POLAROGRAPHY

Electro - analytical technique

DEFINATION

- **Polarography is a method of analysis in which the solution to be analyzed is electrolyzed under diffusion controlled condition.**

- **The graph of current (generated) as a function of voltage (applied) is known as POLAROGRAM.**

  The technique is known as POLAROGRAPHY.

- **It can be used for qualitative as well as quantitative analysis (inorganic, organic and biological samples) without the requirement of prior separation step (in most of the cases).**

HISTORY AND BACKGROUND

Polarography was created by Jaroslav Heyrovsky in Feb. 10th 1922

1922

1959

On December 10th 1959 he was awarded the Nobel Prize.

INTRODUCTION

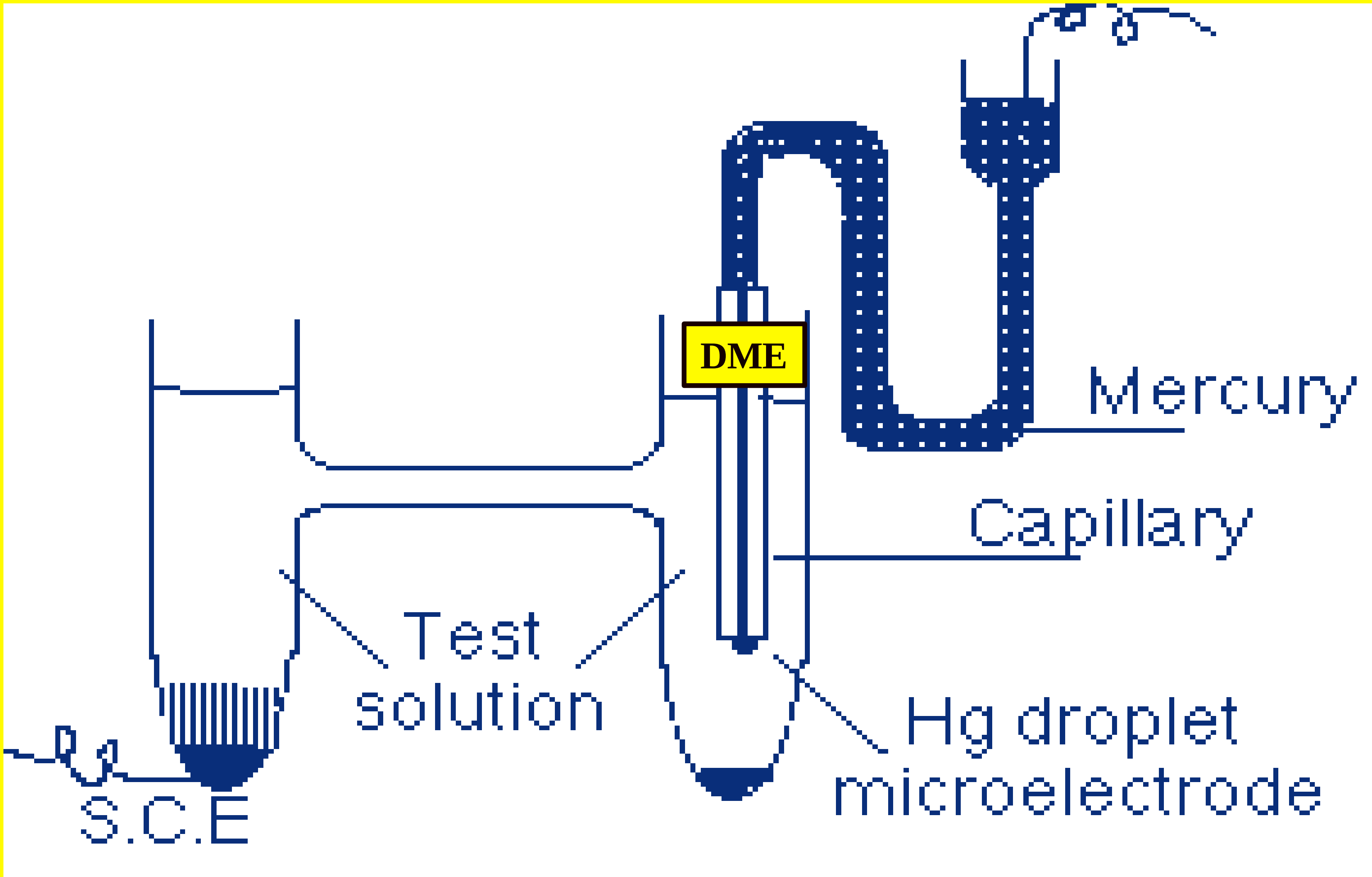
- The basic idea was to pass the current between two electrodes, one having large surface area and other having very small surface area. Both electrodes can be of mercury metal.

