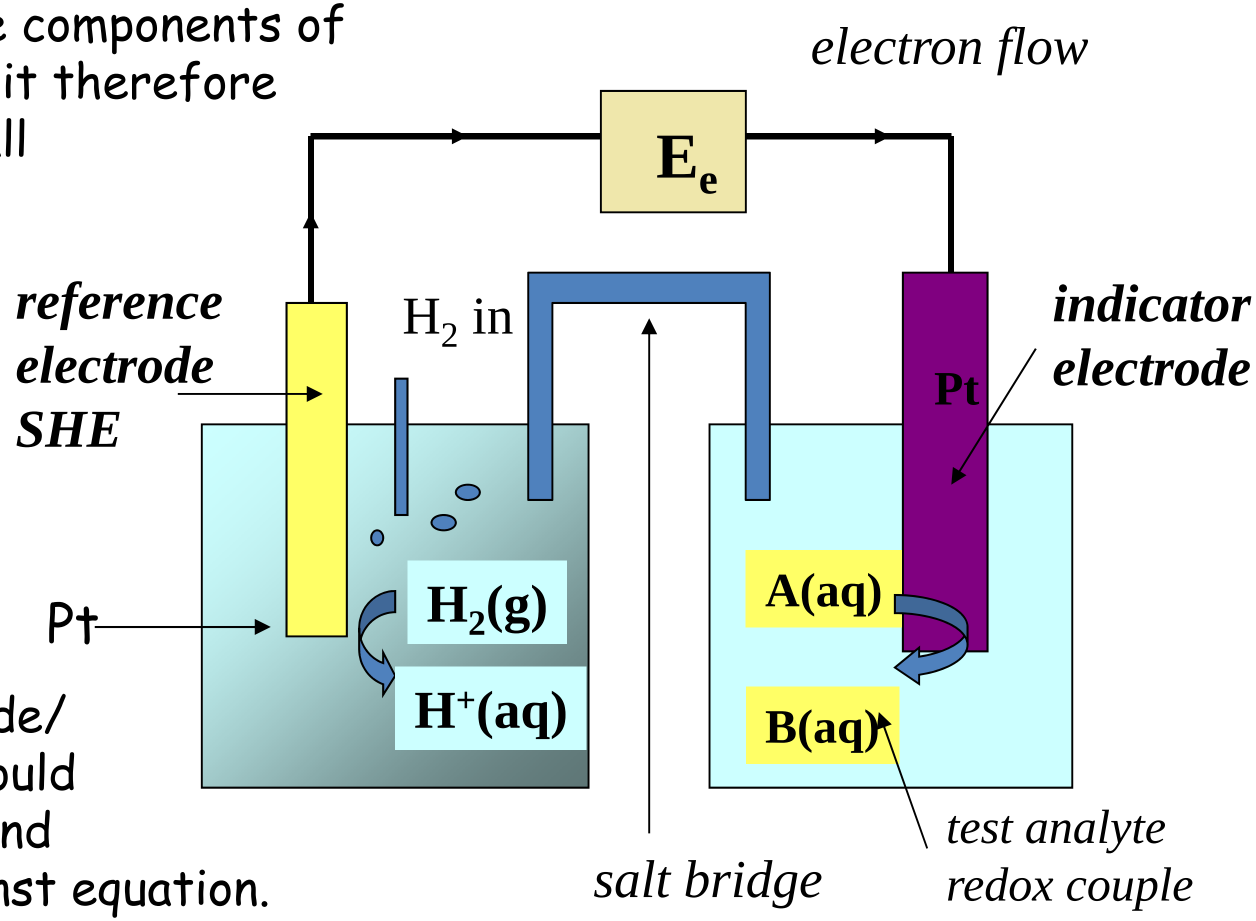
The **potentiometer** is a device which is normally used for the measurement of potentials in low resistance circuits and as a result is only rarely applied.

The **pH meter**, which is a voltmeter, is a voltage measuring device designed for use with high resistance glass electrodes and can be used with both low and high resistance circuits. During a measurement the voltage is converted to a current for amplification via an ac circuit and these are therefore high input impedance devices. (Impedance in an ac circuit is similar to resistance in a dc circuit). Due to the high input resistance very little current flows during the measurement, typically $10^{-13}$ to $10^{-15}$ A, hence the chemical equilibrium remains relatively undisturbed and the criteria for applying the Nernst equation are retained. For convenience when making pH measurements, the voltage reading can be converted directly to pH units.

## Fundamentals of potentiometric measurement : the Nernst Equation.

The potential of the indicator electrode is related to the activities of one or more of the components of the test solution and it therefore determines the overall equilibrium cell potential $E_e$ .

Under ideal circumstances, the response of the indicator electrode to changes in analyte species activity at the indicator electrode/ solution interface should be rapid, reversible and governed by the Nernst equation.




The ET reaction involving the analyte species should be kinetically facile and the ratio of the analyte/product concentration should depend on the interfacial potential difference via the Nernst equation.

The net cell potential at equilibrium is given by the expression across where $E_{ind}$ denotes the potential of the indicator electrode, $E_{ref}$ denotes the reference electrode potential and $E_j$ is the liquid junction potential which is usually small.
The potential of the indicator electrode is described by the Nernst equation.
Hence the net cell potential is given by the expression across,
where k denotes a constant and is given by
The expression outlined.
The constant k may be determined by measuring the potential of a standard solution in which the activities of the oxidised species O and the reduced species R are known. Usually we are interested in determining the concentration rather than the activity of an analyte.
If the ionic strength of all solutions is held constant then the activity coefficient of the analyte will be constant and activities may be replaced by concentrations in the Nernst equation.

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

$$O + ne^- \rightarrow R$$

$$E_{ind} = E^0_{ind} - \frac{2.303RT}{nF}\log\left\{\frac{a_R}{a_O}\right\}$$

$$E_{cell} = k - \frac{2.303RT}{nF}\log\left\{\frac{a_R}{a_O}\right\}$$

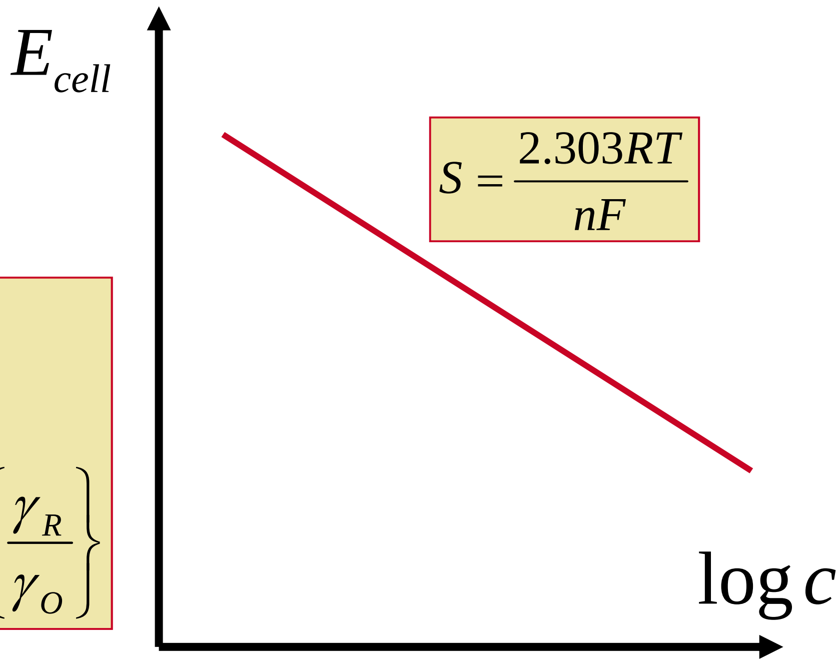
$$k = E^0_{ind} - E_{ref} + E_j$$

$$E_{ind} = E^0_{ind} - \frac{2.303RT}{nF}\log\left\{\frac{\gamma_R c_R}{\gamma_O c_O}\right\}$$
$$= E^0_{ind} - \frac{2.303RT}{nF}\log\left\{\frac{\gamma_R}{\gamma_O}\right\} - \frac{2.303RT}{nF}\log\left\{\frac{c_R}{c_O}\right\}$$

The cell response in the Potentiometric measurement takes the form

$$E_{cell} = k' - \frac{2.303RT}{nF} \log\left\{\frac{c_R}{c_O}\right\}$$

$$k' = E^0_{ind} - E_{ref} + E_j - \frac{2.303RT}{nF} \log\left\{\frac{\gamma_R}{\gamma_O}\right\}$$

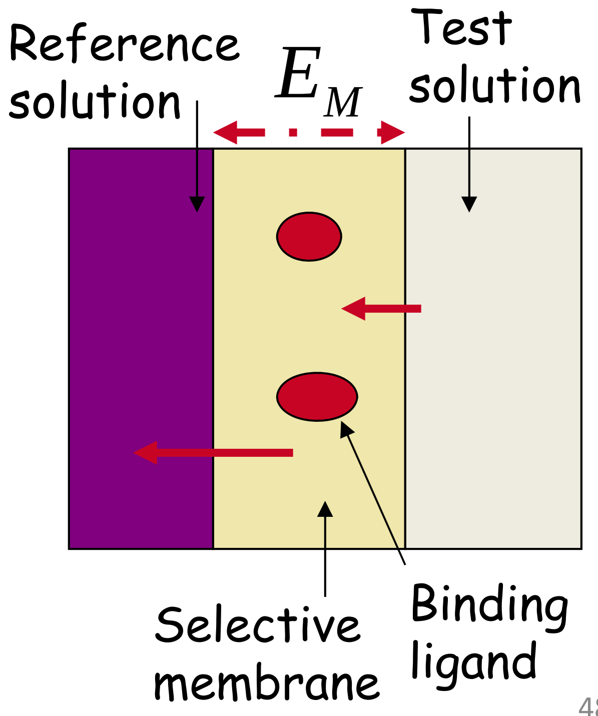



Since the ionic strength of an unknown analyte solution is usually not known, a high concentration of supporting electrolyte is added to both the standards and the samples to ensure that the same ionic strength is maintained.

Practical examples of potentiometric chemical sensor systems include the pH electrode where $E_{cell}$ which mainly reflects a membrane potential, is proportional to log $a_{H^+}$, and ion selective Electrodes where E is Proportional to log $a_{ion}$.

# Ion selective electrodes.

The glass electrode used to measure solution pH is the most
Common example of an ion selective electrode.
Ideally, an ion selective electrode responds only to one target ion
And is unaffected by the presence of other ions in the test solution.
In practice there is always some interference by other ions.
The operation of ISE devices does not depend on redox processes.
The key feature of an ISE is a thin selective membrane across
which only the target ion can migrate.
Other ions cannot
cross the membrane.
The Membrane contains a binding agent
which assists target ion transport across
the membrane. The membrane divides two
solutions. One is the inner reference
solution which contains a low
concentration of the target ion species,
and the other is an outer test solution
containing a higher concentration of
the target ion.



**Glass pH Electrodes**

The glass pH electrode is used almost universally for pH measurements and can be found in a range of environments including hospitals, chemical plants, and forensic laboratories. Its attraction lies in its rapid responses, wide pH range, functions well in physiological systems and is not affected by the presence of oxidising or reducing species. A typical pH electrode and pH meter are shown below.

$$pH = -\log_{10} a_{H^+}$$


Typical pH meter

Typical commercial Glass electrode

When a molecule or ion diffuses (which is facilitated via binding to a mobile ligand which is soluble in the membrane) from a region of high activity $a_1$ to a region of low activity $a_2$ the free energy change is given by the expression across. This diffusional process causes a charge imbalance across the membrane and a potential gradient or membrane potential is developed across the membrane thickness which inhibits further diffusion of target ion. In the steady state, the free energy decrease due to diffusion is balanced by the free energy increase due to coulombic repulsion as outlined across.
If the ion activity $a_2$ in the reference solution is known then the membrane potential is logarithmically dependent on the activity of the target ion.

$$\Delta G = -RT \ln\left\{\frac{a_1}{a_2}\right\}$$

$$-RT \ln\left\{\frac{a_1}{a_2}\right\} = -nFE_M$$

$$E_M = \frac{RT}{nF} \ln\left\{\frac{a_1}{a_2}\right\}$$

Membrane potential

In an ISE device a local equilibrium is set up at the sensor/ test solution interface and a membrane potential is measured. Many ISE materials have been developed utilising both liquid and solid state membranes.
The potentiometric response in all cases is determined by ion exchange reactions at the membrane/solution interface and ion conduction processes within the bulk membrane.
The most important difficulty with ISE systems is the interference from ionic species in solution other than the target analyte.
In general the response of an ISE to both the primary target ion and interferent ion species is given by the **Nikolskii-Eisenmann** equation. In the latter expression $k_{ij}$ denotes the **potentiometric selectivity coefficient** of the electrode against the j th interfering ion.

$$E = E^0_{cell} + S\log\left\{a_i + \sum_j k_{ij} a^{z_i/z_j}\right\}$$

Primary & Interferent ion valencies

Primary ion activity

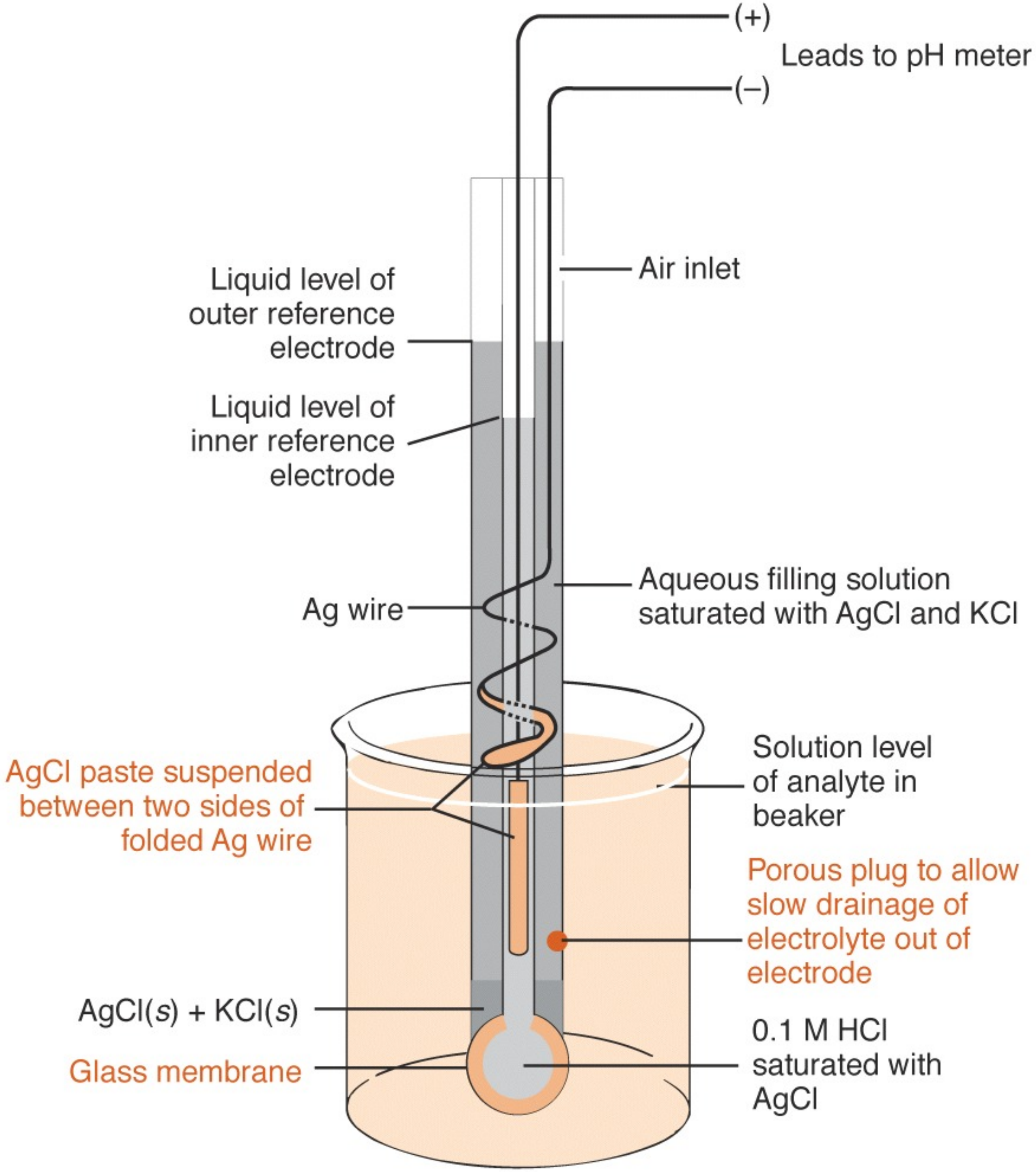
Nernst slope S

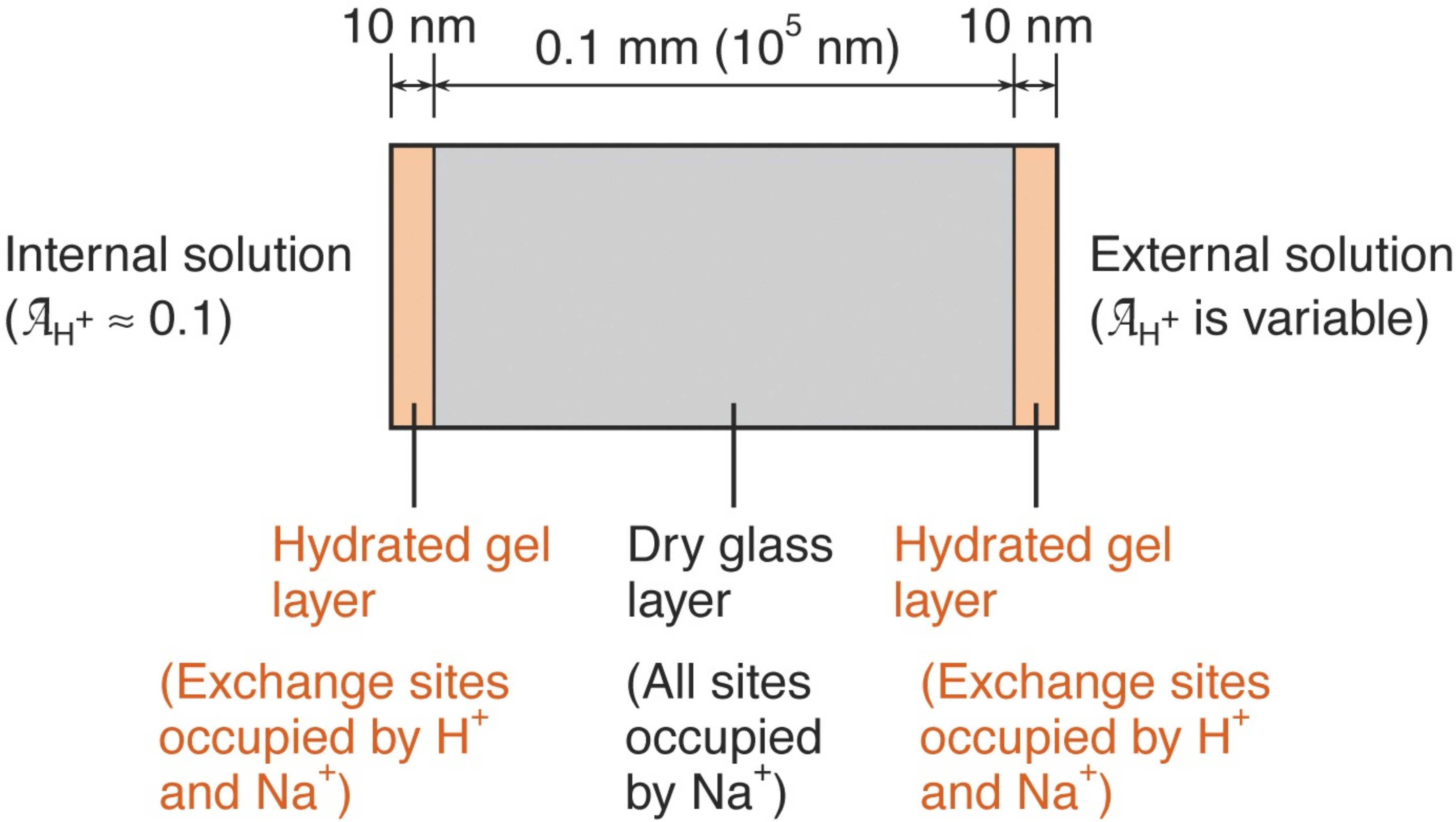
Selectivity coefficient $k_{ij}$ must be minimized

$$k_{ij} = \frac{u_j}{u_i} K_{ij}$$

Electrochemical Mobility of ions i and j

Equilibrium constant for process j(s) + i (m) -> j (m) + i (s)


(+)
Leads to pH meter
(–)
Air inlet
Liquid level of outer reference electrode
Liquid level of inner reference electrode
Aqueous filling solution saturated with AgCl and KCl
Ag wire
Solution level of analyte in beaker
AgCl paste suspended between two sides of folded Ag wire
Porous plug to allow slow drainage of electrolyte out of electrode
AgCl(s) + KCl(s)
0.1 M HCl saturated with AgCl
Glass membrane


10 nm
0.1 mm ($10^5$ nm)
10 nm
Internal solution
($\mathcal{A}_{H^+} \approx 0.1$)
External solution
($\mathcal{A}_{H^+}$ is variable)
Hydrated gel layer
(Exchange sites occupied by $H^+$ and $Na^+$)
Dry glass layer
(All sites occupied by $Na^+$)
Hydrated gel layer
(Exchange sites occupied by $H^+$ and $Na^+$)

3D network of silicate groups. There are sufficient cations within the interstices of this structure to balance the negative charge of silicate groups. Singly charged cations such as sodium are mobile in the lattice and are responsible for electrical conductance within the membrane.

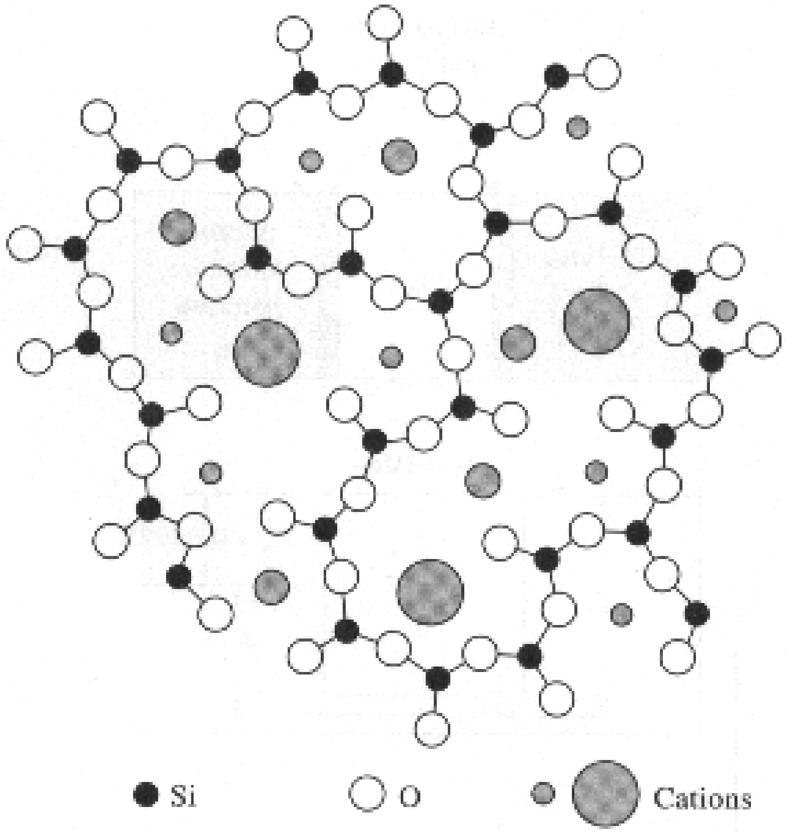



**Figure 23-5** Cross-sectional view of a silicate glass structure. In addition to the three Si—O bonds shown, each silicon is bonded to an additional oxygen atom, either above or below the plane of the paper. *(Adapted with permission from G. A. Perley, Anal. Chem., **1949**, 21, 395. Copyright 1949 American Chemical Society.)*

# Calibrating pH Electrodes

All pH electrodes require calibration prior to use. This usually takes the form of a two point calibration using appropriate buffer solutions. For example to calibrate the electrode for acidic measurements it is usual to:

- Use a pH = 7.0 buffer (typically a phosphate buffer)
- A pH = 4.0 buffer (typically phthalate solutions)

For alkaline measurements the recommended buffers are:

- A pH = 7.0 buffer
- A pH =10.0 buffer.