- The large electrode can be a pool of mercury at the bottom of the cell.

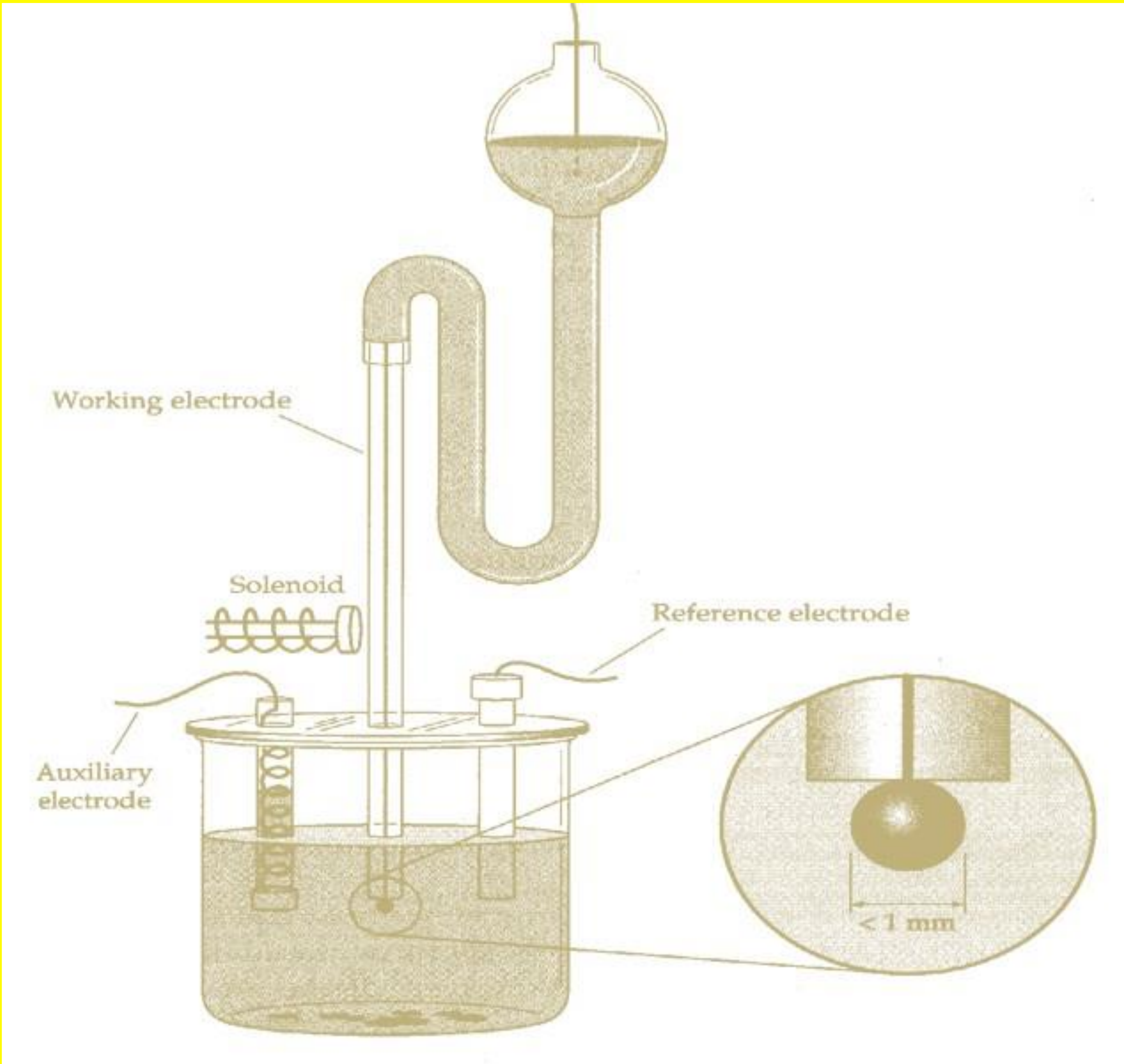
- Small electrode is a drop of mercury coming out of a very fine capillary tube, DME.

- Thus, if a steady voltage is applied to such a cell, it is possible to construct a reproducible current voltage curve.

DROPPING MERCURY ELECTRODE

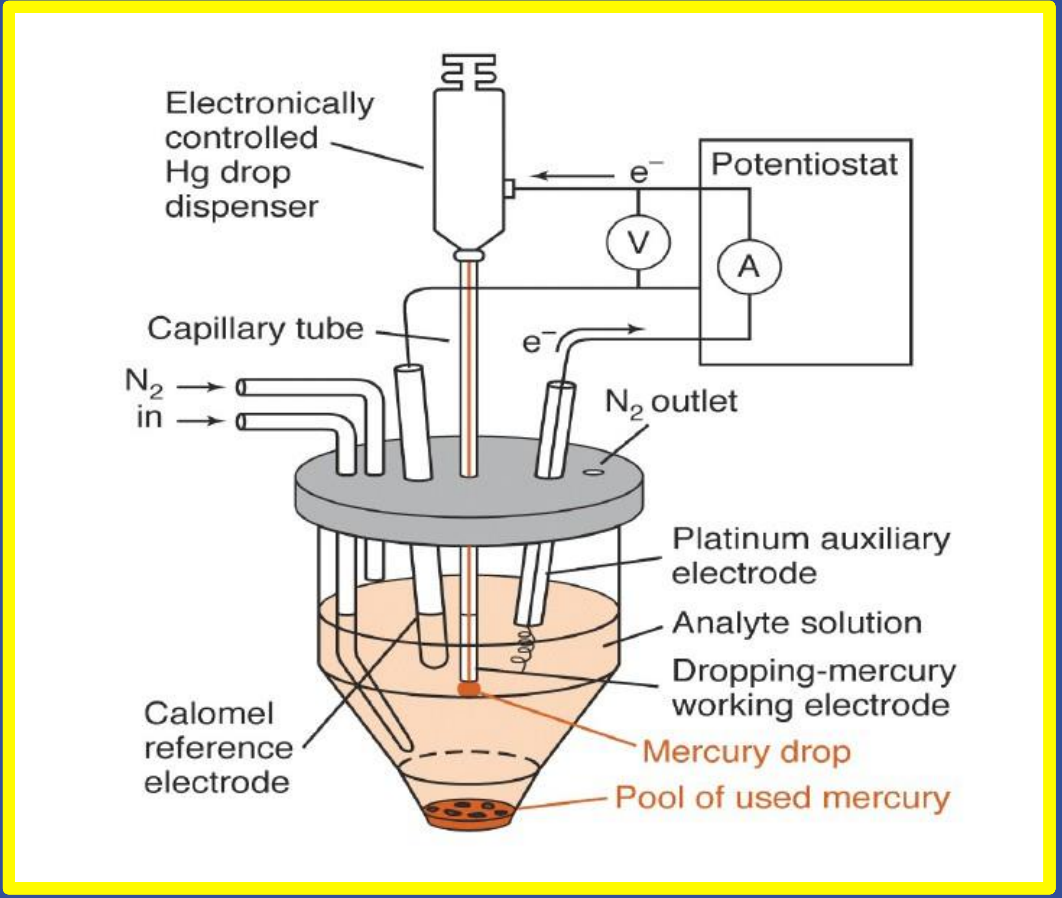


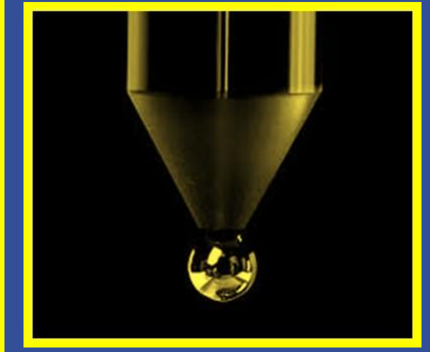
INSTRUMENTATION



Polarography uses regularly renewed mercury drop electrode for analysis

INSTRUMENTATION





Polarography uses regularly renewed mercury drop electrode for analysis.