All of these buffers are generally purchased from the manufacturers and are based on the NIST (National Institute of Standards and Technology) certified standard buffers. [**A extended list of pH buffers can be found at :** *http://www.nist.gov/cstl/analytical/inorganic/ph.cfm*]. Prior to calibrating the pH electrode it is important to adjust the temperature to compensate for temperature effects. Some pH meters include a temperature probe which allows for automatic temperature compensation (ATC).

# Potentiometric indicators/titrations

Titrations carried out using potentiometric indicators are normally referred to as **potentiometric titrations**. This form of titration may be applied across all of the types of titration reaction, provided a suitable electrode is available that can detect either the analyte or the titrant. Table (9.6) lists the measured species in this form of titration and the electrodes normally employed to perform the measurement.

| **Titration type** | **What is measured** | **Type of electrode** |
|---|---|---|
| Acid/base | $[H^+]$ | Glass electrode |
| Redox | Ratio of $\frac{[\text{oxidised}]}{[\text{reduced}]}$ | Inert metal wire electrode – normally Pt or Au |
| Complexometric | [specific metal ion] | Ion-selective electrode |
| Precipitation | $[Ag^+]$ | Silver wire electrode |

Table 9.6 - comparison of potentiometric titrations

The instrumental components required in order to perform a potentiometric titration are:

- Source of titrant and mode of delivery;
- Titration vessel;
- Electrochemical cell comprising an indicator and a reference electrode;
- Mechanical stirrer;
- Millivoltmeter which is set to display pH for acid/base reactions;
- Computer controlled read-out device for use with an auto burette

These are combined together as illustrated in figure (9.20)

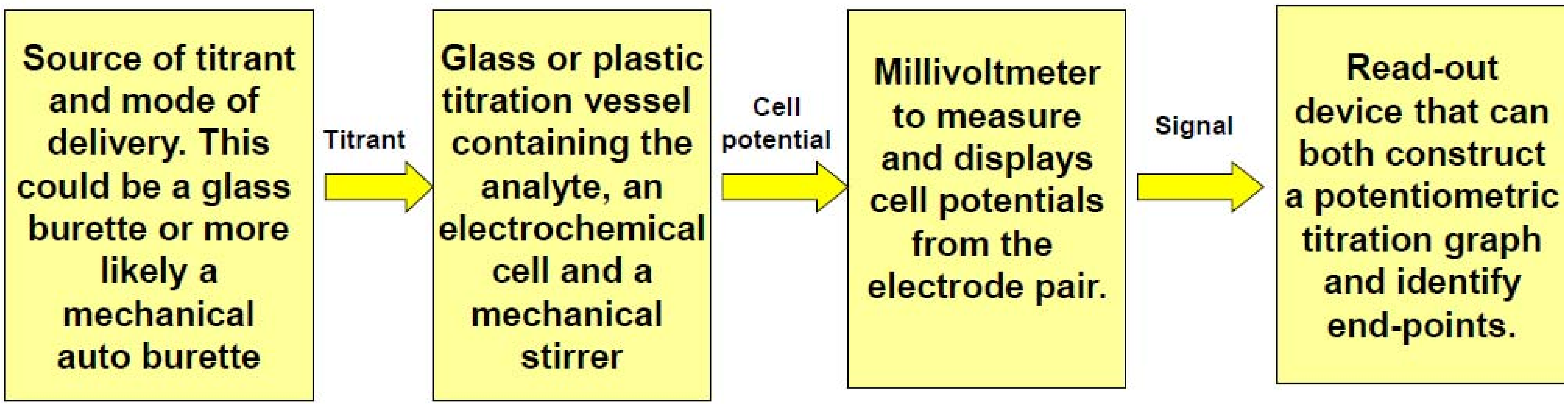



Figure (9.20) - potentiometric titration set-up

## Introduction to the theory underlying potentiometric indicators

The cell potential registered during a potentiometric titration can be expressed as:

$$E_{cell} = E_{indicator(in)} - E_{reference(ref)} \text{ Volts} \qquad \text{Equation (9.24)}$$

The potential of the indicator electrode can be expressed by the Nernst equation:

$$E_{indicator} = E^0 - \frac{0.059}{n} \log \frac{[red]}{[oxid]} \text{ Volts} \qquad \text{Equation (9.25)}$$

Where: $E^0$ represents the standard electrode potential for this half-cell
n is the number of electrons transferred in the redox reaction

For analyte ions where the oxidised or reduced form of the species are in their standard state ( metal or gas for instance), this simplifies to equation (9.26) as either:

$$E_{in} = E^0 + 0.059/n \log [cation] \quad \text{or}$$

$$E_{in} = E^0 - 0.059/n \log [anion] \quad \text{Volts@}20^{o}\text{C} \qquad \text{Equation (9.26)}$$

As the reference electrode chosen for the cell, is assumed to maintain a constant potential throughout the experiment, equation (9.26) may now be expressed as:

$$\mathbf{E_{cell}} = \{E^0 \pm 0.059/n \log [ion] - E_{ref}\}$$

$$= \mathbf{\{const. \pm 0.059/n \log [ion]\} \text{ Volts}} \qquad \text{Equation (9.27)}$$

Thus $\mathbf{E_{cell}}$ **α log [ion]** as all other terms are constant

Whatever the chemical reaction are involved in the titration, all potentiometric titrations produce ‘S’ shaped graphs of the types shown in figure (9.21 A&B)

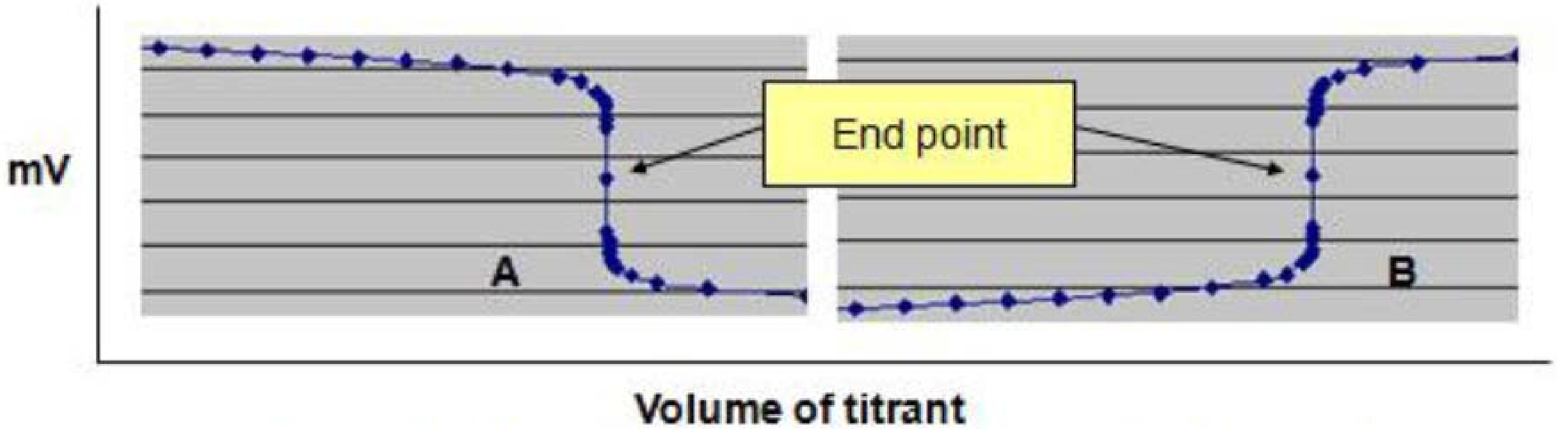



Figure 9.21 – examples of potentiometric titration graphs

One of the main advantages of potentiometric titrimetry, is the ability of the system to be automated, not only to produce titration graphs as illustrated in figure (2b.21), but to calculate and display titration end-points as well. The calculation of end-point location is achieved by use of 1$^{st}$ or 2$^{nd}$ mathematical derivative calculations. These are:

$$\frac{d(mV)}{d(vol)} \textit{ versus } \text{volume of titrant} \quad \text{or} \quad \frac{d^2(mV)}{d(vol)^2} \textit{ versus } \text{volume of titrant}$$

Graphs in these formats are shown on the next slide

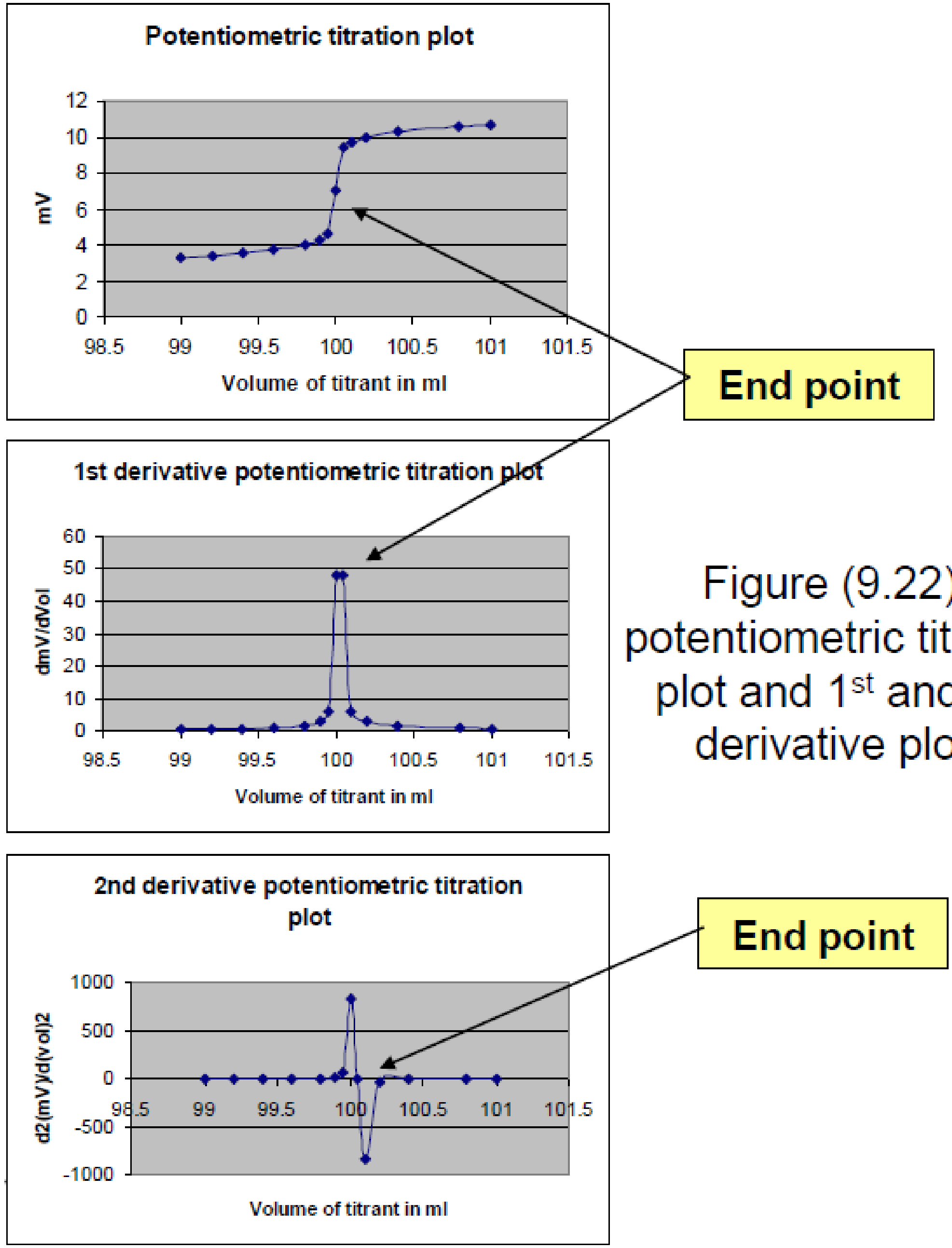
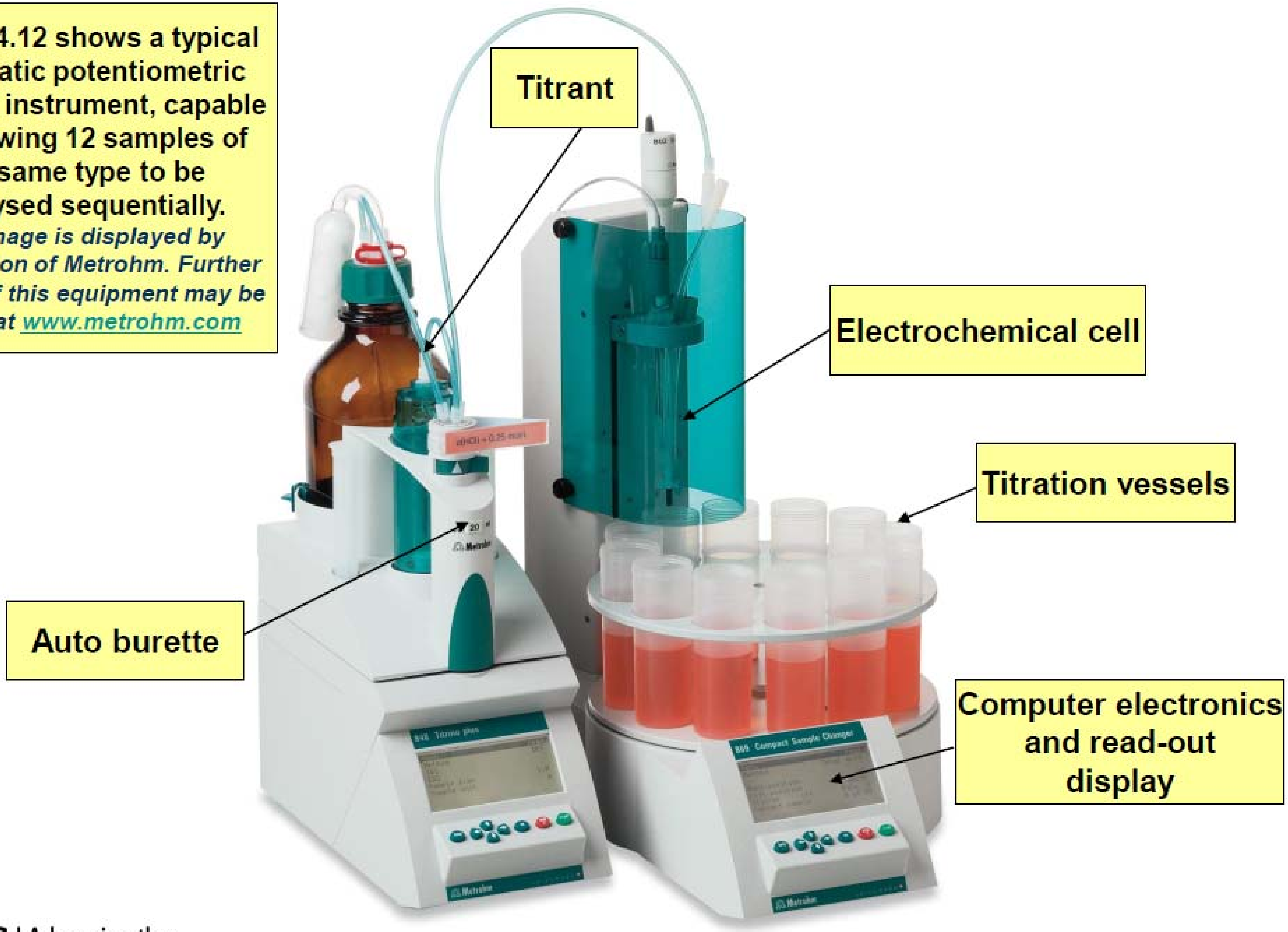



Figure (9.22) - potentiometric titration plot and 1$^{st}$ and 2$^{nd}$ derivative plots

**Potentiometric titration plots are characterised by showing significant changes in slope [d(mV)/d(Vol)] in the immediate vicinity of the end-point. This feature can be utilised to detect the maximum value in a plot of this first derivative *versus* volume of titrant. By going one stage further and calculating the second mathematical derivative, the resultant plot passes through zero at the end point. This can be detected by a computer controlled titrator and displayed as the end-point. Illustrations of these plots are shown in figure (9.22). A typical auto-titrator is shown as figure (9.23) on the next slide**

**Figure 4.12 shows a typical automatic potentiometric titration instrument, capable of allowing 12 samples of the same type to be analysed sequentially.**

***The image is displayed by permission of Metrohm. Further details of this equipment may be found at www.metrohm.com***




RSC | Advancing the Chemical Sciences

Figure 9.23 - typical potentiometric auto-titrator

# Advantages of potentiometric over visual indicators

There are number of advantages offered by potentiometric indicators over visual indicators to follow the progress of titrimetric reactions and detect end-points. These are:

- Ability to function is highly coloured solutions;

- Ability to find multiple end-points when samples contain more than one titratable species. For instance, a sample containing both weak and strong acids or polyprotic acids (eg: orthophosphoric acid $H_3PO_4$) where there is a significant difference between the $K_a$ values of the titratable protons. **See example (9.i) on the next slide**

- Offers opportunities for automation for both detection of end-points and for the analysis of multiple samples dispensed from auto-samplers.

**Example (9.i)** – titration of orthophosphoric acid solution with standardised NaOH

The 3 protons are all titratable, however only the first two will be detectable potentiometrically, as the $K_a$ value of the 3rd proton is too low to be detectable.

$$H_3PO_{4(s)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_2PO_4^-{}_{(aq)} \quad K_{a1} = 7.5\times10^{-3}$$ - 1st end point

$$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HPO_4^{2-}{}_{(aq)} \quad K_{a2} = 6.2\times10^{-8}$$ - 2nd end point

$$HPO_4^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + PO_4^{3-}{}_{(aq)} \quad K_{a3} = 2.14\times10^{-13}$$

**Figure (9.24), shows a typical potentiometric titration plot for a polyprotic acid. For orthophosphoric acid on its own, the volume of titrant required for the second end point should be exactly double that to the first.**

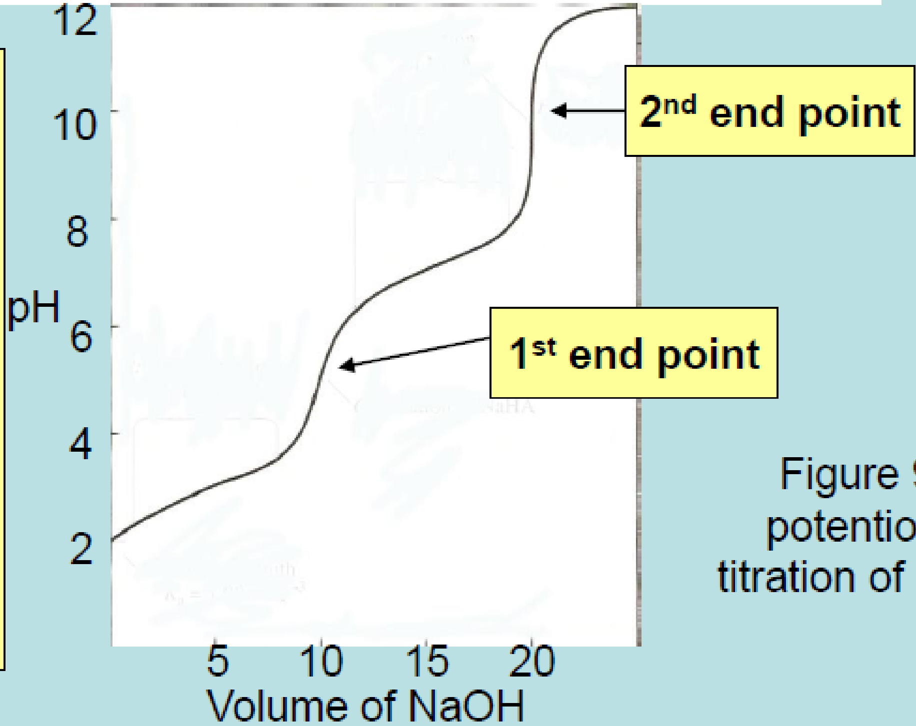



Figure 9.24 – typical potentiometric plot for titration of a polyprotic acid

# Ion-Selective Electrodes

Since the introduction of the pH electrode during the 1930s chemists have sought membrane materials which are sensitive to ions other than hydrogen ions. This has led to a number of membrane electrodes being developed based around;

- Glass membranes
- Plastic membranes
- Solid state electrodes

Generally these electrodes are useful for the direct measurement of ions at low concentrations. They are especially suited to measurements in biological media as they are not impaired by proteins, which has seen a rapid growth in medical applications. The most significant drawback of the electrodes is that they are **not specific but only selective** for the measurement of individual ion activities. Therefore they are more correctly referred to as **ion- selective electrodes**

# Glass membranes

Glass membranes are made from an ion-exchange type of glass (mainly silicate based). This type of ISE has good selectivity, but only for several single-charged cations eg: $H^+$, $Na^+$, and $Ag^+$. The glass membrane has excellent chemical durability and can work in very aggressive media. The most common example of this type of electrode is the pH glass electrode. Gas sensing electrodes (which are also based on pH electrodes), are available for the measurement of a limited range of gases. These diffuse across a thin polymeric membrane to alter the pH of a thin film of buffer solution which is itself in contact with a pH glass electrode.

## Solid State membranes

These membranes are made from mono- or polycrystallites of a single substance. They have good selectivity, because only ions which can introduce themselves into the crystal structure can interfere with the electrode response. Selectivity of crystalline membranes can be for both cation and anion of the membrane-forming substance. An example is the fluoride selective electrode based on $LaF_3$ crystals.

# Polymer Membrane Electrodes

Polymer membrane electrodes consist of various ion-exchange materials incorporated into an inert matrix such as PVC, or silicone rubber. After the membrane is formed, it is sealed to the end of a PVC tube. The potential developed at the membrane surface is related to the concentration of the species of interest. Electrodes of this type include potassium, calcium, chloride,  nitrate, perchlorate, potassium, and one for water hardness.

| Ion to be measured | Type of membrane | Cconcentration range/M | Optimum pH | Interfering ions | Selectivity const. k1,2 |
|---|---|---|---|---|---|
| $Na^+$ | Glass | $1 – 10^{-5}$ | >7 | $H^+$<br>$Cs^+$, $Li^+$<br>$K^+$ | $10^2$<br>0.002<br>0.001 |
| $Br^-$ | Solid-state | $1 – 5 X 10^{-6}$ | 2 – 12 | $S^{2-}$, $I^-$, $CN^-$ | ~ $10^6$ |
| $Cl^-$ | Solid-state | $1 – 5 X 10^{-5}$ | 2 - 11 | $I^-$, $CN^-$<br>$S^{2-}$<br>$Br^-$ | ~ $10^6$<br>~ $10^6$<br>~ $10^5$ |
| $F^-$ | Solid state | $1 – 10^{-6}$ | 5 -8 | $OH^-$ | ~ $10^4$ |
| $Ca^{2+}$ | PVC-gel | $1 – 5 X 10^{-7}$ | 6 - 8 | $Zn^{2+}$<br>$Pb^{2+}$<br>$Mg^{2+}$ | 3.2<br>0.063<br>0.014 |
| $NO_3^-$ | PVC-gel | $1 – 7 X 10^{-6}$ | 3 - 10 | $ClO_4^-$<br>$I^-$<br>$Br^-$<br>$NO_2^-$<br>$Cl^-$ | ~ $10^6$<br>20<br>0.1<br>0.04<br>0.004 |
| $CO_2$ | Gas-sensing | $10^{-2} – 10^{-4}$ | | Volatile, weak acids interfere | |
| $NH_3$ | Gas-sensing | $1 – 10^{-6}$ | | Volatile amines interfere | |



Table 2b.5
Examples of commercial ion selective electrodes

Figure (9.17) is a schematic representation of a cell arrangement for use of an ISE. Figure (9.18) shows some typical membranes. Figure (9.19) shows schematically, the fundamental features in a gas sensing electrode

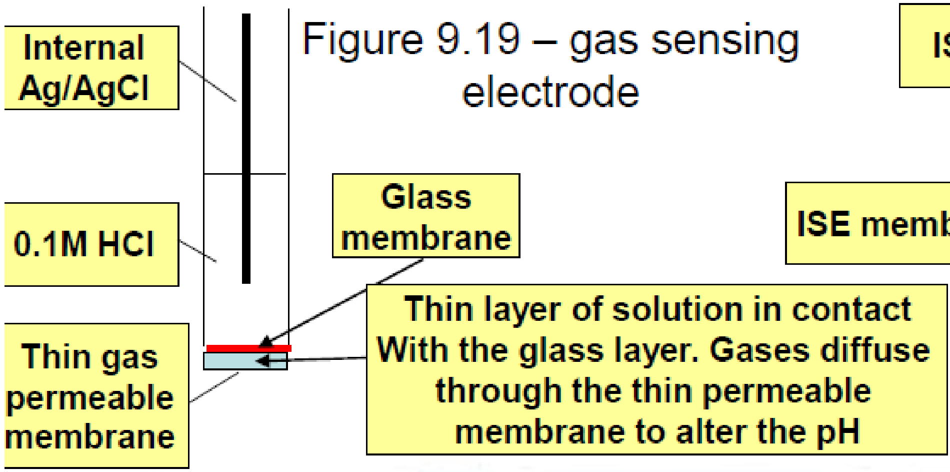



Figure 9.19 – gas sensing electrode

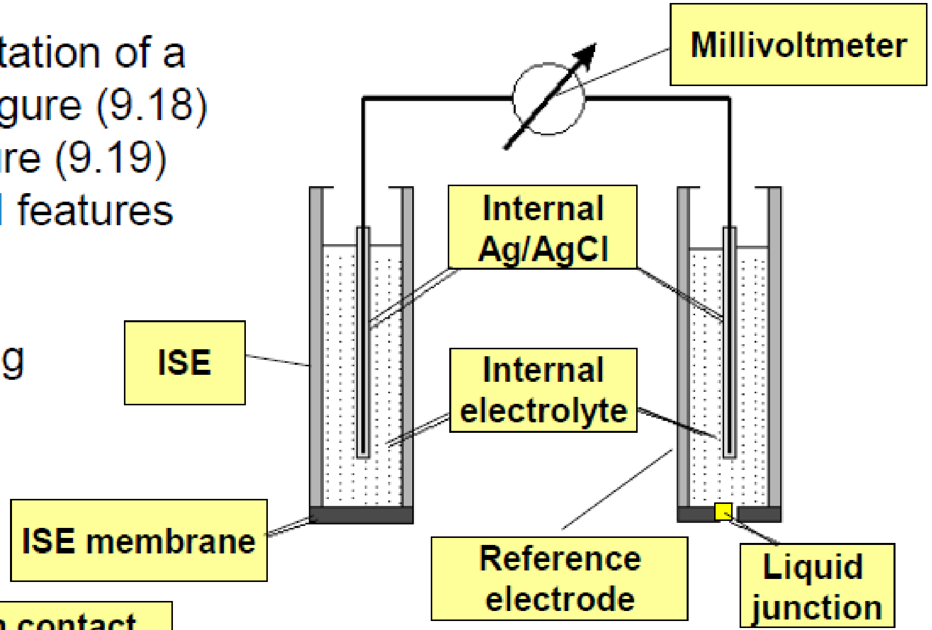



Figure 9.17 – cell arrangement for ISE

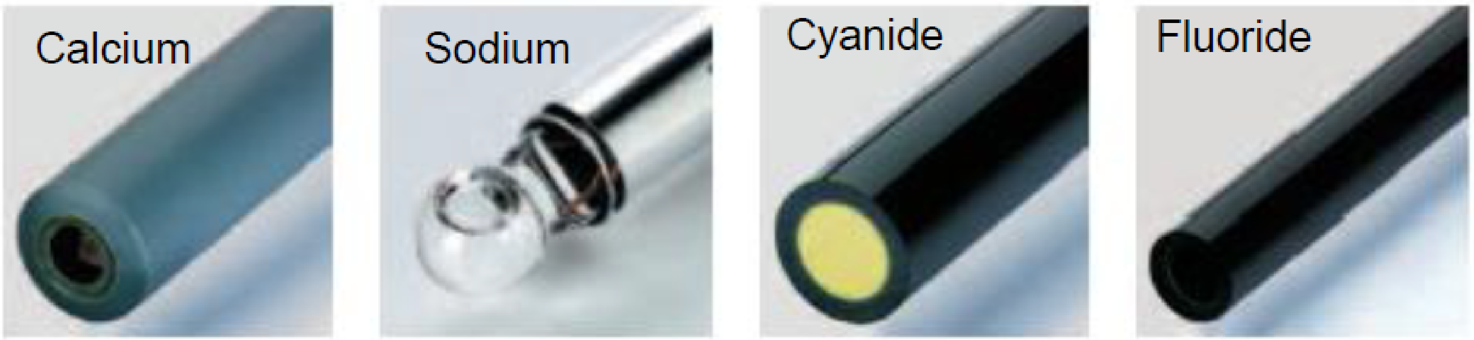



Figure 9.18 – examples of commercial ion selective electrodes

The potential of an ion selective electrode in the presence of a single ion follows a variation of the Nernst equation with n being replaced by z the charge on the ion being measured.

$$E_{ise} = k + \frac{2.303RT}{zF} \log a_{cation} \qquad \text{Equation (9.21)}$$

Note: +ve for cations, -ve for anions

$$E_{ise} = k - \frac{2.303RT}{zF} \log a_{anion} \qquad \text{Equation (9.22)}$$

The constant $k$ depends on the nature of the internal reference electrode, the filling solution and the construction of the membrane and is determined experimentally by measuring the potential of a solution of the ion of known activity.

In table (9.5) a different $k$ value is quoted $k_{1,2}$ or $k_{a,b}$. This is known as the selectivity coefficient for the electrode and is an indication of the how significantly other listed ions will interfere with the measurement of the target ion. This value is obtained from the **Nicolsky equation**, equation (9.23).

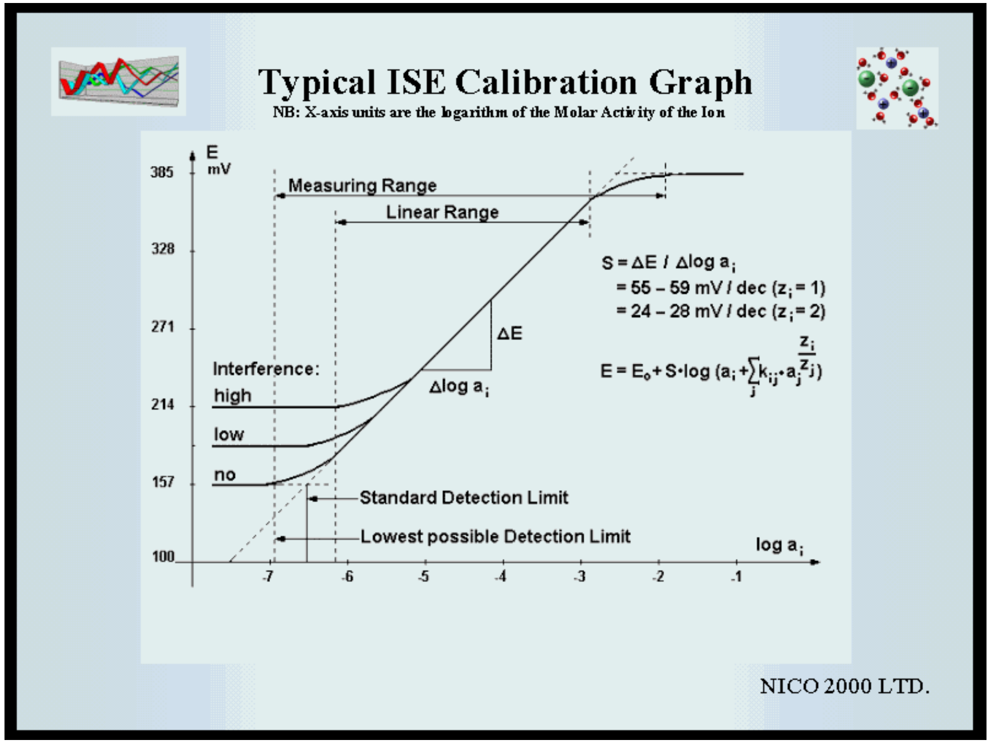
# The Nicolsky Equation

A general equation can be written for mixtures of two ions where the ion to be measured is designated ion A and the potential interfering ion as ion B.

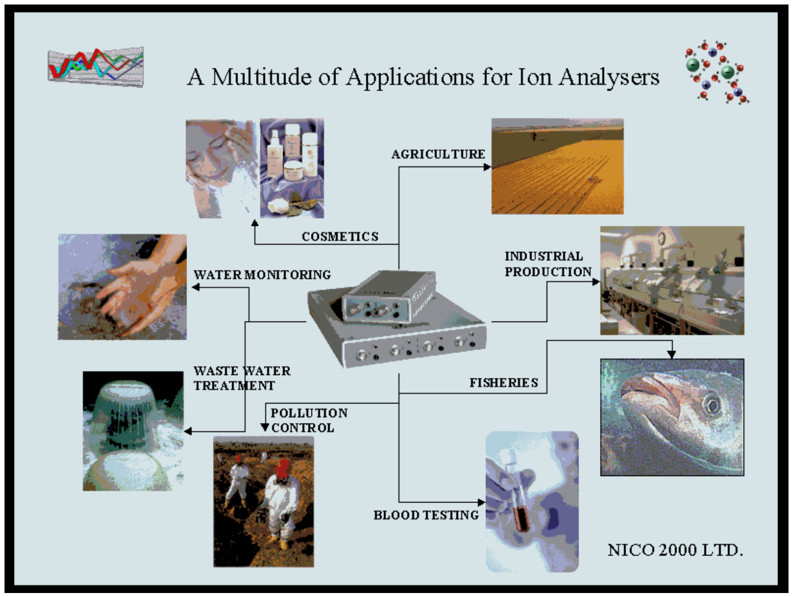
$$E_{AB} = k_A - \frac{2.303RT}{z_A F} \log (a_A + K_{AB} a_B^{z_A/z_B}) \qquad \text{Equation (9.23)}$$

A value for K can be obtained by making measurements of the potential of two different standard solutions of known activity and then solving the two simultaneous equations for the two constants.

One problem with selectivity coefficients is that they are not really constant and therefore vary with relative concentration. Hence they should only be treated as an indicator of possible problems as the absolute magnitude may be incorrect. Alternative methods such as the mixed solution method involves a graphical extrapolation to estimate K. In practise it usually unnecessary to determine this value experimentally as it should be quoted on the manufacturer's literature.



Typical ISE Calibration Graph
NB: X-axis units are the logarithm of the Molar Activity of the Ion
E
mV
385
328
271
214
157
100
Measuring Range
Linear Range
S = ΔE / Δlog a$_i$
= 55 – 59 mV / dec (z$_i$ = 1)
= 24 – 28 mV / dec (z$_i$ = 2)
ΔE
Δlog a$_i$
Interference:
high
low
no
Standard Detection Limit
Lowest possible Detection Limit
log a$_i$
-7
-6
-5
-4
-3
-2
-1
NICO 2000 LTD.

A Multitude of Applications for Ion Analysers
AGRICULTURE
COSMETICS
INDUSTRIAL PRODUCTION
WATER MONITORING
WASTE WATER TREATMENT
FISHERIES
POLLUTION CONTROL
BLOOD TESTING
NICO 2000 LTD.

# ISE Applications.

- Ion-selective electrodes are used in a wide variety of applications for determining the concentrations of various ions in aqueous solutions. The following is a list of some of the main areas in which ISEs have been used.
- Pollution Monitoring: CN, F, S, Cl, $NO_3$ etc., in effluents, and natural waters.
- Agriculture: $NO_3$, Cl, $NH_4$, K, Ca, I, CN in soils, plant material, fertilisers and feedstuffs.
- Food Processing: $NO_3$, $NO_2$ in meat preservatives.
- Salt content of meat, fish, dairy products, fruit juices, brewing solutions.
- F in drinking water and other drinks.
- Ca in dairy products and beer.
- K in fruit juices and wine making.
- Corrosive effect of $NO_3$ in canned foods.
- Detergent Manufacture: Ca, Ba, F for studying effects on water quality.
- Paper Manufacture: S and Cl in pulping and recovery-cycle liquors.
- Explosives: F, Cl, $NO_3$ in explosive materials and combustion products.
- Electroplating: F and Cl in etching baths; S in anodizing baths.

# ISE Advantages.

- When compared to many other analytical techniques, Ion-Selective Electrodes are relatively inexpensive and simple to use and have an extremely wide range of applications and wide concentration range.
- The most recent plastic-bodied all-solid-state or gel-filled models are very robust and durable and ideal for use in either field or laboratory environments.
- Under the most favourable conditions, when measuring ions in relatively dilute aqueous solutions and where interfering ions are not a problem, they can be used very rapidly and easily (e.g. simply dipping in lakes or rivers, dangling from a bridge or dragging behind a boat).
- They are particularly useful in applications where only an order of magnitude concentration is required, or it is only necessary to know that a particular ion is below a certain concentration level.
- They are invaluable for the continuous monitoring of changes in concentration: e.g. in potentiometric titrations or monitoring the uptake of nutrients, or the consumption of reagents.
- They are particularly useful in biological/medical applications because they measure the activity of the ion directly, rather than the concentration.
- In applications where interfering ions, pH levels, or high concentrations are a problem, then many manufacturers can supply a library of specialised experimental methods and special reagents to overcome many of these difficulties.
- With careful use, frequent calibration, and an awareness of the limitations, they can achieve accuracy and precision levels of ± 2 or 3% for some ions and thus compare favourably with analytical techniques which require far more complex and expensive instrumentation.
- ISEs are one of the few techniques which can measure both positive and negative ions.
- They are unaffected by sample colour or turbidity.
- ISEs can be used in aqueous solutions over a wide temperature range. Crystal membranes can operate in the range 0°C to 80°C and plastic membranes from 0°C to 50°C.

# Quantitative applications of potentiometry

There are two ways in which the output from potentiometric measurements can be used analytically:

- Directly – termed **Direct Potentiometry**
- Relatively – **Potentiometric titrimetry**

**Potentiometric titrimetry was covered in Chapter 4 of this teaching and learning programme and is reproduced here in slides 47 - 54**

Direct potentiometry provides a rapid and convenient method of determining the activity of a variety of cations and anions. The technique requires only a comparison of the cell potential developed between the indicator and reference electrodes, when immersed in the analyte solution compared to that developed when immersed in one or more standard solutions of known analyte concentration The best example of this, is of course, the measurement of pH using a typical pH meter calibrated against two buffer solutions. A useful on-line application is the monitoring of nitrate levels in river waters using a nitrate ISE. A continuous read out of nitrate levels is provided over long period of time.

# Amperometry

## Introduction

**Amperometry** refers to the measurement of the current flow resulting from an electrochemical oxidation or reduction of an electroactive species. The measurement technology normally uses a potentiostatic circuit (see next slide) and is created, by maintaining a **constant potential** at the working electrode (normally Pt, Au or C based), that is sufficient to bring about the redox transition of interest. The potential chosen will be on the plateau region of the current/voltage Voltammogram (refer to slide 64). Under normal conditions, the current flow is directly proportional to the concentration of the species being measured.

The technique may be used:

- To act as a means of detecting end points in a redox (or in some instances a precipitation or a complexometric) titration;
- As the basis of an electrochemical detector for HPLC;
- As a basis for measurement in some types of biosensor.

All three of these application are described in the next few slides.

# Applications of Amperometry

## Instrumentation

In the majority of applications, a potentiostatic cell arrangement is used. Figure (9.30) shows a typical cell arrangement. A potentiostatic cell comprises three electrodes:

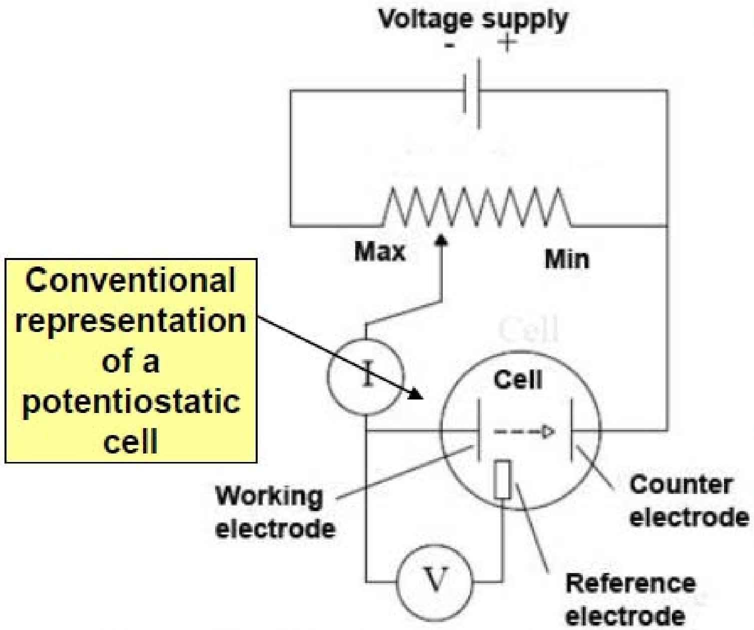



Figure 9.30 - Arrangement for a potentiostatic cell

- Working [where the redox reaction occurs]
- Reference [generally calomel or Ag/AgCl]
- Auxiliary / Counter [generally Pt]

The potential of the working electrode is controlled with respect to the reference electrode whilst the current flows between working and the auxiliary electrodes. The advantage of this cell design over a simpler two electrode design (cathode and anode), is that it avoids any 'back emf' (potential) caused by the IR drop. Note: the IR drop is normally only an issue in solutions of high resistance (low conductance)

# Amperometric titrations

This represents a form of end-point detection in a titration reaction, where the end-point is determined by the measurement of current flows just before and just after the end point, when the concentration levels are low. The end point is then calculated mathematically by finding the point of intersection between the best straight lines drawn through these two sets of points. The measurement voltage is selected such that either the analyte, the titrant or both are electroactive. Figures (9.31) below show typical of graphs that can be obtained.

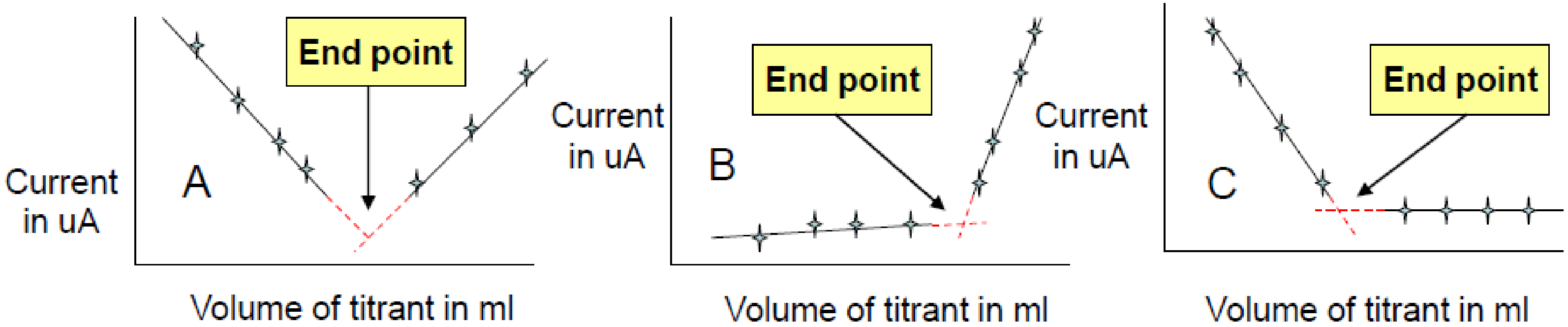



Figure 9.31 – typical amperometric titration plots

**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.**
**Note: The initial line in 'B' and the second line in 'C' may well not be horizontal, reflecting other features of the electrochemistry, not considered in this discussion.**

| Advantages | Disadvantages |
| --- | --- |
| ▪ Avoids the use of difficult end-point detection using colour indicators;<br>▪ Rapid titration as only a few measurements are required around the end point;<br>▪ Ease of automation to carry out titration and detect end point;<br>▪ Offers some selectivity by choice of applied potential;<br>▪ Applicable to redox, precipitation & complexometric reactions.<br>▪ Requires relatively inexpensive electrochemical equipment | ▪ Requires specific equipment;<br>▪ Need to have voltammetric information so as to choose appropriate applied potential;<br>▪ Working electrode can be contaminated by products of reduction or oxidation, requiring cleaning to restore inert effectiveness. |

Table 9.7 – advantages and disadvantages of amperometric titrations

# Electrochemical detector for HPLC

The most popular detection mechanism for HPLC remains UV absorption, however there some applications where the detector in not sufficiently sensitive for the analysis required. Amperometry can provide an extremely sensitive method of detection for compounds that can be oxidised or reduced at a **polarized** working electrode. A typical flow cell is shown in figure (9.32):

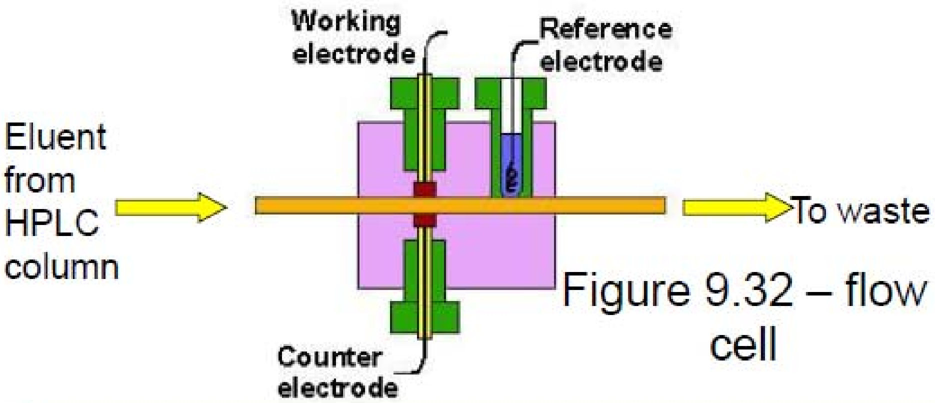



Figure 9.32 – flow cell

The most popular material for a working electrode in this context is 'Glassy Carbon', a non-porous carbon based substrate, whose electrode surface can be highly polished and may be used over a wide +ve and -ve voltage range.

One example for the application of electrochemical detection, is the detection of very low levels of nitro-compounds used as accelerants and explosives. Organic nitro-compounds can be analysed very sensitively by voltammetric techniques. The nitro grouping is reduced in two possible stages:

$$-NO_2 \xrightarrow{4e^-} -NHOH \xrightarrow{2e^-} -NH_2$$

Note: by careful choice of the applied potential at the working electrode, additional selectivity may be introduced into the analysis

# Analysis of dissolved oxygen using an amperometric sensor

A typical oxygen electrode is shown in figure (9.33). Oxygen diffuses through the thin polymer (Teflon) membrane to reach the platinum or gold cathode to which is applied sufficient negative potential to bring about oxygen reduction according to the equations shown below:

Cathode reaction $O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$

$H_2O_2 + 2e^- \rightarrow 2OH^-$

Anode reaction $Ag + Cl^- \rightarrow AgCl + e^-$

Total reaction $4Ag + O_2 + 2H_2O + 4Cl^- \rightarrow 4AgCl + 4OH^-$

Figure (9.33) shows a typical oxygen electrode of a simple two electrode type. Oxygen diffuses through the membrane and is reduced at the cathode. The rate of diffusion of oxygen to the cathode is proportional to its partial pressure in the sample in which the electrode is placed, and the amperometric current produced by the reduction is proportional to this. The electrode is calibrated by exposure to solutions of known oxygen content. Further details on this type of electrode may be found at: http://www.eutechinst.com/techtips/tech-tips16.htm and http://en.wikipedia.org/wiki/Clark_oxygen_sensor#Electrodes

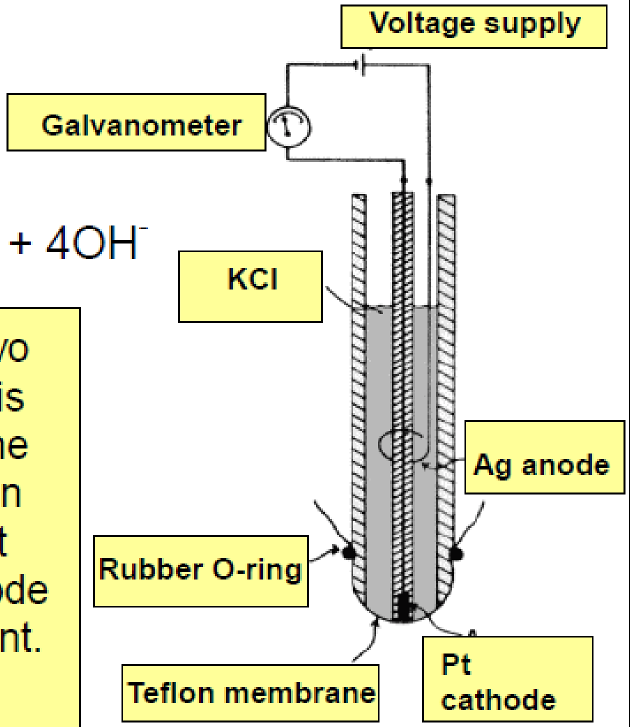



Figure 9.33 – dissolved oxygen electrode

# Biosensors using amperometric transducers

A chemical sensor is a device that transform chemical information, into an analytically useful signal. Chemical sensors normally contain two basic components:

- Chemical (molecular) recognition system (termed a **receptor**);
- A physicochemical **transducer**.