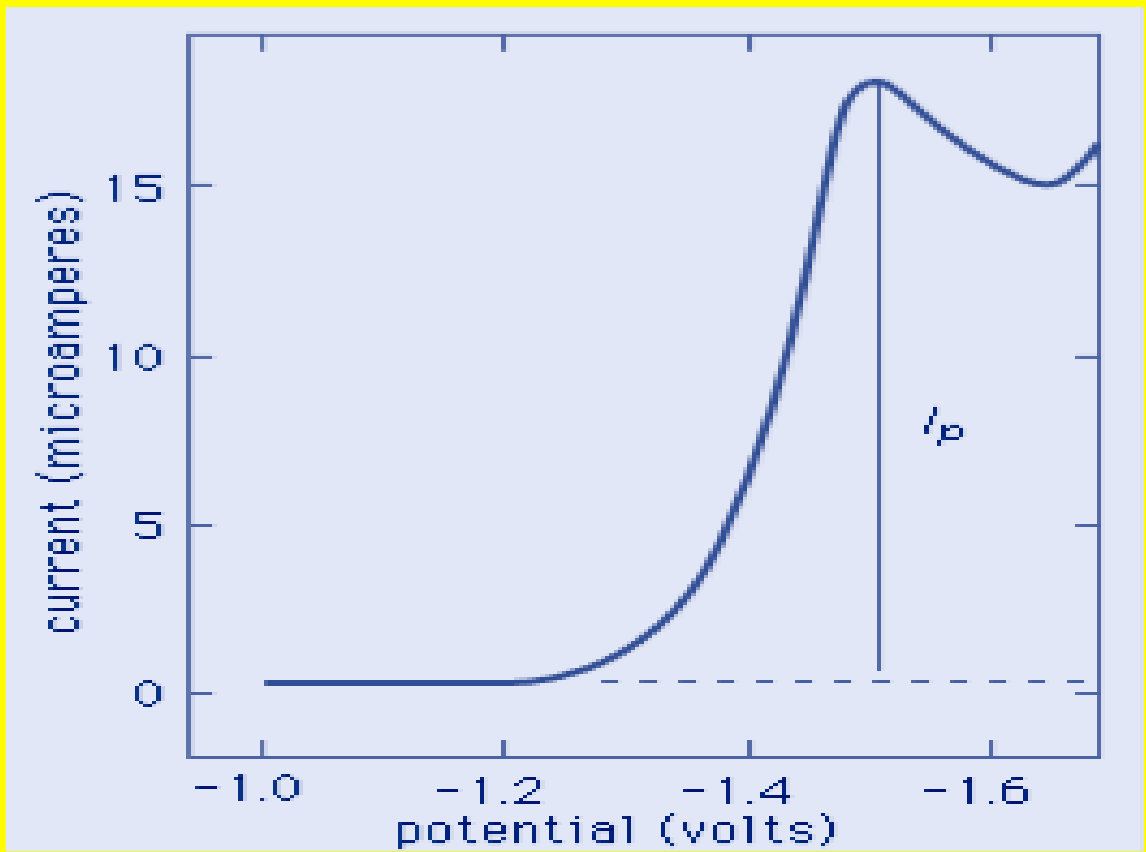
WORKING

- Electrolyte is a dilute solution of electro active material to be analyzed in a suitable medium containing excess of supporting electrolyte.