Biosensors are chemical sensors in which the recognition system utilises a biochemical mechanism. While all biosensors are more or less selective for a particular analyte, some are by design, only class selective. The transducer serves to transfer the signal from an output domain of the recognition system to mostly the electrical domain. One of the most important electrical transducer modes is amperometry. Important working electrode materials are:

- Metal or carbon electrodes;
- Chemically modified electrodes.

Analytes measurable by these systems are:

- Oxygen, sugars, alcohols, sugars, phenols, oligonucleotides

# Glucose biosensor

Enzymes are frequently used to modify an electrode surface and thus to impart selectivity in a measurement system. A good example is the glucose biosensor which uses an enzyme (glucose oxidase). The glucose oxidase is immobilised in a gel (for instance an acrylamide gel) and coated onto the surface of a platinum electrode. The gel also contains an electrolyte (KCl) and makes contact with an Ag/AgCl ring electrode to complete the cell. Figure (9.34) below is a schematic representation of a typical glucose biosensor type electrode

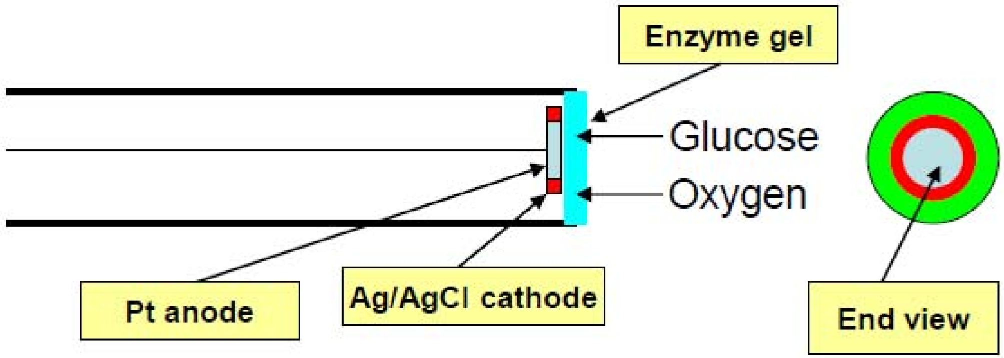



Figure 9.34 – schematic diagram of a glucose biosensor

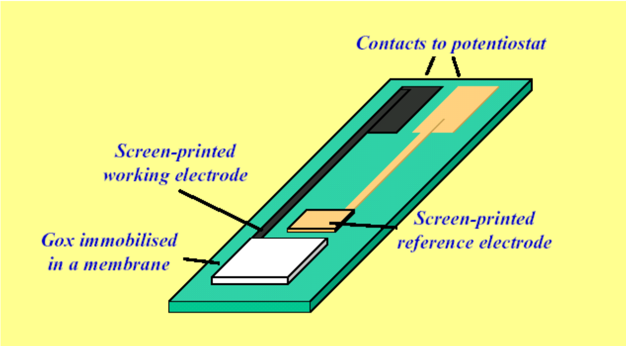
Glucose and oxygen diffuse from the analysis solution into the gel, where the reaction is catalysed to produce $H_2O_2$. Part of this diffuses to the Pt anode where it is oxidised to $O_2$. The reactions are shown in equations (9. 39 & 40) below. To bring about the oxidation shown in equation (9.40), requires a voltage or ca. +0.6 V wrt a Ag/AgCl reference electrode

$$\text{Glucose} + O_2 + H_2O \longrightarrow \text{gluconic acid} + H_2O_2 \qquad \text{Equation (9.39)}$$

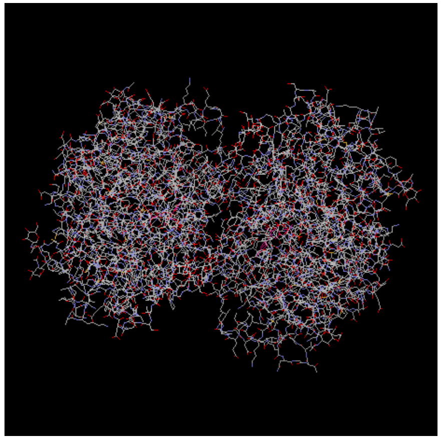
$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^- \qquad \text{Equation (9.40)}$$

# 3 generations of enzyme biosensor electrodes.

- **1st generation**: Charge shuttling via $O_2/H_2O_2$.
- **2nd generation** : Synthetic electron shuttles (redox mediators) used.
- **3rd generation** : No mediator used , enzyme wiring.







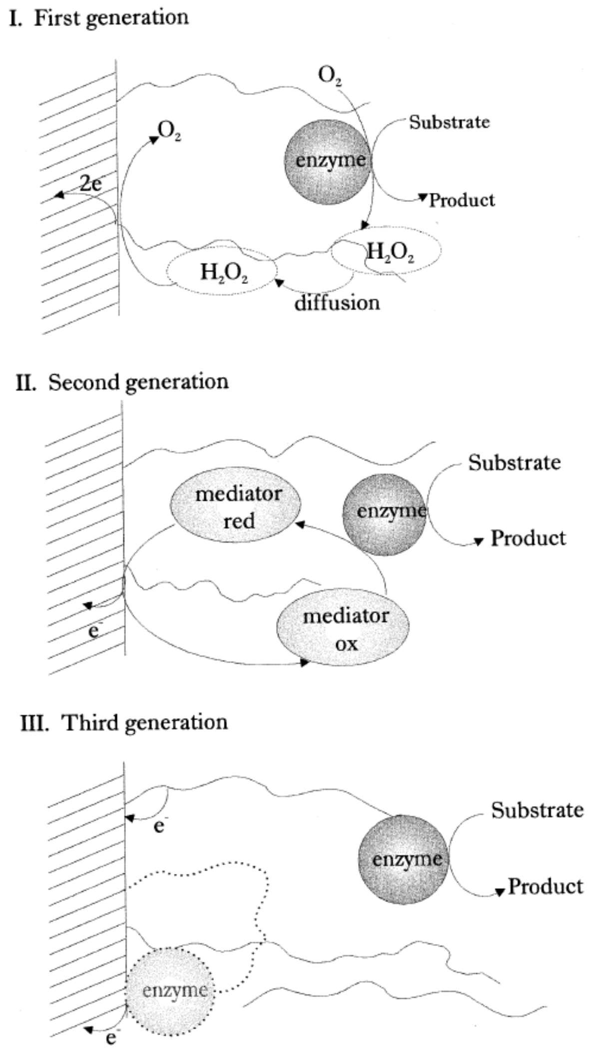



Fig. 2. Schematic representation of the three generations of enzyme electrodes.

*W. Schuhmann / Reviews in Molecular Biotechnology 82 (2002) 425–441*

# Enzyme communication with electrodes.

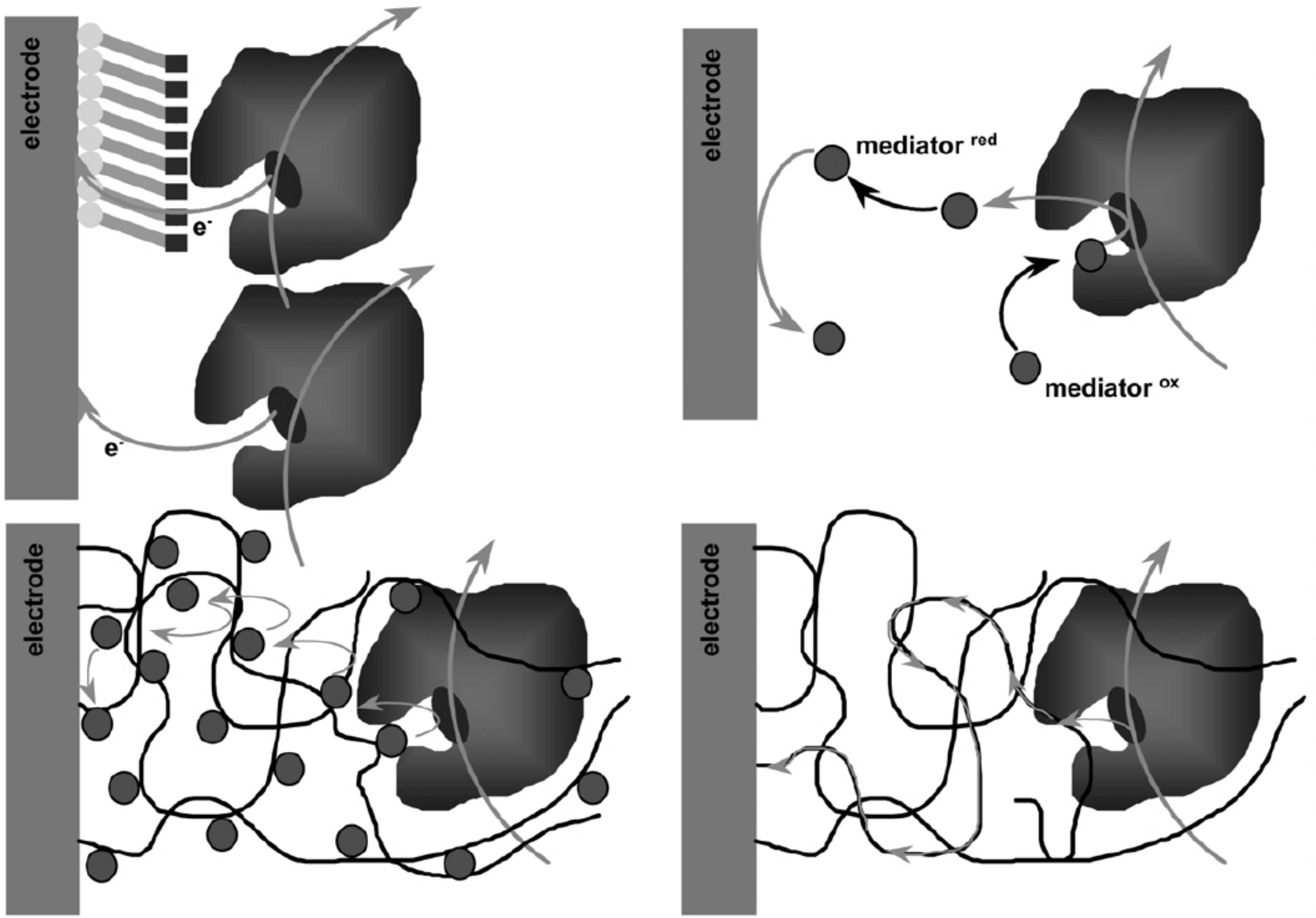
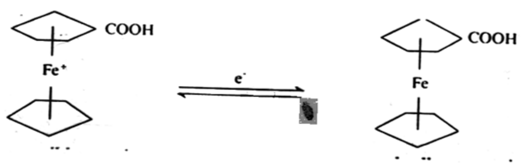



Fig. 1. Schematic representation of ET possibilities between enzymes and electrodes. (a) Direct ET at a bare or monolayer-modified electrode. (b) Shuttle mechanism based on free-diffusing redox species. (c) Electron hopping in a redox-relay modified polymeric hydrogel. (d) ET via a conducting polymer chain.

*W. Schuhmann / Reviews in Molecular Biotechnology 82 (2002) 425–441*

# Homogeneous mediation using substituted ferrocene.

Mediator redox couple reasonably insoluble in aqueous solution, hence is located close to electrode.




$$G + FAD \rightarrow GL + FADH_2$$
$$FADH_2 + 2Fe(Cp)_2^+ \rightarrow FAD + 2Fe(Cp)_2 + 2H^+$$
$$2Fe(Cp)_2 \rightarrow 2Fe(Cp)_2^+ + 2e^-$$

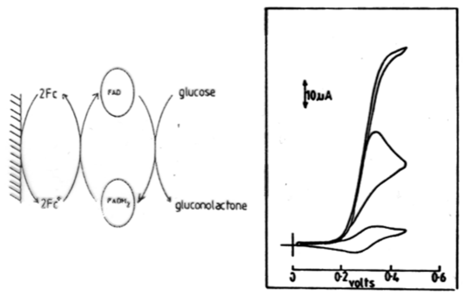
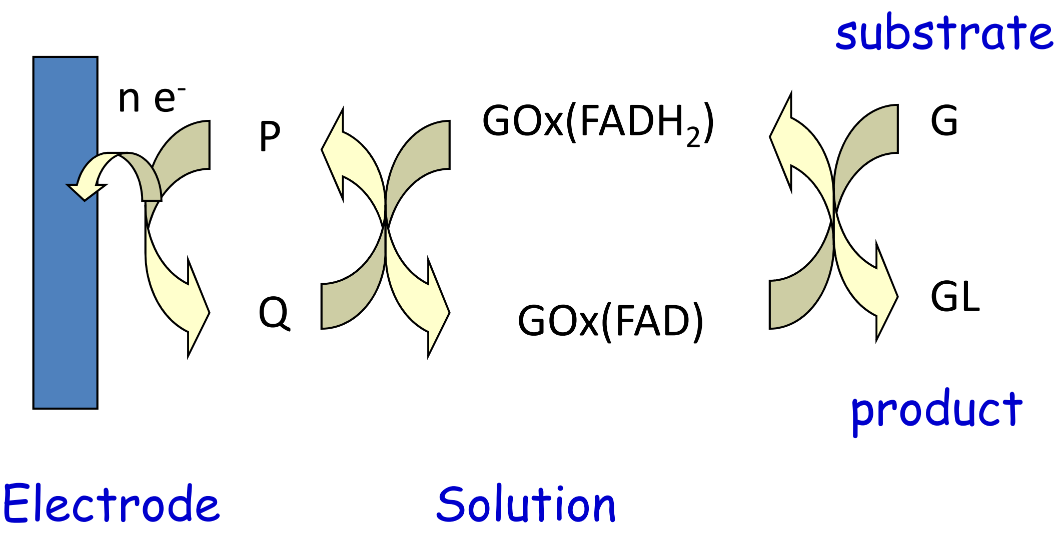
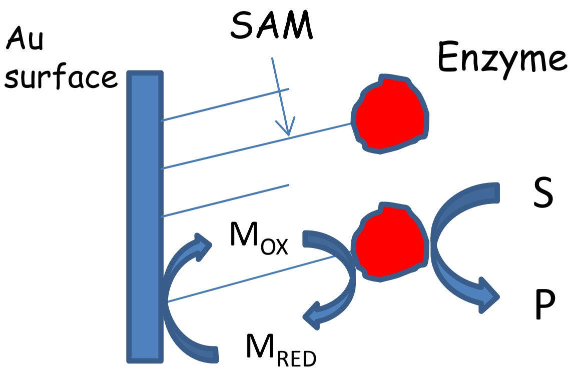


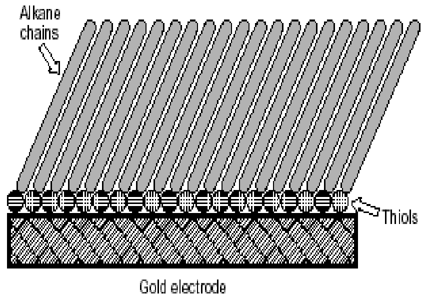

FIGURE 17. The scheme for the homogeneous mediation of glucose oxidase oxidation by ferrocenes. The inset shows typical cyclic voltammetric results for the system in the presence of increasing concentrations of glucose. The data were recorded at a glassy carbon electrode electrode (area 0.05 $cm^2$) in 0.085 mol $dm^{-3}$ phosphate buffer pH 7.0 containing 0.5 mmol $dm^{-3}$ ferrocene monocarboxylic acid and 38 mol $dm^{-3}$ glucose oxidase at a sweep rate of 5 mV $s^{-1}$, potentials are vs. SCE. a) No glucose, b) 0.5 mmol $dm^{-3}$ glucose, c) 2.5 mmol $dm^{-3}$ glucose.




P,Q represents reduced and oxidised forms of redox mediator (ferrocene and ferricinium); G = glucose, GL = gluconolactone. GOx ($FADH_2$) = reduced form of glucose oxidase; GOx(FAD) = oxidised form of glucose oxidase.




## SAM



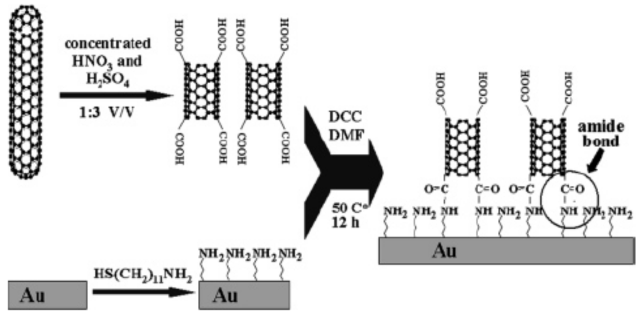
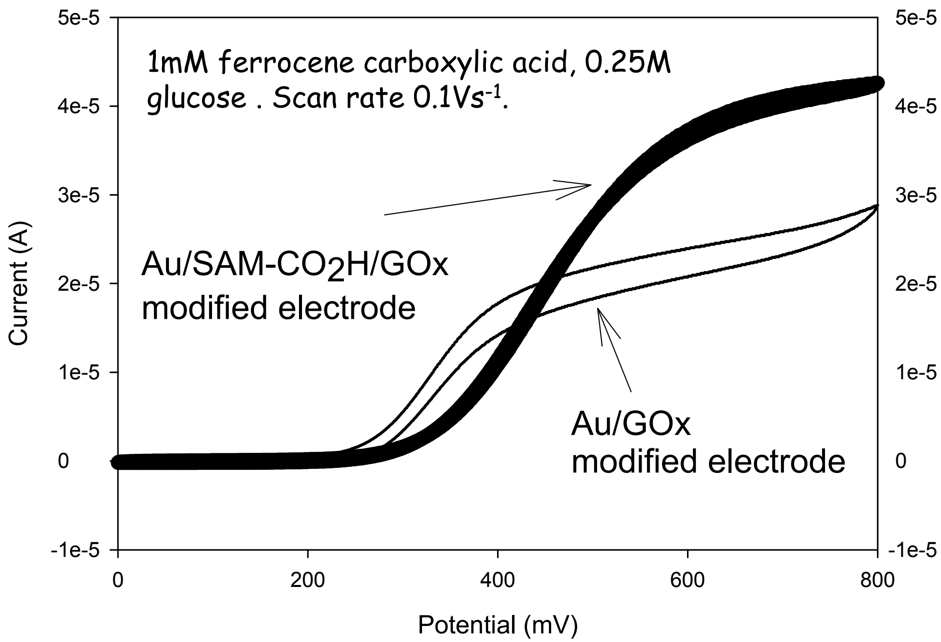
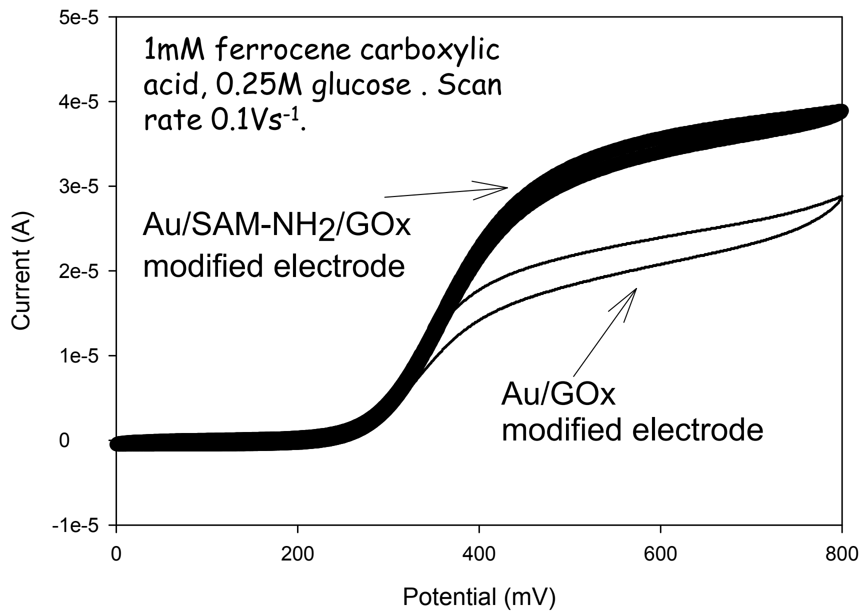




**Figure 2.** Schematic representation of the formation of SWNT assemblies.





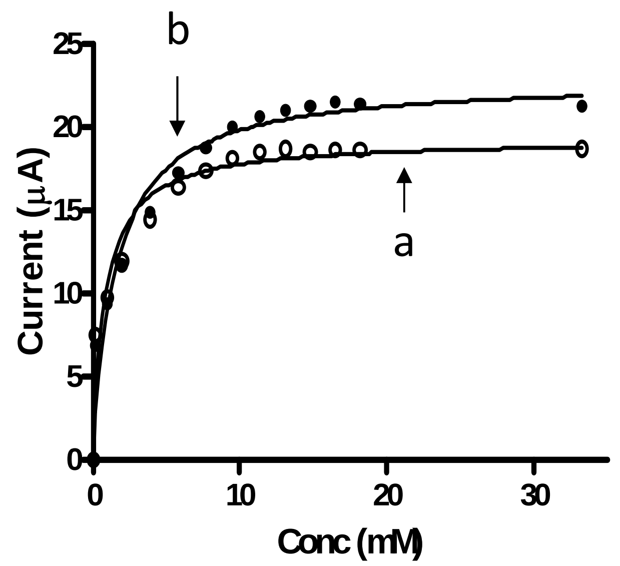

Glucose bio-sensing via immobilized redox enzyme using self assembled monolayer (SAM)

# Analysis of immobilized enzyme kinetics.

Enzyme/substrate kinetics well described By Michaelis-Menten model.

| System | $V_{max}$ /μA | $K_M$/mM |
|---|---|---|
| Au/GOx | 19 | 1.5 |
| Au/MUA/GOx | 23 | 0.8 |

$$f_\Sigma = \frac{i_{SS}}{nFA} = \frac{v_{max} c}{K_M + c} = \frac{k_c e_\Sigma c}{K_M + c}$$

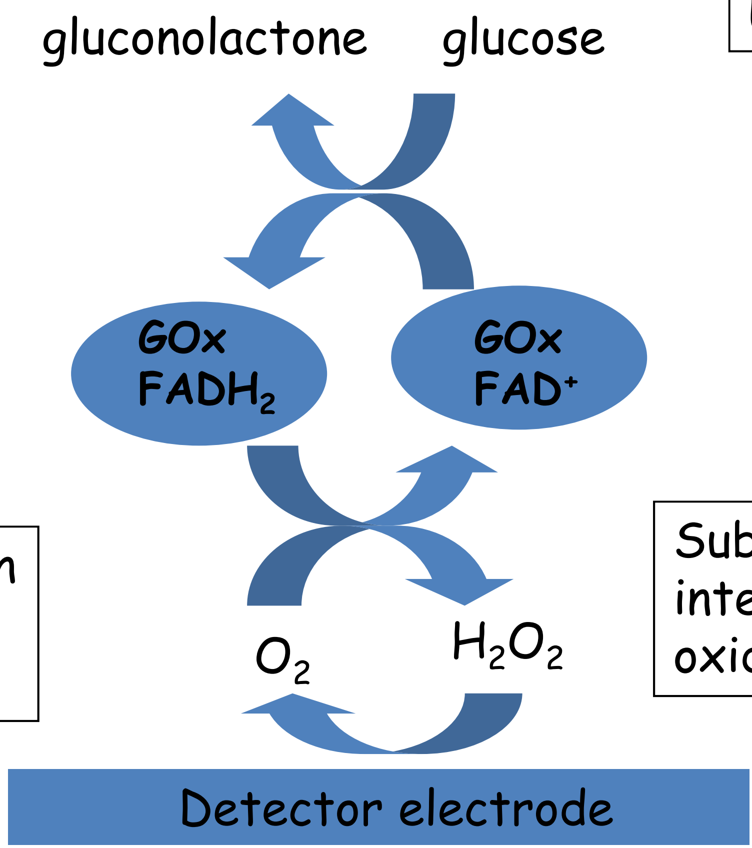



Steady state current vs concentration data
(a) Au/glucose oxidase,
(b) Au/SAM-$CO_2H$/glucose oxidase.
Data fit to simple Michaelis-Menten kinetic equation using NLLS fitting program.

# Amperometric glucose detection via traditional oxygen mediation.

$E_{appl}$ = + 0.8 V

Ping pong mechanism for the oxidation of glucose by oxygen catalysed by glucose oxidase.

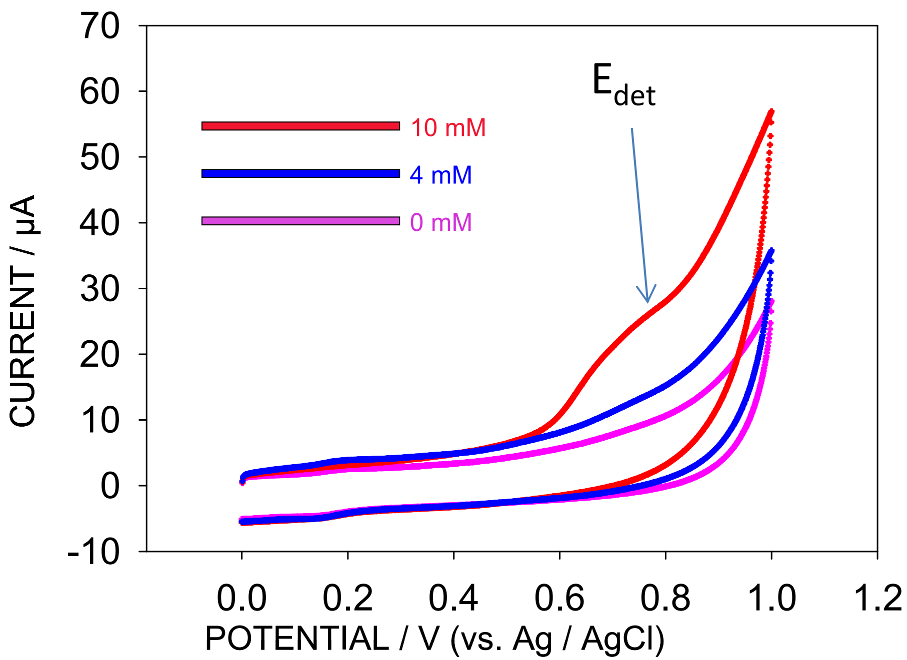


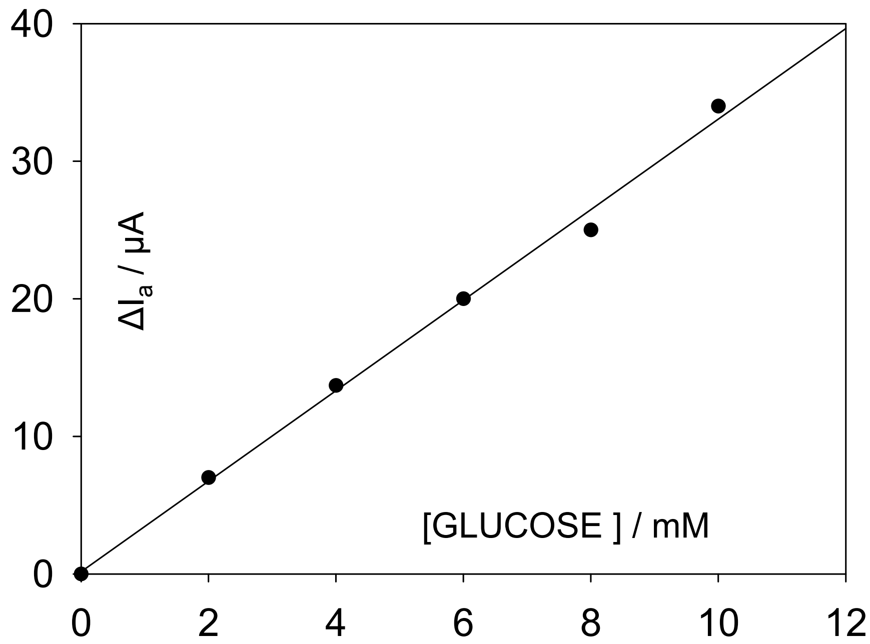

Amperometric detection via oxidation of Hydrogen peroxide.

Subject to considerable interference by oxidizable substances.

# Au/SWCNT/Nafion/GOx modified electrode : amperometric glucose detection at positive potentials.

Amperometric detection of $H_2O_2$
Produced at detector electrode.



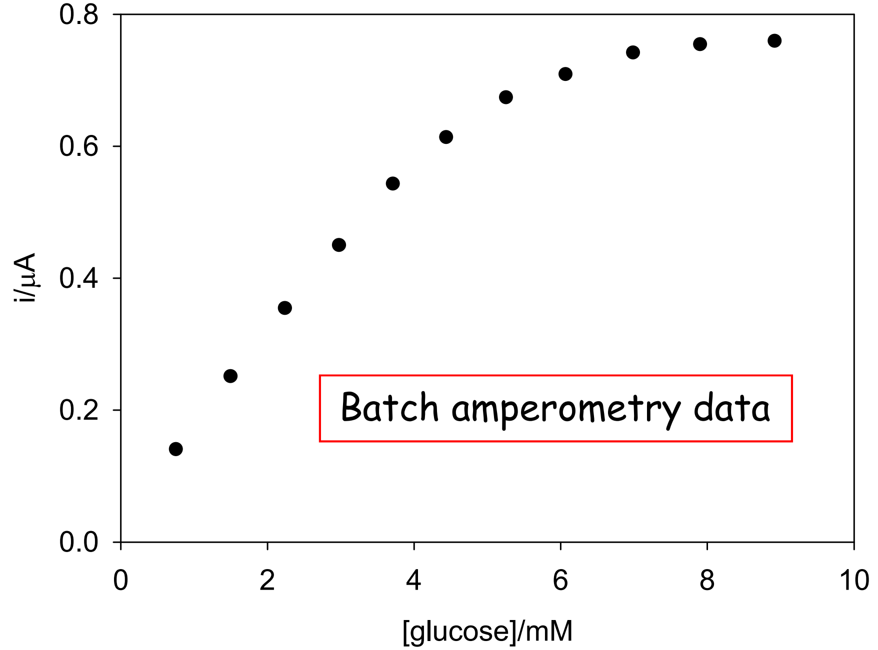

Amperometric detection potential fixed at + 0.8 V

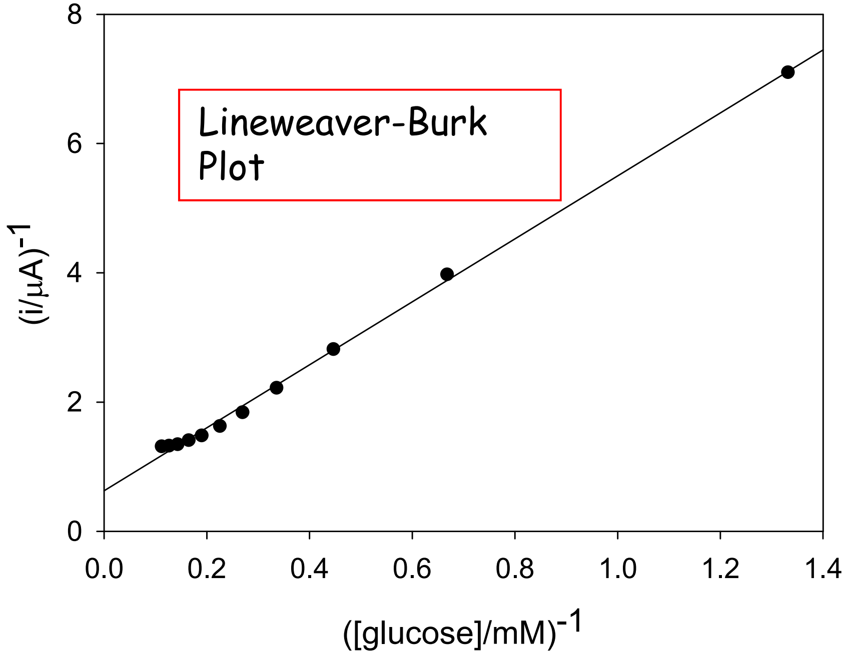
# Amperometric glucose detection via traditional oxygen mediation.

Linear Region
0.3-2 mM
$R^2$=0.998 (N=9)
Detection limit (S/N=3)
= 0.1 mM
Response time = 17s
Sensitivity
0.17 μA/mM

Detection potential E = 0.8 V

Hydrogen peroxide oxidation at SWCNT surface.



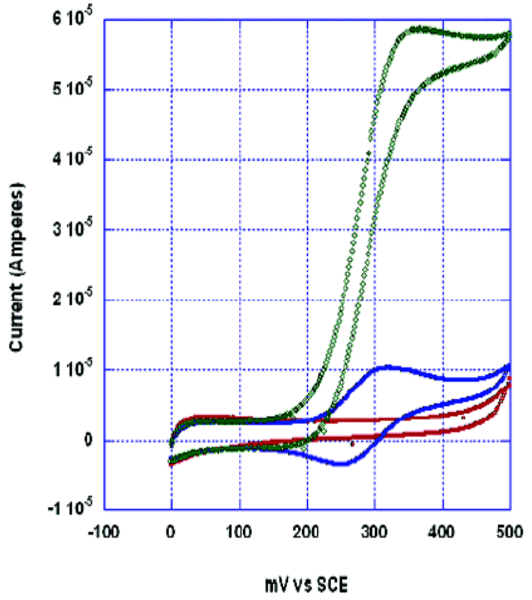



*Figure 4.* Voltammetric response of a GOX-SWNT-modified GC electrode in the absence (red) and presence (blue) of 0.5 mM FMCA. The catalytic response (green) is observed on the addition of 50 mM glucose.

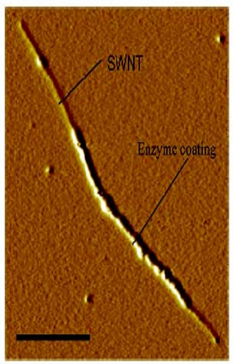



*Figure 3.* Amplitude AFM image of a glucose oxidase-modified SWNT. Scale bar = 200 nm.

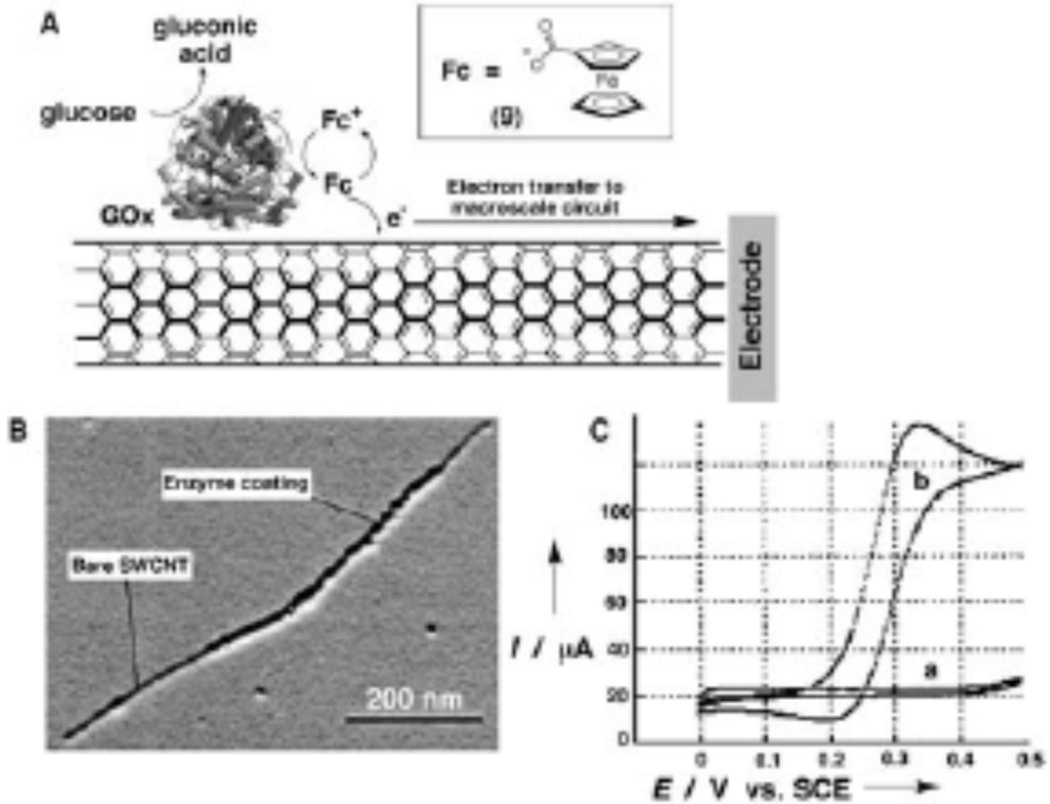
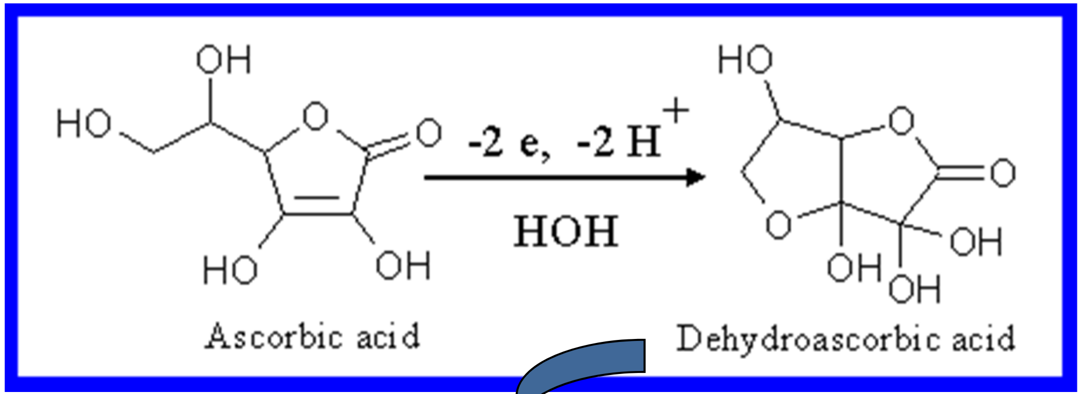



*Figure 14. A) Electrical contacting of GOx loaded onto SWCNT sidewalls through a diffusional mediator (ferrocene monocarboxylic acid). B) An AFM image of a SWCNT loaded with GOx on the sidewall. C) Voltammetric responses of GOx-modified SWCNTs with ferrocene monocarboxylic acid as the diffusional electron relay: a) in the absence of glucose; b) in the presence of glucose. (Adapted from ref. [93a], Figures 7 and 8, with permission).*

Davis et al. J. Am. Chem. Soc., 2002, 124, 12664-12665.




An example of an EC process is the electrochemical oxidation of ascorbic acid (vitamin C) and its subsequent reaction with water (the solvent) to yield electrochemically inactive dehydroascorbic acid.

Sensor response to ascorbate injections

current direct measure of ascorbate concentration

detection potential

polymer film electronically conducting at this potential

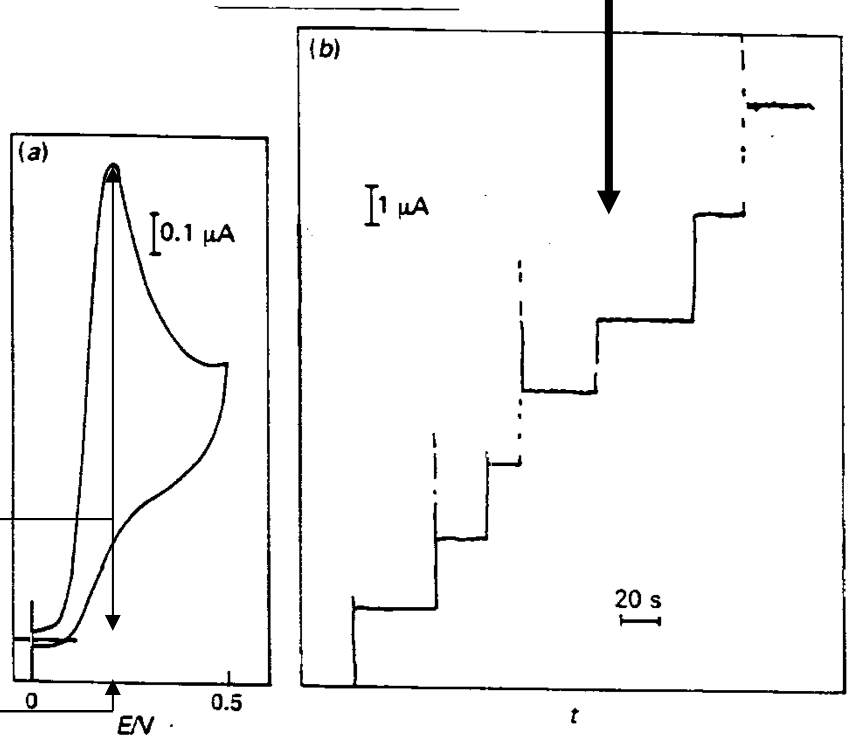



**Fig. 1** (*a*) Cyclic voltammogram of a dilute ascorbate solution (0.3 mmol dm$^{-3}$, 0.1 mol dm$^{-3}$ NaCl) recorded at a sweep rate of 10 mV s$^{-1}$ at a PP–DBS$^-$ electrode. (*b*) Evaluation of the modified electrode response to a sequence of ascorbate injections in the amperometric mode. The stock ascorbate solution was 8 mmol dm$^{-3}$ in 0.1 mol dm$^{-3}$ NaCl, and the volumes added in sequence to the cell were 5 × 50 μl followed by 2 × 75 μl .

| Amperometric Application | Advantages | Disadvantages |
|---|---|---|
| HPLC electrochemical detection | Very sensitive detection technique;<br>Offers additional layer of separation as only those substances which are electrochemically redox active at the chosen potential will be detected.. | Experimentally more difficult to manage than UV detection;<br>Eluent must contain a dissociated electrolyte;<br>WE can be contaminated by some products of oxidation |
| Oxygen sensor | Wide linear range : $10^{-4}$ – 1 atmosphere partial pressure;<br>Relatively inexpensive equipment required;<br>Can be used to measure $O_2$ in both gaseous and solution environments;<br>Can be calibrated by using air and pure oxygen;<br>Can be used for blood oxygen determinations;<br>Can be used in batch or flow cell environments | Temperatures must be carefully controlled;<br>$O_2$ present in solution will be affected by presence of organic solvents; |
| Biosensors | Selectivity towards individual analytes of medical importance eg: glucose;<br>Can be used to measure pesticides, bacteria, mycotoxins;<br>Relatively inexpensive equipment required; | Response time to target analytes not as fast as with chemical sensors. |

Table 9.8 – advantages and disadvantages of some amperometric sensors

## Further aspects of voltammetry.

- Depending on the shape of the potential/time perturbation signal and on the mode of the analyte transport, voltammetric techniques can be classified as
    - **Linear potential sweep & cyclic voltammetry** (LPSV, CV)
    - **Potential Step Methods** (chrono-amperometry,)
    - **Hydrodynamic voltammetry** (rotating disc, rotating ring/disc voltammetry, flow injection analysis, wall/jet voltammetry)
    - **Stripping Voltammetry** (ASV,CSV).
- Voltammetric techniques are distinct analytical tools for the determination of many inorganic and organic substances which can be reduced or oxidised at indicator electrodes at trace levels. the simultaneous determination of a number of analytes is possible using voltammetric techniques.
- Usually the volume of the sample solution used is large and the size of the indicator electrode is small, and the measurement time is short, so the bulk concentration of the analyte does not change appreciably during the analysis. Thus repeated measurements can be performed in the same solution.
- The selectivity of the technique is moderate and can be largely enhanced by the combination of a separation step such as liquid chromatography with electrochemical detection (LCEC).

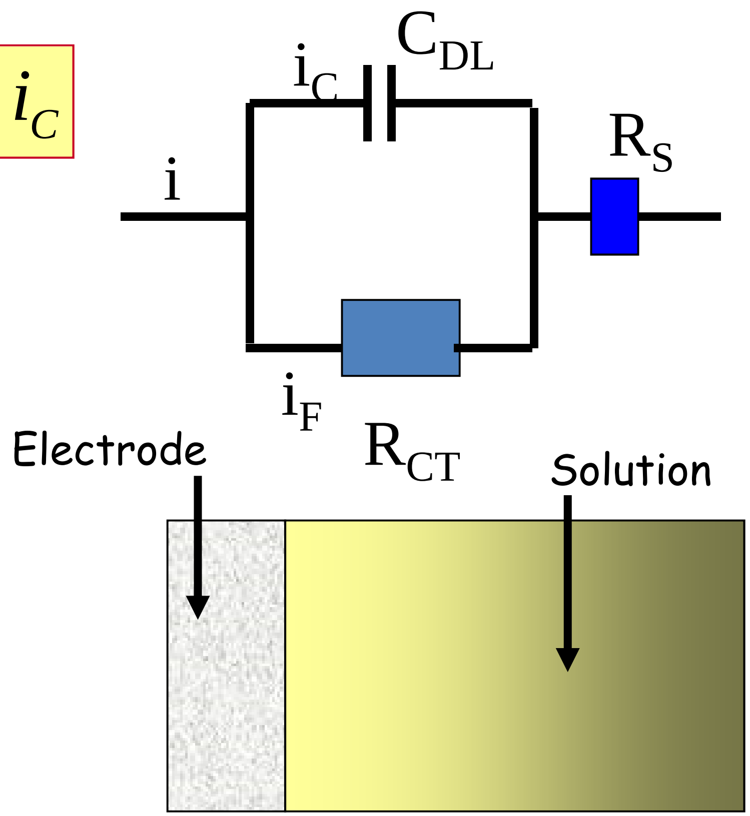
## Some practical considerations in voltammetry.

Choice of working electrode depends on specific analytical situation. Mercury working electrodes (DME, SMDE, MFE) useful for trace metal analysis in which reduction of metal ions (e.g. $Cd^{2+}$, $Zn^{2+}$ etc) occurs at Hg surface. Hg exhibits a large overpotential for $H_2$ gas evolution, and so the potential window available in aqueous solution for metal ion reductions is quite large (-2.7 to ca. + 0.3 V vs SCE).
Hg electrodes not useful for oxidations because Hg oxidises at low potentials via $2Hg \rightarrow Hg_2^{2+} + 2e^-$. Also there is concern over toxicity of Hg.
Instead solid electrodes such as Pt, Au and C (graphite, glassy carbon) are employed for oxidative analysis. These electrodes are electronically conductive and the surface can be readily renewed.
The potential window available in analysis will be determined by the solvent adopted as well as on the supporting electrolyte used. The upper potential limit in aqueous media is ca. + 1.5 V (vs SCE) and is set by the onset of $O_2$ evolution.

# Charging and Faradaic currents.

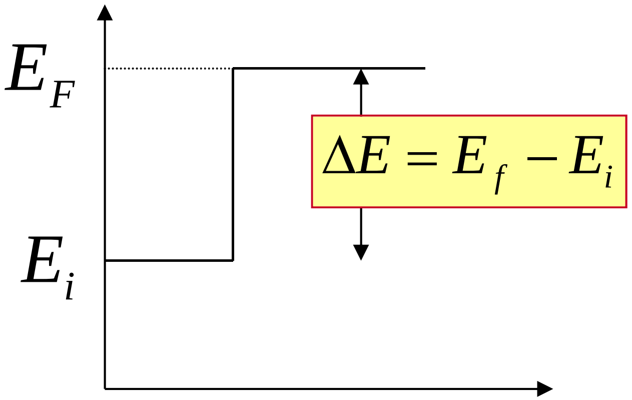
Voltammetric measurements rely on the examination of ET processes at solid/liquid interfaces.
Analytical uses of voltammetry rely on measuring current flow as a function of analyte concentration.
However applying a potential programme to an electrode necessitates the charging of the solid/liquid interface up to the new applied potential. This causes a current to flow which is independent of the concentration of analyte.
Hence the observed current is the sum of two contributions, the **charging current** and the **Faradaic current**.
The Faradaic current $i_F$ is of primary analytical interest since this quantity is directly proportional to the bulk concentration of the analyte species of interest.