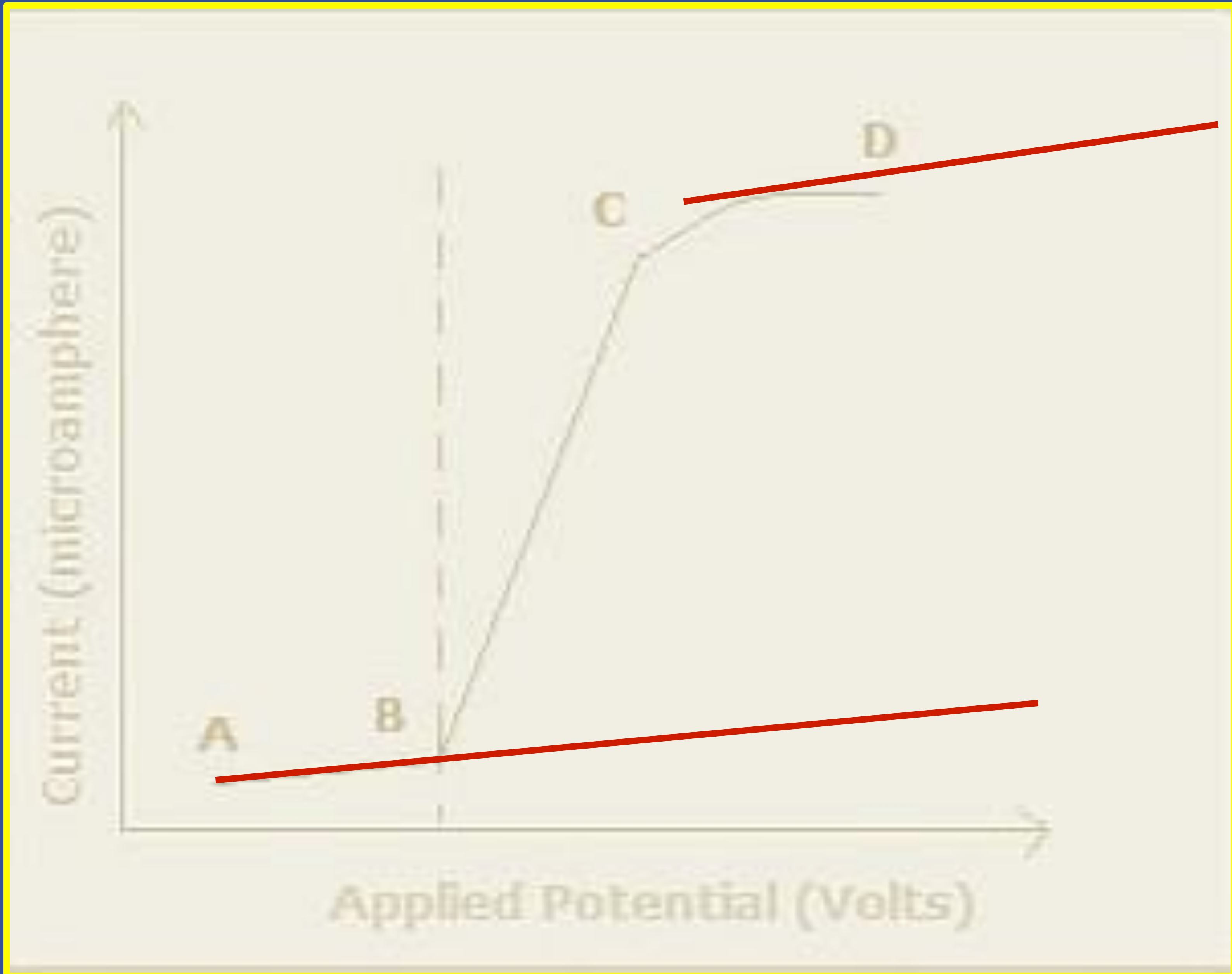
- Consider a Polarographic cell, containing a solution of cadmium chloride, to which an external E.M.F is applied.

- The positively charged ions present in the solution will be attracted towards the mercury drop of the dropping mercury electrode (DME).