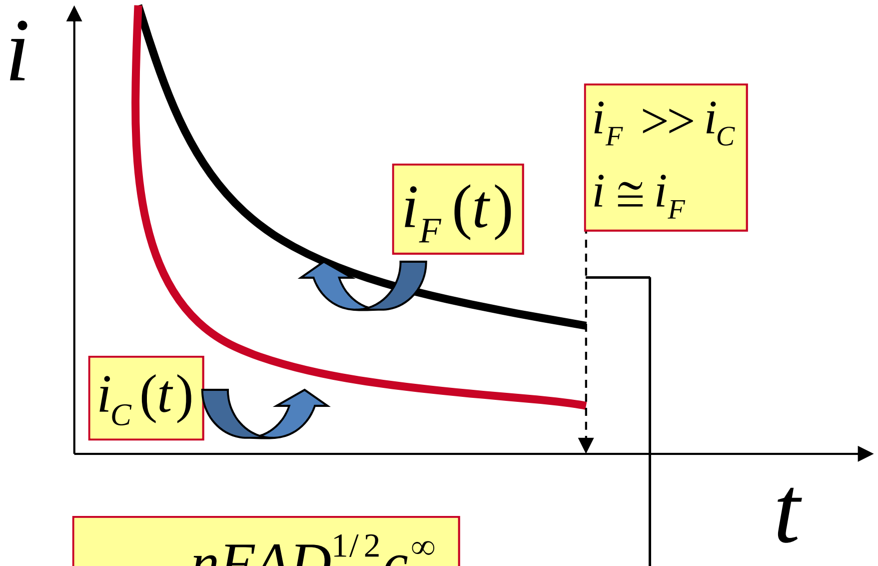
$$i = i_F + i_C$$




The objective is to **maximise $i_F$** and **minimise $i_C$** . Note that $i_C$ is always present and has a constant residual value.
As the concentration of analyte decreases $i_F$ decreases and will approach the value of the residual value of $i_C$. This places a lower limit on analyte detection and hence on the use of voltammetry as an analytical application.

Charging current and Faradaic current contribution can be computed for various transient electrochemical techniques




$$i_C = \frac{\Delta E}{R_S} \exp\left[-\frac{t}{R_S C_{DL}}\right]$$

$$i_F = \frac{nFAD^{1/2} c^{\infty}}{\pi^{1/2} t^{1/2}}$$

Take reading when $i_C$ is small.

Potential step technique.

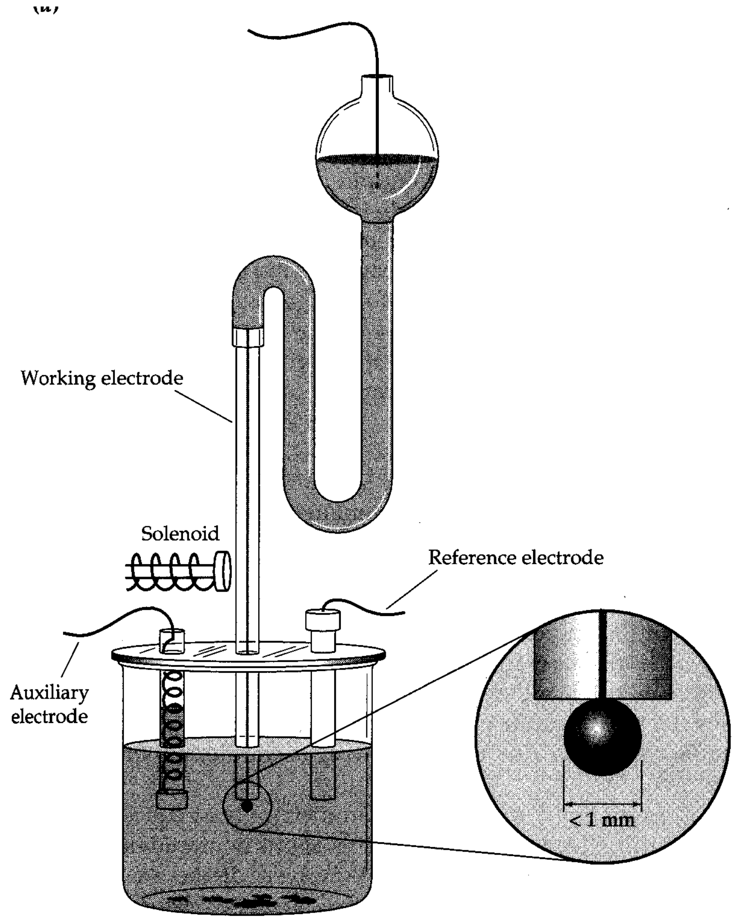
A similar quantitative analysis can be done for DC polarography and linear potential sweep voltammetry.

# Polarography : voltammetry at mercury electrodes.

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.



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.

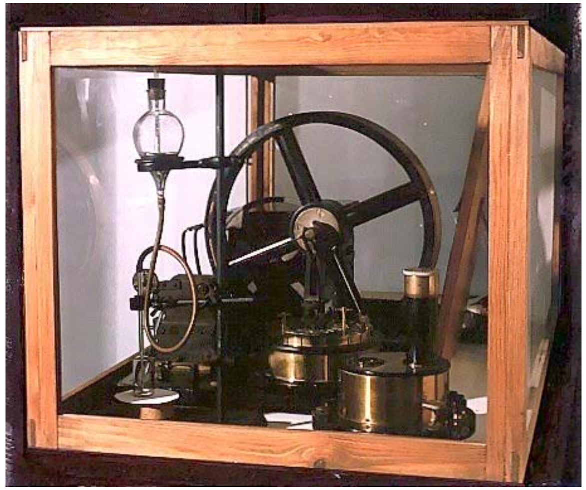
All modern voltammetric methods used now in

electroanalytical chemistry originate from polarography.

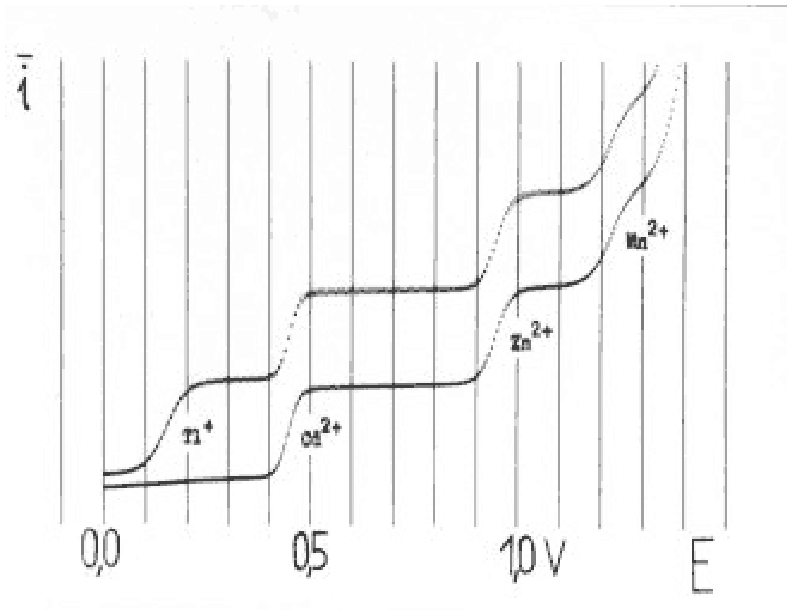
Swedish king Gustav Adolf VI awards the Nobel Prize to Heyrovský in Stockholm on 10.12.1959

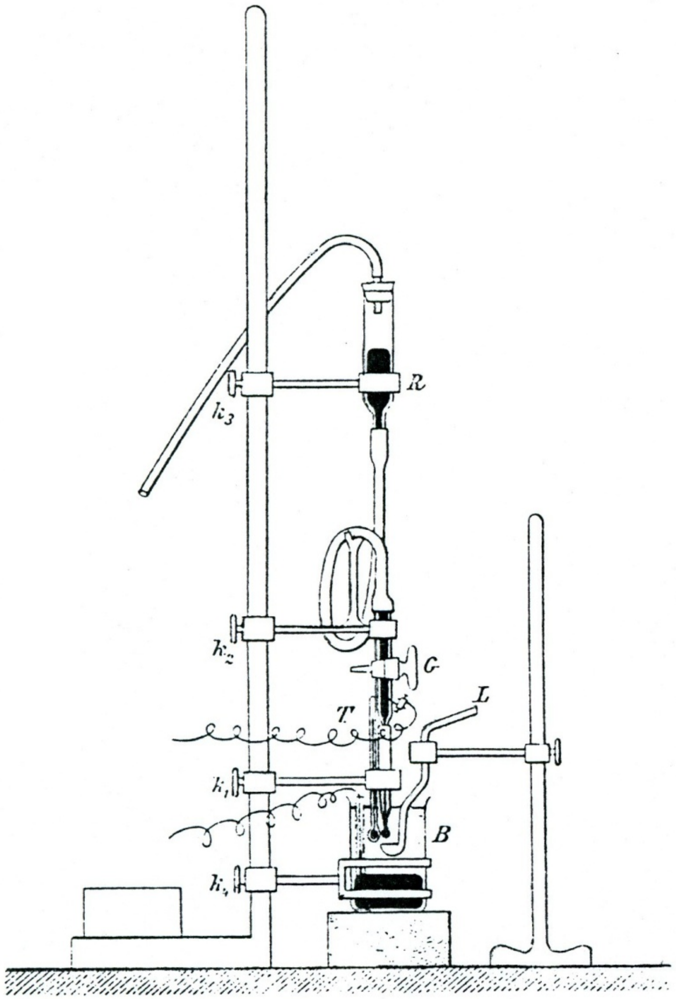
On February 10, 1922, the "polarograph" was born as Heyrovský recorded the current-voltage curve for a solution of 1 M NaOH.

Heyrovský correctly interpreted the current increase between -1.9 and -2.0 V as being due to deposition of $Na^+$ ions, forming an amalgam.

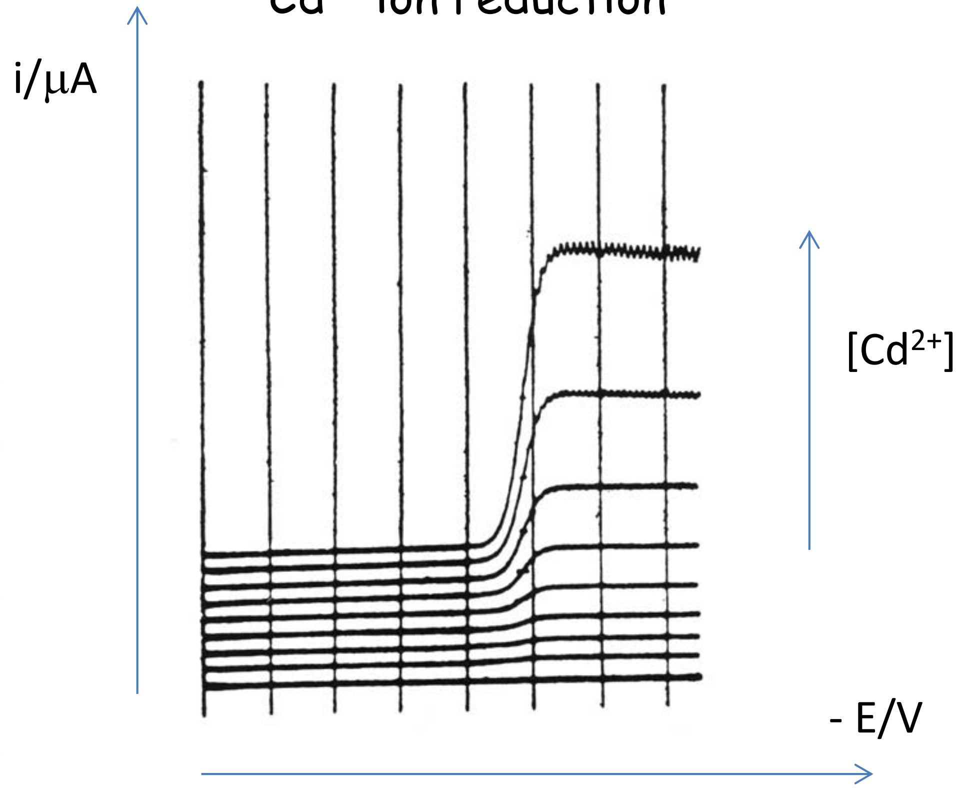


Typical polarographic curves (dependence of current **I** on the voltage **E** applied to the electrodes. The small oscillations indicate the slow dropping of mercury): lower curve - the supporting solution of ammonium chloride and hydroxide containing small amounts of cadmium, zinc and manganese, upper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






## $Cd^{2+}$ ion reduction




$Cd^{2+} + 2e^{-} \rightarrow Cd(Hg)$

**Voltammograms** (voltammetric waves) are graphs of current (i) vs. applied voltage ($E_{appl}$)

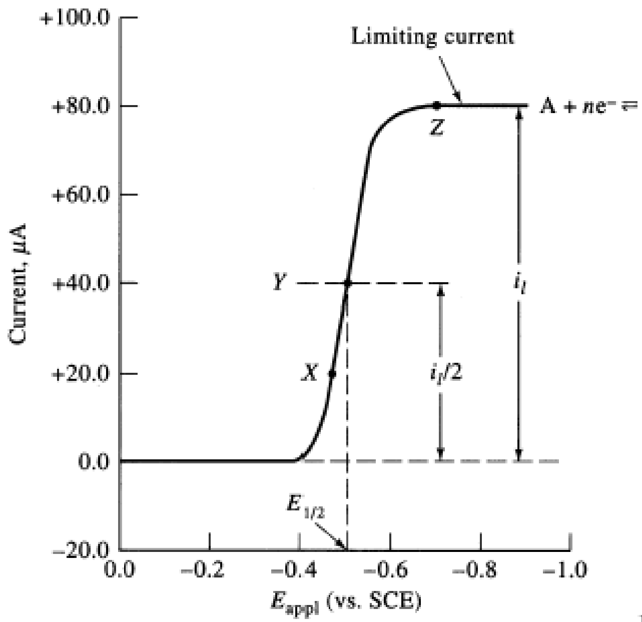


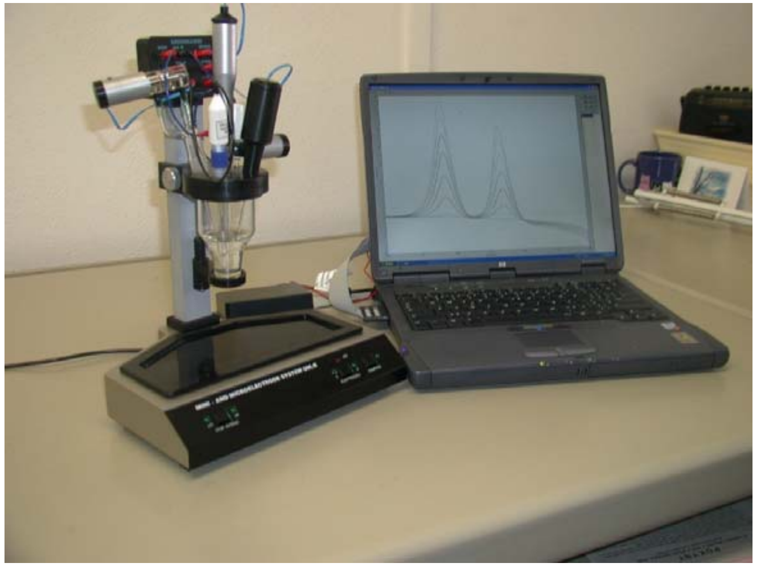

Fig 25-5

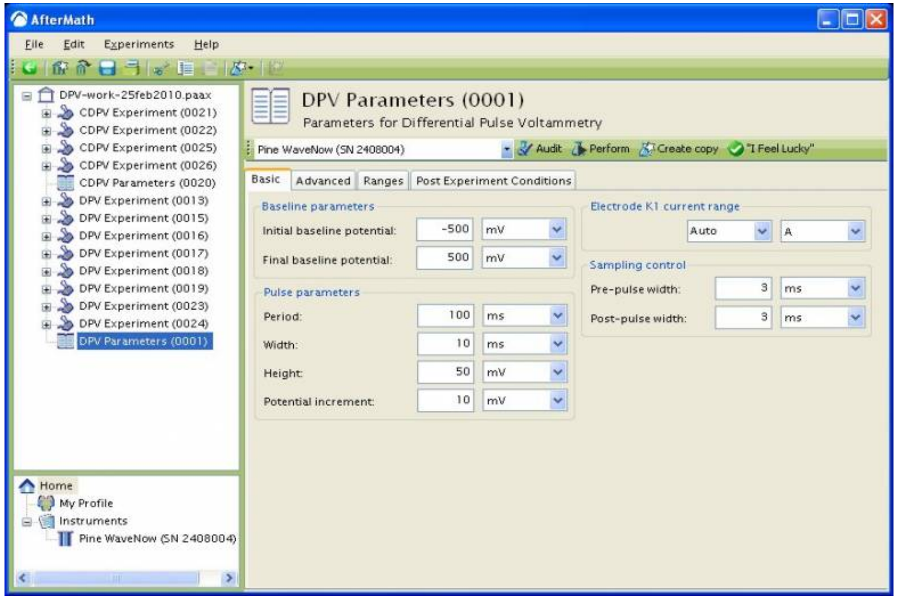
Hg microelectrode is cathode -ve terminal in above

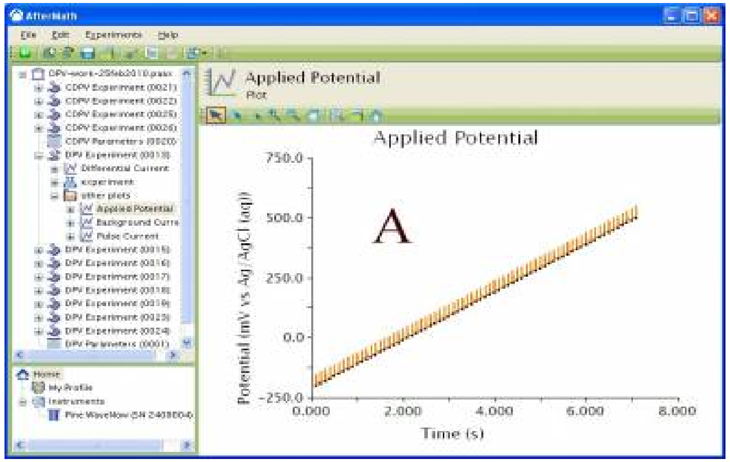
$$A + ne^- \leftrightarrow P \qquad E^0 = -0.26\ V$$

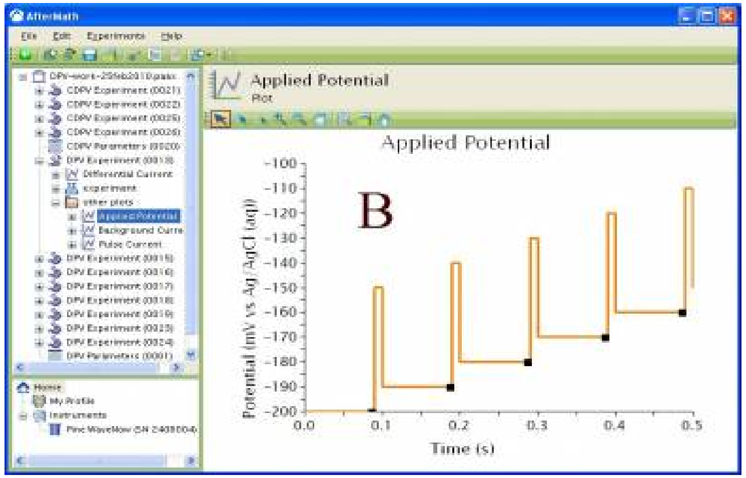
Increase in current at potential at which A can be reduced (reaction demands electrons, supplied by potentiostat)

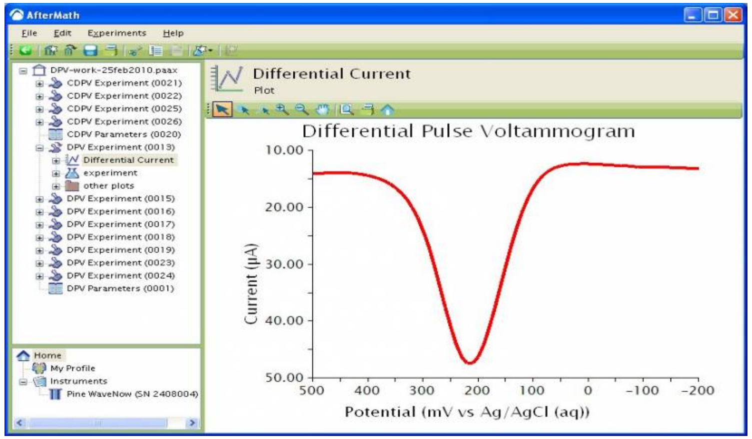
# Differential pulse voltammetry (DPV)



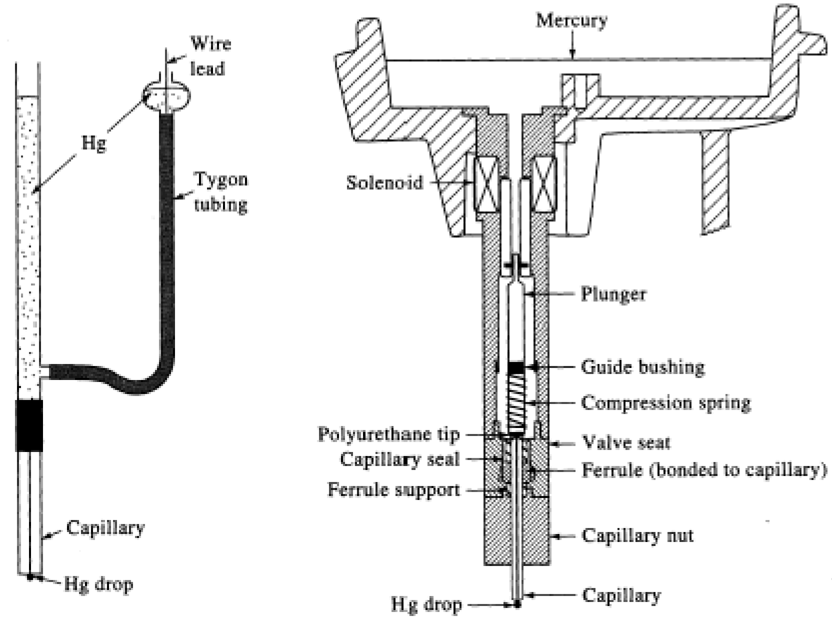


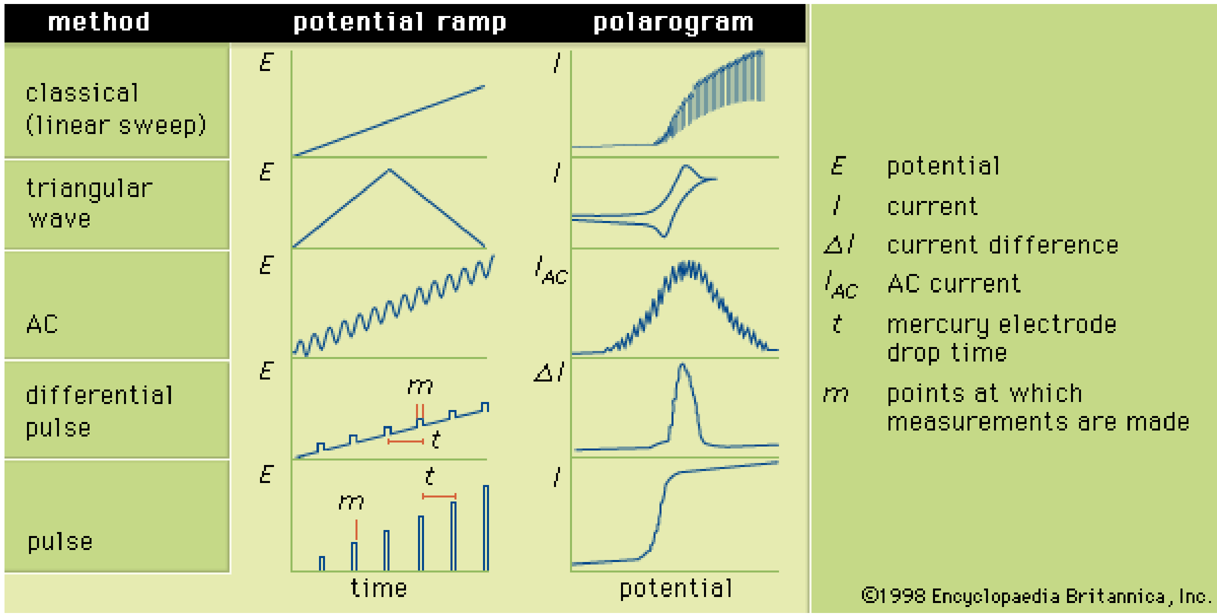



# Mercury working electrodes



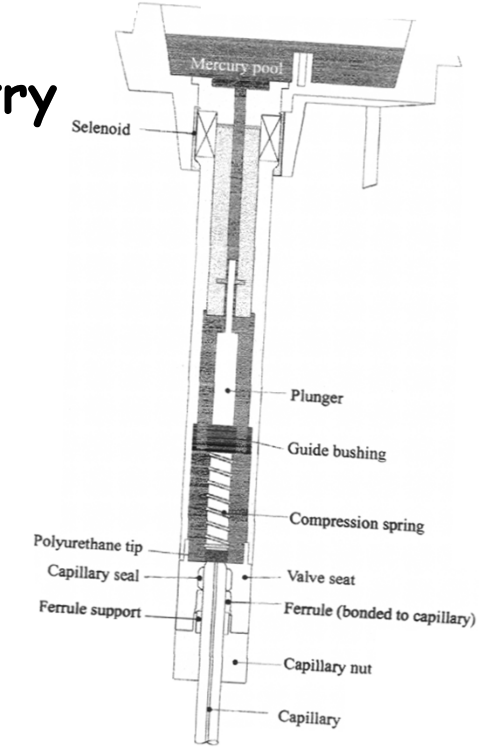

(c) (d)

Most common waveforms used
in voltammetry.



# Polarography : voltammetry using Hg as a working electrode.

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.




**Electrode schematic.**

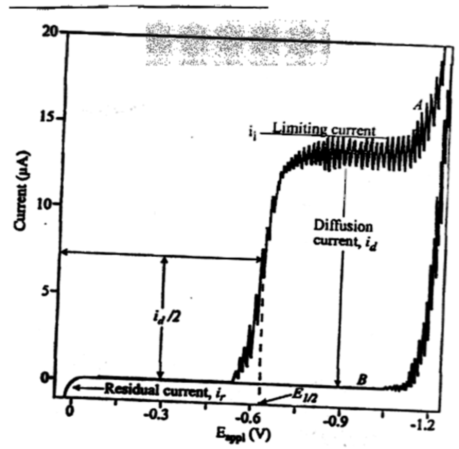



**Fig. 7.3-18.** Polarograms recorded (A) in a solution containing $5 \times 10^{-4}$ mol/L $Cd^{2+}$ and 1 mol/L HCl and (B) in a 1 mol/L HCl solution. (Adapted from Sawyer, D.T. and Roberts Jr., J.L. (1980), *Experimental Electrochemistry for Chemists*, New York: Wiley, with permission)

**Typical current/voltage polarograms.**

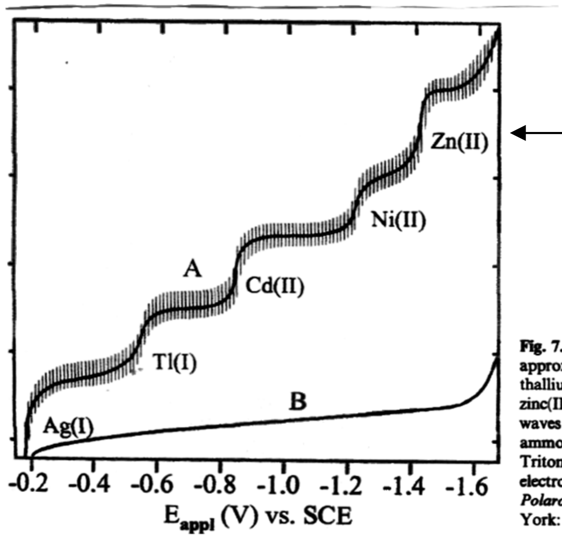
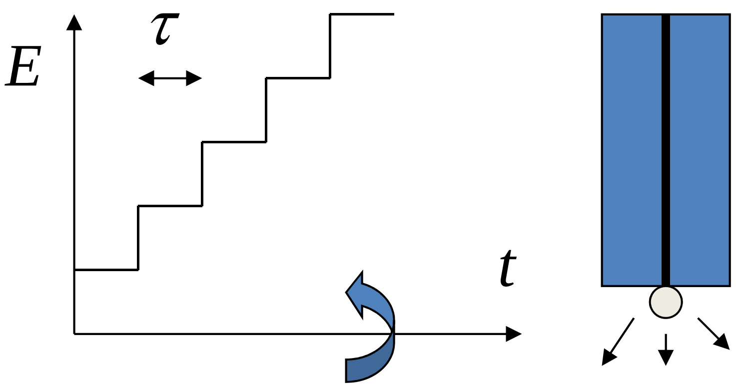



**Fig. 7.3-19.** Polarograms of (A) approximately 0.1 mmol/L each of silver(I), thallium(I), cadmium(II), nickel(II), and zinc(II), listed in the order in which their waves appear, in 1 mol/L ammonia/1 mol/L ammonium chloride containing 0.002% Triton X-100 and (B) the supporting electrolyte alone. (From Meites, L. (1967), *Polarographic Techniques*, 2nd ed., New York: Wiley, p. 164, with permission)



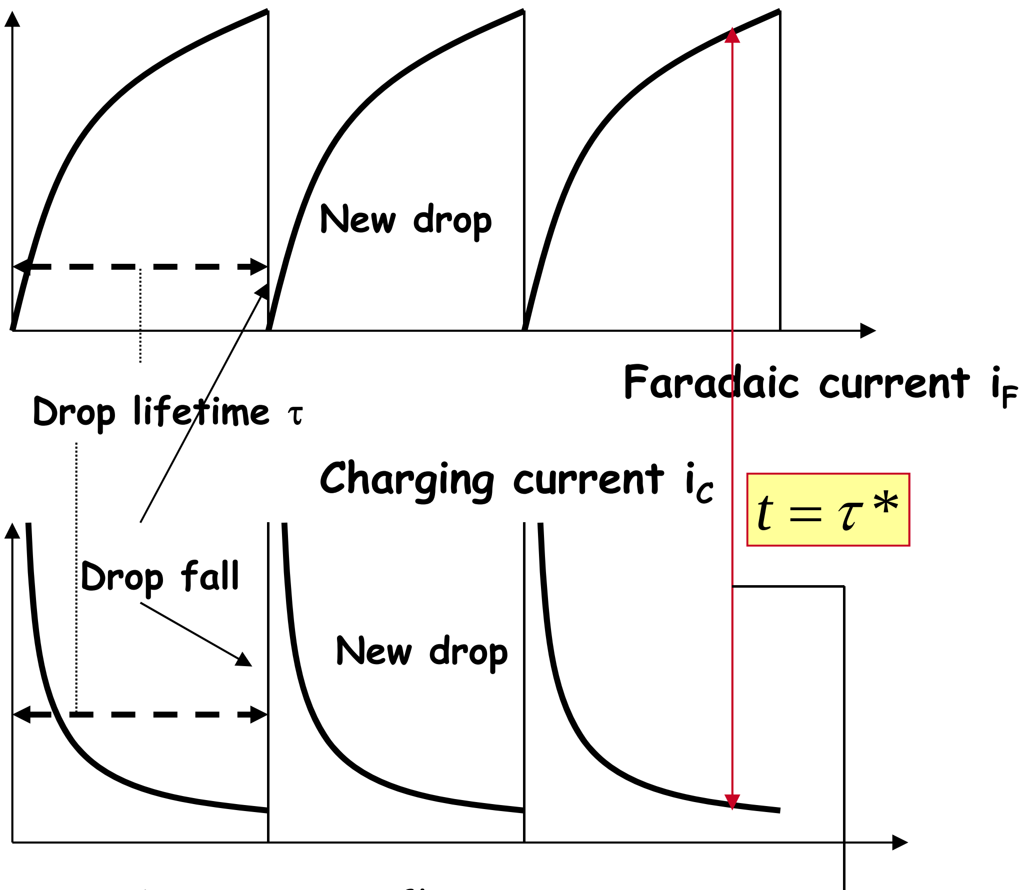

$$A = F(t)$$

Apply sequence of little potential steps to a series of growing Hg drops and measure current flowing as a function of drop lifetime.
Resulting current response given by the Cottrell equation.

$$i_D = nFA(t)c^{\infty}D^{1/2}\pi^{-1/2}t^{-1/2}$$

The drop area is a function of time, and also the diffusion layer thickness gets thinner as a result of the expanding drop. Taking these effects into account gives the Ilkovic equation.

$$i_D = \left\{4\sqrt{\frac{7\pi}{3}}F\left(\frac{3}{4\pi\rho_{Hg}}\right)^{2/3}\right\}nD^{1/2}c^{\infty}m^{2/3}t^{1/6}$$




Net current flowing consists of **Faradaic** current $i_F$ of analytical significance and a **charging** current $i_C$ arising from the electrical properties of electrode/solution interface.

Best to sample current at a time τ* just before the end of the drop life when $i_F$ is maximum and $i_C$ is minimum for optimum sensitivity.

# Polarography

First voltammetric technique

Differs from hydrodynamic

- unstirred (diffusion dominates)
- dropping Hg electrode (DME) is used as working electrod

current varies as drop grows then falls off

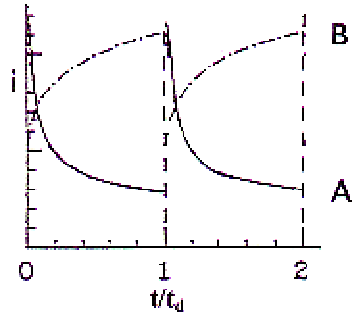
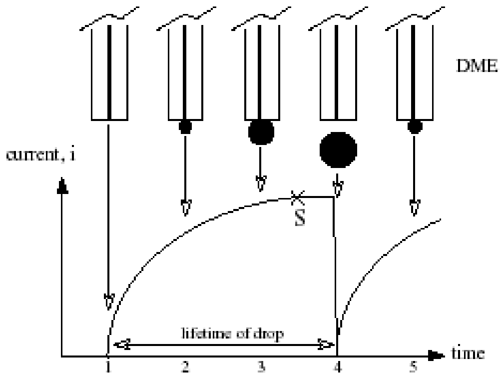



**FIGURE 3-3** Variation of the charging (curve A) and diffusion currents (curves B) during the lifetime of a drop.




$$i = i_c + i_D = Kt^{-1/3} + K't^{1/6}$$

Charging current

$$i_c = 0.00567(E - E_{pzc})C_{DL}m^{2/3}t^{-1/3}$$

Ilkovich equation

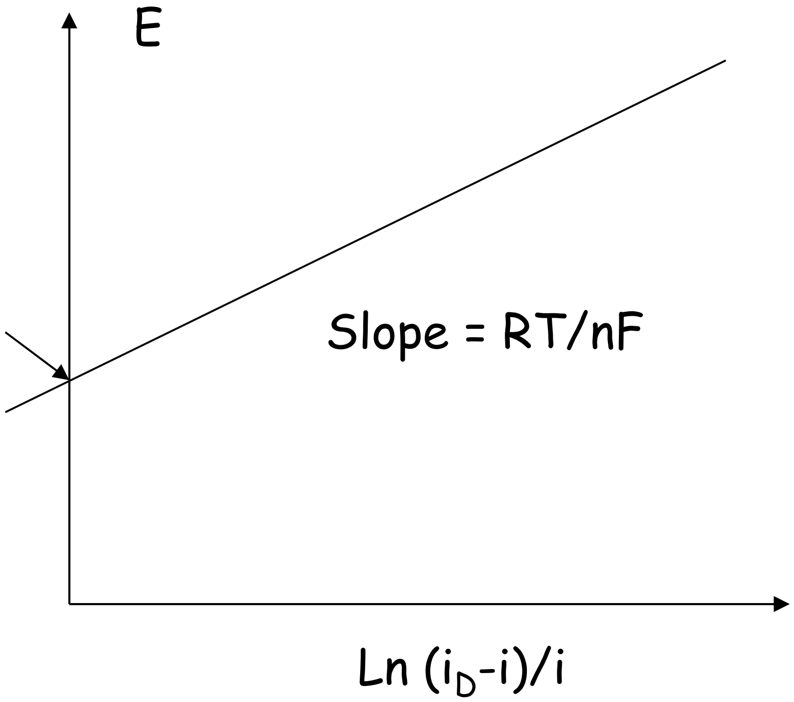
Drop time

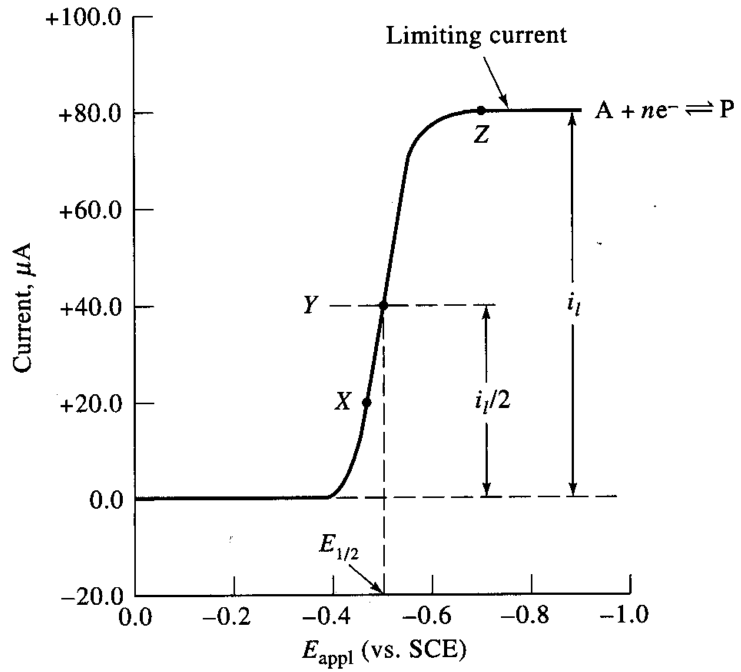
$$i_D = 607nD^{1/2}m^{2/3}t^{1/6}c^{\infty}$$

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

Heyrovsky-Ilkovich equation.

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_D - i(E)}{i(E)}$$



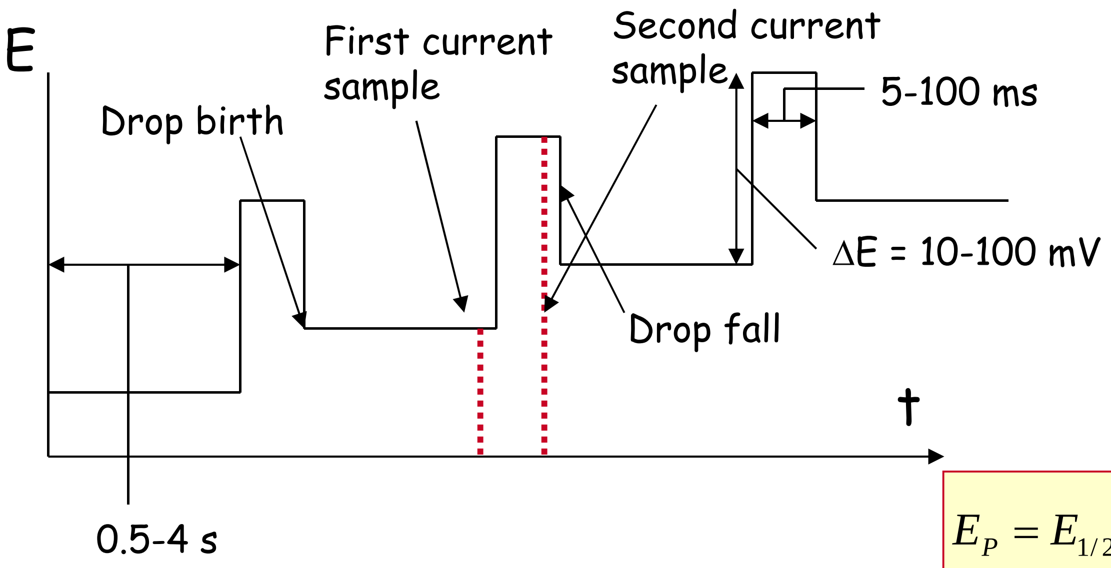



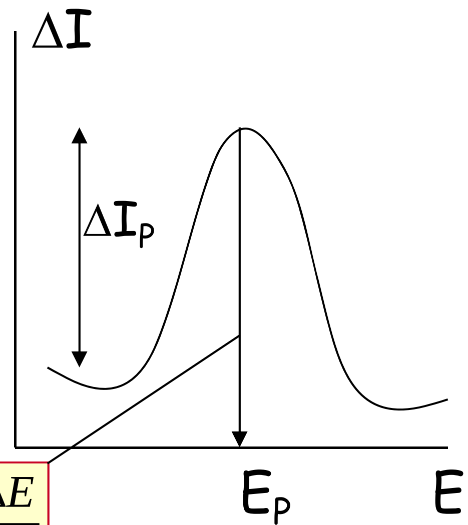

Can evaluate n and $E_{1/2}$ via Heyrovsky Ilkovich plot.

## Differential pulse voltammetry.

Ordinary voltammetry has a LOD of ca. 1 μM. To obtain greater sensitivity (LOD ca. $10^{-8}$M) we can develop a more sophisticated potential waveform such as that used in **differential pulse polarography**.

Charging current contribution minimized : hence greater sensitivity.




$$E_P = E_{1/2} - \frac{\Delta E}{2}$$

Apply series of potential pulses of constant amplitude ΔE with respect to a linearly varying base potential E.
We plot $\Delta I = I(\tau) - I(\tau')$ where $\tau'$ denotes the time immediately before application of pulse and $\tau$ is the time, late in the pulse just before drop is dislodged, as a function Of base potential E.

A plot of ΔI vs E is peaked, the height of which is proportional to the bulk concentration of analyte.

$$\Delta I_P = \frac{nFAD^{1/2}c^{\infty}}{\pi^{1/2}(\tau - \tau')^{1/2}}\left\{\frac{1-\sigma}{1+\sigma}\right\}$$

$$\sigma = \exp\left[\frac{nF\Delta E}{2RT}\right]$$

## **Stripping Voltammetry**.

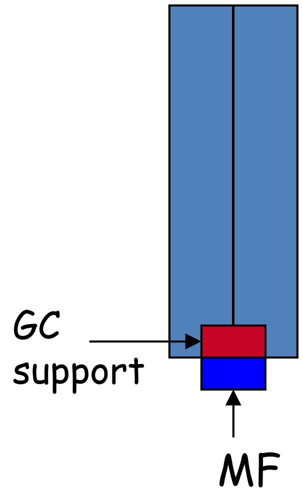
Trace and ultratrace determination of analyte species in complex matrices of environmental, clinical or industrial samples pose a significant challenge.
Resolution of these analytical problems is often obtained by use of **preconcentration** techniques.
One such technique is stripping voltammetry.
This is a two stage technique.

1. **Preconcentration** or **accumulation** step. Here the analyte species is collected onto/into the working electrode
2. **Measurement step** : here a potential waveform is applied to the electrode to remove (strip) the accumulated analyte.

SV is the most sensitive of the available electroanalytical techniques and very low detection limits are possible (< $10^{-9}$M, < ppb).
The technique results in greatly enhanced faradaic current, while the charging current contribution remains unchanged.
Hence the ratio $i_F$ / $i_C$ is increased resulting in enhanced sensitivity.

- The concentration of metal atoms in the amalgam depends on the deposition current and on the deposition time. We need to maximise $c_M$ to obtain maximum analytical sensitivity.
- This can be done by using long deposition times or by increasing the deposition current by increasing the stirring rate/rotation rate or flow rate. One can also increase the electrode surface area while maintaining a constant electrode volume.
- The hanging mercury drop electrode HMDE is used for ASV studies. Its advantages are good reproducibility but disadvantages include the necessity of using low stirring rates during pre-concentration and the HMDE has a low surface area to volume ratio which limits sensitivity.
- The **mercury thin film electrode** (MFE) is also used in ASV. This consists of a thin film of Hg deposited on an inert support electrode such as C, Pt, Ir via $Hg^{2+} + 2e^- \rightarrow Hg$. Typically the Hg film is 1-1000 nm thick. The advantages of the MFE is a high surface area to volume ratio hence excellent sensitivity. The MFE exhibits great stability so one can use very high stir or rotation rates during pre-concentration.
- Generally we use the MFE for analyte concentrations less than $10^{-7}$ M and the HMDE for higher analyte concentrations.
- The stripping peak current varies linearly with the sweep rate and the peaks are thin and sharp.

$$c_M = \frac{i_{dep} t_{dep}}{nFV_{Hg}}$$




MF thickness

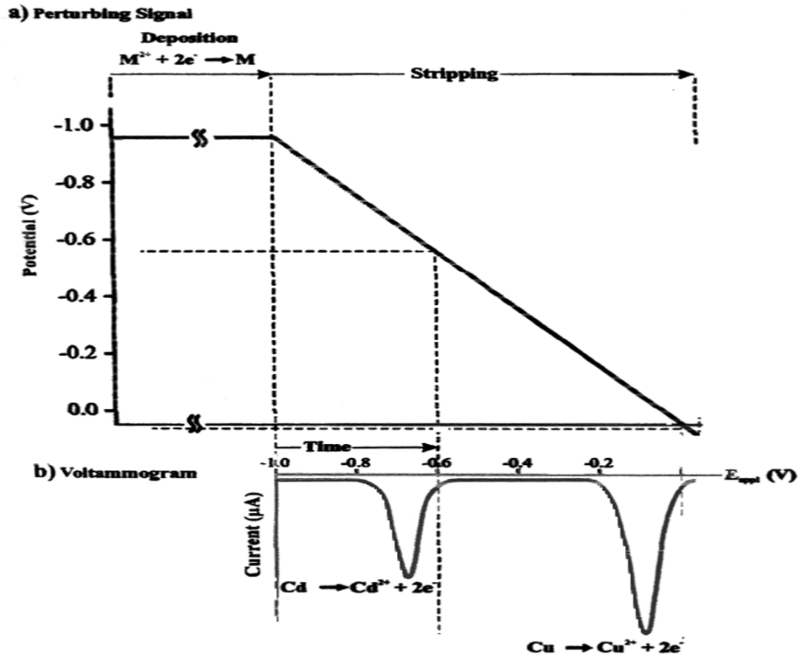
$$i_p = \frac{n^2 F^2 \upsilon A L c_M}{2.7RT}$$

- SV has a number of variants ; these are classified by the nature of either the stripping step or the preconcentration step :
  - Anodic stripping voltammetry
  - Cathodic stripping voltammetry
  - Adsorptive stripping voltammetry
  - Abrasive stripping voltammetry

**Anodic Stripping Voltammetry (ASV).**

- **Accumulation** : employs electrolytic preconcentration ; have reduction to metal ions and amalgamation $M^{n+} + ne^- \rightarrow M(Hg)$ where $M^{n+} = Pb^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Cu^{2+}$ etc. Have preconcentration from a large volume of solution into a small volume Hg electrode, with solution stirring. This is an example of electrochemical extraction.
- **Measurement** : this is the stripping step, and employs a positive directed potential waveform which causes oxidation of any metals present in the Hg electrode : $M(Hg) \rightarrow M^{n+} + ne^-$. Oxidation is an anodic process and hence the term anodic stripping.

ASV is used primarily for the determination of amalgam forming metals. A schematic representation of the ASV experiment is presented across.




The shape of the stripping peak will depend on the type of electrode used, the voltammetric waveform, and the kinetics of the electrode reaction.

Note that the order in which metals are stripped from the amalgam is that of the metal ion/amalgam couple formal potential. This allows the metal to be identified on the basis of the stripping peak potential.

The choice of the deposition potential is made such that the current is limited by mass transfer, not ET kinetics. Also one selects a potential 0.2-0.3 V more negative than the polarographic $E_{1/2}$ value of the redox couple. The choice of $E_{dep}$ also allows selectivity in the stripping voltammogram.

## Cathodic Stripping Voltammetry (CSV).

- The pre-concentration step employs electrolytic formation of a sparingly soluble salt between oxidised electrode material and the analyte. The salt is deposited on the surface of the electrode.

Examples :

- Halides : $2Hg + 2 X^- \rightarrow Hg_2X_2 + 2e^-$
- Thiol compounds : $2 Hg + 2 RSH \rightarrow Hg(SR)_2 + 2 H^+ + 2 e^-$

- The stripping step involves the reduction of the salt formed (a cathodic step) .

Example :

- $Hg_2X_2 + 2 e^- \longrightarrow 2 Hg + 2 X^-$

## Adsorptive Stripping Voltammetry (AdSV).

- Pre-concentration involves **adsorption** of an organic compound or a metal complex onto an electrode surface. This is a non electrolytic pre-concentration process : no ET is involved.
- The stripping step involves determination of the adsorbed species by reduction or oxidation as appropriate using a suitable potential programme (LSV, DPV, SWV methods).

# Example : ADSV of metal complexes.

AdSV uses the formation of an appropriate metal chelate, followed by its controlled interfacial accumulation onto the working electrode via adsorption. Subsequently, the adsorbed metal chelate is reduced by a negative going potential scan. The reduction can proceed via the metal or the ligand L of the complex. The resultant adsorptive stripping response reflects the corresponding adsorption isotherm, as the surface concentration $\Gamma$ of the analyte is proportional to its bulk concentration. In many cases the Langmuir adsorption isotherm is used in quantitative data analysis. Hence calibration plots often exhibit deviations from linearity at high concentrations due to saturation of surface coverage.

$$\Gamma = \Gamma_m \left\{ \frac{Kc}{1+Kc} \right\}$$

Langmuir adsorption isotherm

complexation → $M^{n+} + p\,L \rightleftharpoons [ML_p]^{n+}$

adsorption → $[ML_p]^{n+}(aq) \rightleftharpoons [ML_p]^{n+}\ (surf)$

reduction → $[ML_p]^{n+}\ (surf) + n\,e^- \longrightarrow M + p\,L$

## Potentiometric stripping analysis (PSA).

- Potentiomtric stripping analysis is another attractive version of stripping analysis.
- The pre -concentration step in PSA is the same as for ASV. The metal is electrolytically deposited via reduction onto the Hg electrode (which is in tin film form).
- The stripping is done by chemical oxidation, e.g. using oxygen or mercury ions in solution.
    - M(Hg) + oxidant → $M^{n+}$ + Hg
- Alternatively it is possible to strip the metal off by application of a constant anodic current through the electrode. The potential of the electrode, when monitored as a function of time, produces a response analogous to a redox titration curve, which contains qualitative and quantitative information.
- A sudden change in the potential when all the metal deposited in the electrode has been depleted from the surface. The time required to reach the "equivalence point" is proportional to the bulk concentration of the metal ion.
- For constant current PSA the stripping time is inversely proportional to the stripping current.

$$\tau \propto \frac{c_M t_D}{c_{ox}}$$

- Note that the use of PSA circumvents serious interferences characteristic of AV, such as oxygen or organic surfactants.

**Further comments.**

- The choice of analysis waveform used during the stripping step can also affect the shape and ultimate sensitivity of the output curve obtained in the various types of stripping experiments.

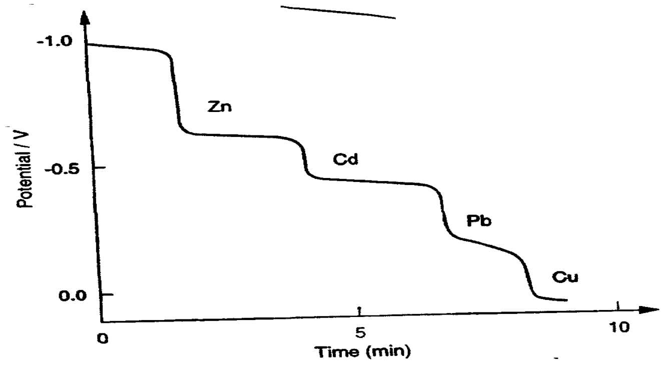



**Figure 24.4** Potentiometric stripping analysis of a solution containing $1.5 \times 10^{-6}$ M $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$, and $Cu^{2+}$, using 3-min deposition and mercury as an oxidant.

- In recent years use has been made of chemically modified electrodes for pre-concentration and stripping analysis of a variety of analyte species. This is a extensive research area at the present time.

# Coulometric methods

Coulometric methods are electrolytic methods performed by accurately measuring the quantity of electrical charge (number of electrons) required to quantitatively bring about a redox transformation in accordance with equation (9.41):

$$[\text{Oxid}] + ne^- \rightleftharpoons [\text{Red}] \qquad \text{Equation (9.41)}$$

The main advantage this technology offers is that the analyses can be termed as **absolute** and thus require no prior calibration, the accurate quantitative measurement being based upon accepted physical constants. The accuracy obtainable is equivalent to that of gravimetric and volumetric procedures, with the added advantage that the technology can be completely automated. The two important terms that need defining are:

**Coulomb**

Defined as the quantity of electrical charge (Q) transported by a constant current of 1 amp flowing for 1 second [$Q = It$]

**Faraday**

The quantity of charge that corresponds to one mole or 6.022 X $10^{23}$ electrons. The Faraday constant is 96,485 coulombs/mole of electrons

As will be shown later, the technology can be used in one of two modes:

- At a constant current, where;

  $Q = I t$ Equation (9.42)

- With a controlled potential where;

  $Q = \int_0^t i \, dt$ Equation (9.43)

Where 'i' represents the variable current flowing during the total time 't' for the completion of the reaction.

**Example (2b.ii)**

**Example (9.iii)** nt of copper deposited on a platinum electrode by the passage of a constant current of 0.800 A over a period of 6.2 min

The equation for the reaction is: $Cu^{2+} + 2e^{-} \longrightarrow Cu$

Total charge transferred 'Q' is $Q = It = 0.8 \times 6.2 \times 60 = 297.6$ C
From the equation for the reaction, 63.55 g Cu would be deposited by 2 X 96,485 C
Thus weight of copper deposited:
[297.6 / (2 X 96485)] X 63.55 g
= **0.098 g**

# Controlled potential coulometry

This technique is better termed **potentiostatic** coulometry to reflect the circuitry required to perform the process. The potential of the working electrode is controlled with respect to a reference electrode so that **only the analyte** is responsible for the transfer of charge across the electrode solution interface. The number of coulombs required to convert the analyte to its reaction product is then determined by recording and integrating the current *versus* time graph as indicated in figure (9.35). The cell arrangement is very similar to that shown as figure (9.30) on slide 68, with additional circuitry to allow for the integrator. See figure (9.36)

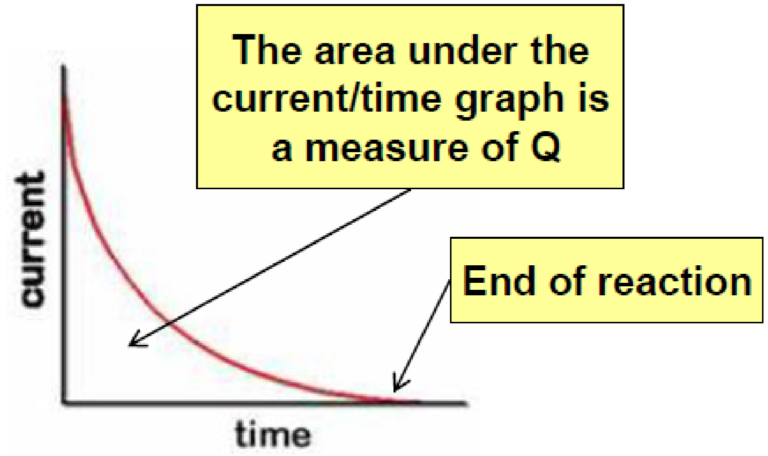



Figure 9.35 – current/time exponential relationship

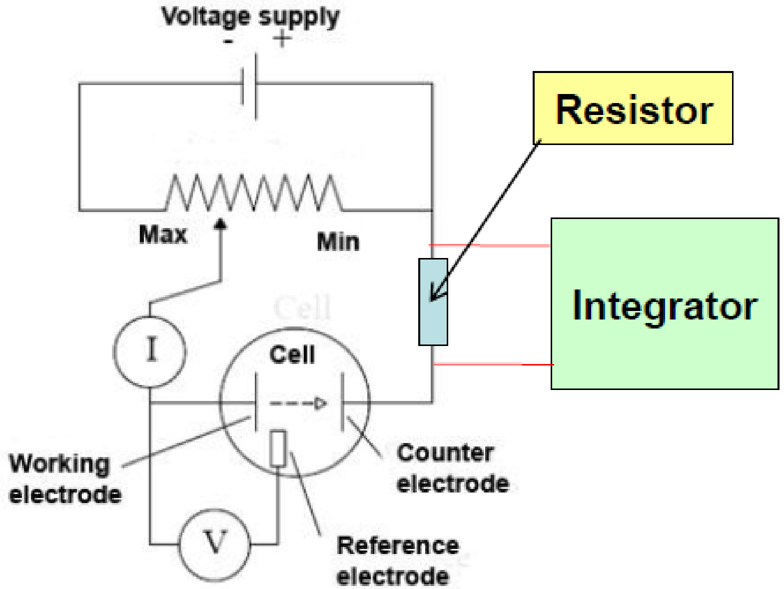



Figure 9.36 – circuit for Potentiostatic coulometry





Continued on the next slide

Two types of cell are frequently used for potentiostatic coulometry.

The first consists of a platinum gauze (large surface area) working electrode together with a platinum counter electrode and a calomel reference. It is important to physically separate the counter and working electrodes via a salt bridge, in order to avoid products generated at the counter electrode from diffusing into the analyte solution and causing interference. To avoid large liquid junction potentials, the salt bridge frequently contains the same electrolyte as is present in the analyte solution.

One of the main problems encountered when using acidic solutions to perform analyte reductions at negative potentials (see the earlier section on voltammetry), is that the reduction of hydrogen ion to hydrogen gas can lead to serious interference. This can be overcome by the use of a pool of mercury as the cathode, as the production of hydrogen at the mercury electrode is subject to a large **overpotential.** So a mercury cathode forms the basis of the second type of cell arrangement.

# Constant current coulometry

This technique is sometimes referred to as amperostatic coulometry. The cell requires only the working and counter electrodes, again separated from each other so as to avoid the reaction products generated at the counter electrode reacting at the working electrode – see figure (9.37)

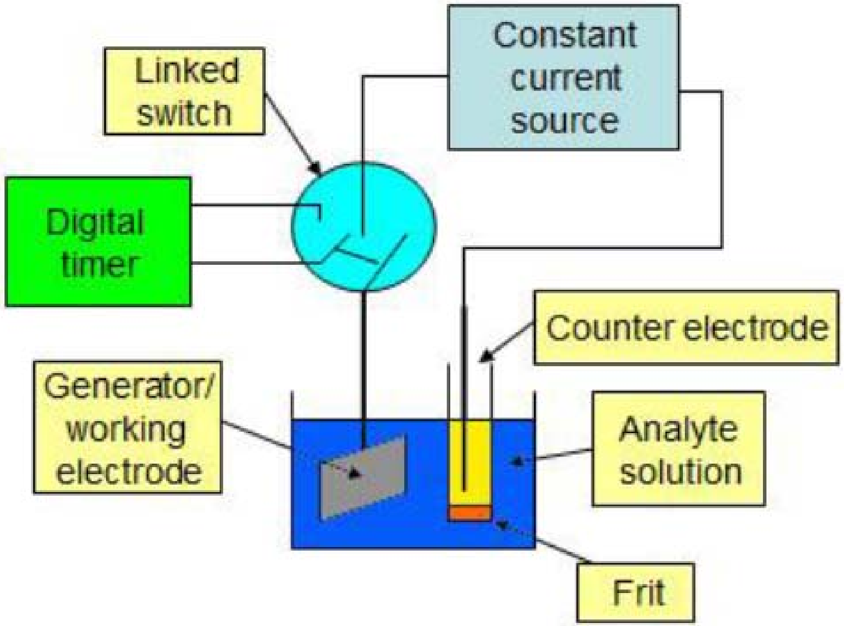



Figure 9.37 – apparatus arrangement for constant current coulometry

The potential at the working electrode will remain constant provided there is sufficient reactant to maintain the set current flow. This could be:

- The size of the electrode where the product of the redox reaction is oxidation of the electrode itself;
- The concentration of reagent in the analyte solution.

The main application of constant current coulometry is the generation of reagents for use in coulometric titrimetry

# Coulometric titrimetry

This form of titrimetry generates the reagent in-situ by use of constant current coulometry. The only measurements required are current and time. The end point in the titration may be detected by any of the usual methods, however electrical methods are favoured (potentiometric, amperometric or conductometric) as these methods can lead to the total automation of the system.

Since **concentration polarisation** is inevitable in coulometric titrimetry, it is preferable for most of the titration reaction to take place away from the electrode surface. If this is not the case, the system will have to continuously increase the potential at the working electrode in order to maintain the production of titrant. An example of this is the use of $Fe^{2+}$, generated from $Fe^{3+}$ to titrate a range of strong oxidising agents such as permanganate ($MnO_4^-$) and chromate ($CrO_4^{2-}$).

Although redox type reactions would seem to be the obvious application of coulometric titrimetry, neutralisation, precipitation and complexometric reactions can also be carried out by using this technique. Table (9.9) on the next slide gives some examples of reagents that can be generated coulometrically, together with examples of uses to which they can be put.

| Species/substance being determined | Generator electrode reaction | Titration reaction |
|---|---|---|
| Acids | $2H_2O + 2e \rightarrow 2OH^- + H_2$ | $OH^- + H^+ \rightarrow H_2O$ |
| Bases | $H_2O \rightarrow 2H^+ + ½ O_2 + 2e$ | $H^+ + OH^- \rightarrow H_2O$ |
| Chloride, bromide iodide, mercaptams | $Ag \rightarrow Ag^+ + e$ | $Ag^+ + X^- \rightarrow AgX(s)$<br>$Ag^+ + RSH \rightarrow AgSR(s) + H^+$ |
| Calcium, copper, zinc & lead ions | $HgNH_3Y^{2-} + NH_4^- + 2e \rightarrow Hg(l) + 2NH_3 + HY_3^-$ | $HY_3^- + Ca^{2+} \rightarrow CaY^{2-} + H^+$ |
| Olefines, As(III), Ti(I), I-, mercaptams | $2Br^- \rightarrow Br_2 + 2e$ | $>C=C< + Br_2 \rightarrow > CBr - CBr<$<br>$2I^- + Br_2 \rightarrow I_2 + 2Br^-$ |
| $H_2S$, ascorbic acid, thiosulphate | $2I^- \rightarrow I_2 + 2e$ | $C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2I^- + 2H^+$ |
| Cr(VI), Mn(VII), V(V),Ce(IV) | $Fe^{3+} + e \rightarrow Fe^{2+}$ | $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ |
| Fe(III), V(V), Ce(IV) | $TiO^{2+} + 2H^+ + e \rightarrow Ti^{3+} + H_2O$ | $Ti^{3+} + H_2O + Ce^{4+} \rightarrow TiO^{2+} + 2H^+ + Ce^{3+}$ |

Note: the generated titrant is shown in red



Table 9.9 – examples of coulometrically generated titrants and possible applications

# The Karl Fischer reaction

One of the most widely used titration reactions in industry is the Karl Fischer titration for the determination of water present in solids (particularly pharmaceuticals) and organic liquids. The reaction is considered specific for water and is based upon a redox reaction involving iodine.

The Karl Fischer reagent which can be purchased from most chemical suppliers consists of iodine, sulphur dioxide and an organic base (pyridine or imidazole) dissolved in dry methanol or alternative alcohols. The chemical reaction underlying the titration is shown in equation (9.44)

$$C_5H_5N{\cdot}I_2 + C_5H_5N{\cdot}SO_2 + C_5H_5N + H_2O \Longrightarrow 2\ C_5H_5NH^+I^- + C_5H_5N^+SO_3^- \qquad \text{Equation(9.44)}$$

$$C_5H_5N^+SO_3^- + CH_3OH \Longrightarrow C_5H_5NH^+(CH_3OSO_3)^-$$

Thus 1 mol of $I_2$ ≡ 1 mol of $SO_2$ ≡ 3 mols of base ≡ 1 mole of water

The reagent will normally contain an excess of both $SO_2$ and base and thus it is the **iodine content which is proportional to the water.** The end point in the titration may be determined colorimetrically (excess brown colour of the reagent) however the end point is mostly determined electrically.

Karl Fischer (K/F) reagent decomposes on standing and it is thus usual to standardise the reagent against a standard solution of water in dry methanol on a daily basis.

Great care must be exercised to keep all of the glassware used in the titration free from contamination by water, particularly atmospheric moisture.

The titration can be carried out either:

- Directly – dissolve sample in dry methanol and titrate directly with the reagent;
- Indirectly – addition of an excess of K/F reagent followed by back titration with standard water in methanol.

When the sample is totally soluble in methanol, a direct titration is usually possible. However, when the sample is only partially soluble in methanol, the back titration is likely to give more accurate results. The method is very sensitive allowing small amounts of water ($mg/dm^3$) to the determined accurately.

Modern Karl Fischer titration equipment is now based upon the coulometric generation of iodine using a constant current type source, with linked electrochemical detection. This process is described on the next slide with a schematic diagram of the apparatus required as figure (9.38)

A schematic diagram of a typical coulometric titrator is shown in figure (9.38). The main compartment of the titration cell contains the anode solution. The anode is separated from the cathode by an ion permeable membrane. The cathode is in contact either with the same anode solution or a specially prepared cathode solution. Two other Pt electrodes are immersed in the anode compartment and connected to the indicating meter. The reaction at the anode generates $I_2$ which reacts with the water in the sample. When all of the water has been titrated, the excess $I_2$ is sensed by the indicator electrodes, which stops any further generation. The reaction at the cathode generates hydrogen. The bi-potentiometric indicator works by a combination of voltammetry and potentiometry.

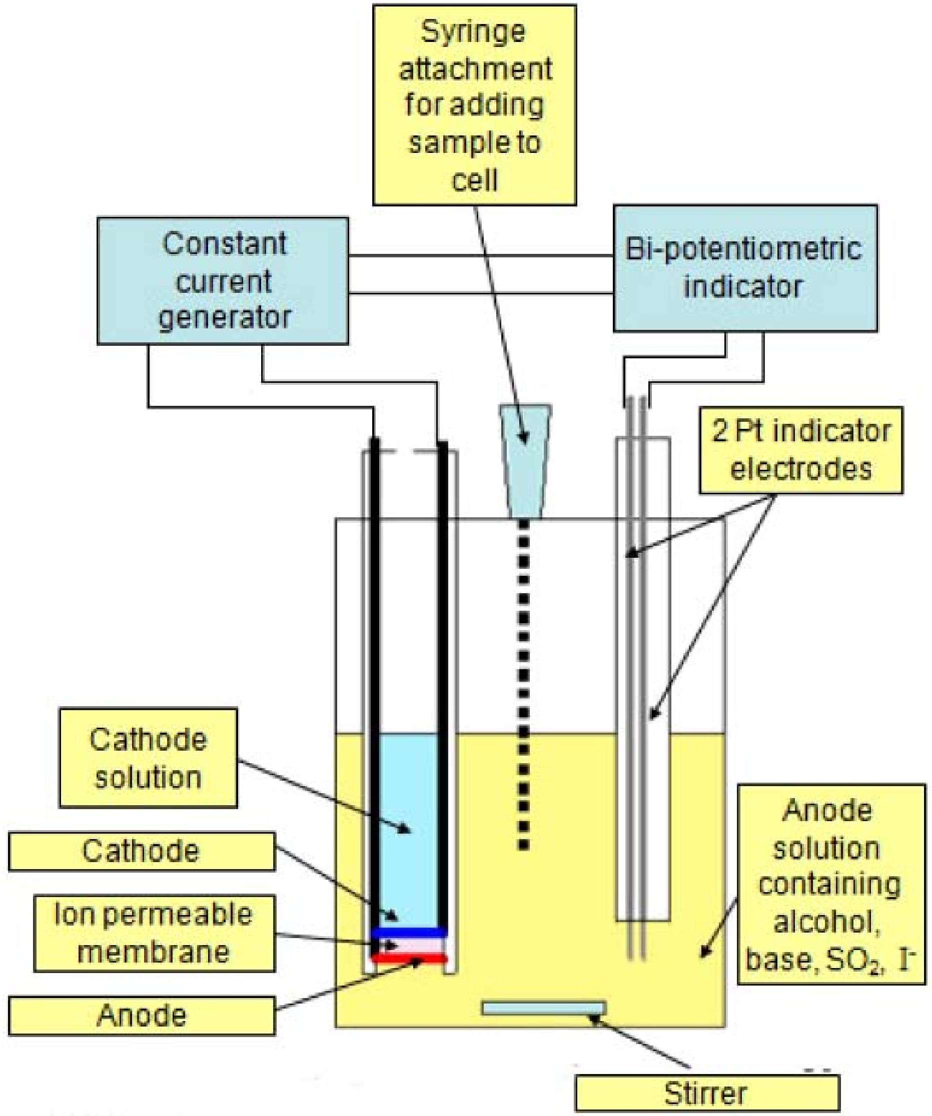



Figure 9.38 – schematic diagram of a K/F coulometric titrator

# Applications of coulometric Karl Fischer titrations

The technique may be applied to measure the water contents of a wide range of inorganic and organic matrices. Where solubility in methanol is a problem then other alcohol type solvent can be added to increase solubility for instance decanol or hexanol. In order to avoid opening the anode compartment to the air, samples are usually dissolved in a suitable dry solvent and then added via a syringe into the reagent in the compartment. The quantity added will depend upon the level of water expected. The current generator is also set to correspond to expected water levels.

As indicated in equation (9.44) 1 mole of iodine ≡ 1 mole of water

1 mole of iodine is generated by 2 X 96485 C of power
Thus 18 g of water ≡ 192,970 C
Thus **1 mg of water** ≡ 0.001/18 X 192970 C = **10.72 C**

This factor may be used to calculate water contents of all samples analysed.

An example is shown as example (9.1v) on the next slide.

**Example (9.iv)**

0.10 g of a sample of an essential oil was added to the anode compartment and analysed for its water content. A pulsed current of 40 mA was used and the total time that the current was flowing was measured as 35.0 s. Calculate the quantity of water in the oil expressing the answer as ppm w/w

The total charge transferred (Q) = 40/1000 X 35.0 = 1.4 C

From the relationship given on the previous slide, 10.72 C ≡ 1 mg of water

Thus 1.4 C ≡ 1.4/10.72 mg of water = 0.1305 mg of water

0.10 g of the oil contained 0.1305 mg of water

Thus 1 kg of oil contains 1305 mg of water = 1305 ppm

Given that the sample was weighed initially only to 2 significant figures the result should be quoted as **1300 ppm**

# Measurement of metal plated film thickness

One other important example of the use of constant current coulometry is the measurement of average film thickness of a plated metal film. This is obtained by measuring the quantity of electricity needed to dissolve a well defined area of the coating.

The film thickness (T) is proportional to the total charge transferred (Q), the atomic weight of the metal (M), the density of the metal (ρ) and the surface area (A) from which the metal is removed. (n) is the number of electrons transferred in the oxidation of the metal from the surface to the solution

The anode reaction is: Metal + $ne^-$ = $(\text{Metal ion})^{n+}$

$$T = \frac{Q}{n \times 96485} \times \frac{M}{\rho A}$$

Equation (9.45)

The cell comprises the sample as the **anode** with a platinum cathode. The reaction Is followed potentiometrically using the sample as the indicator electrode together with a suitable reference electrode. The example on the next slide illustrates how the measurements are made to determine when all of the coating has been removed.

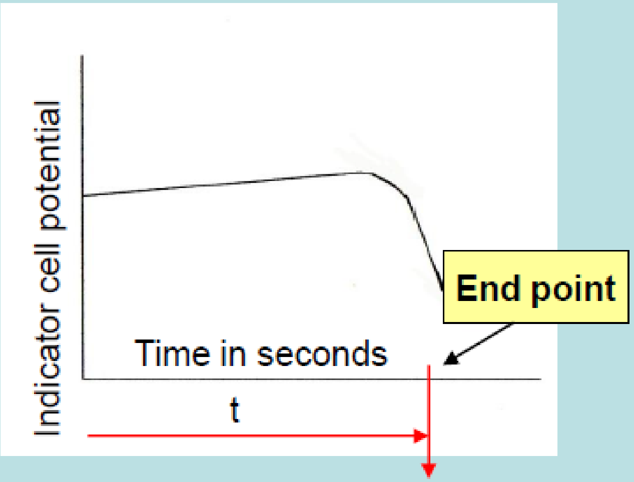
**Example (9.v)**

Consider a silver coating on a copper base.  The half cell reactions are:

$Ag^+ + e^- \Rightarrow Ag$ $\quad E^o = +0.799$

$Cu^{2+} + 2e^- \Rightarrow Cu$ $\quad E^o = +0.337$

Once the reaction commences the indicator electrode detects the $Ag^+/Ag$ half cell and gradually changes potential reflecting the gradual increase in $Ag^+$ concentration in the solution.  As soon as all of the silver has been removed, the copper begins to dissolve in order to maintain the current flow and the indicator cell begins to recognise the present of the $Cu^2/Cu$ half-cell. If the potential of the indicator cell is plotted as a function of time, a graph will be produced which is similar to that obtained from a potentiometric titration.  Figure (9.39) illustrates a typical graph for this reaction.




If the current applied was 'I' amps and the time 't' was measured, then Q = It
If the area deplated is measured and the Density of silver is known, then the Thickness of the film can be calculated.

**Figure 9.39 – potential/time graph for plating thickness measurement**