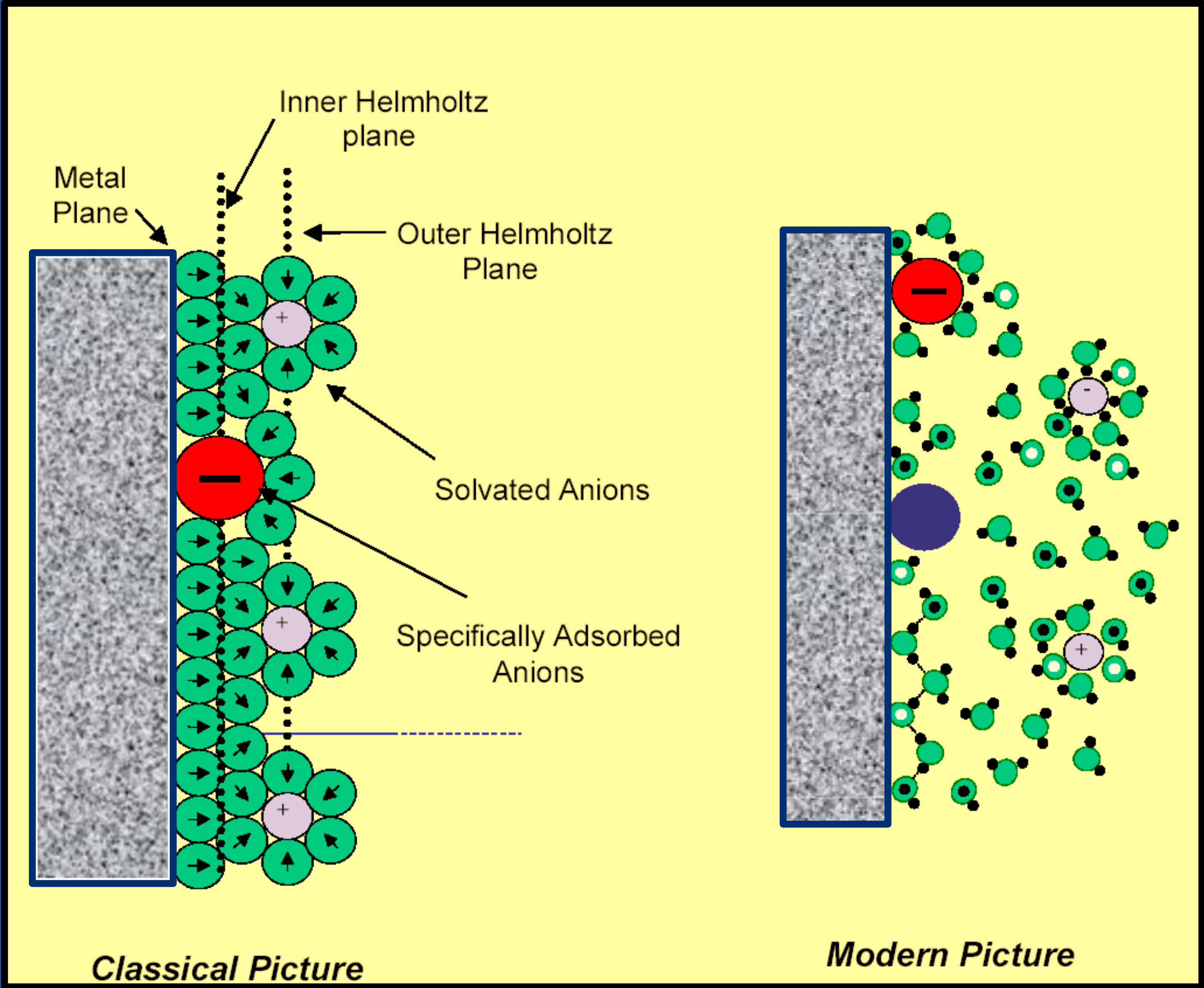
- The total current flowing through the cell may be regarded as being the " sum of the electrical and diffusive forces."
- When the applied voltage is increased and the current is recorded a graph will obtained.



CURRENT VOLTAGE CURVE



$$i_{nf} = \frac{dQ}{dt} = A\frac{d(C_{dl} \cdot E)}{dt} = A\left(E\frac{dC_{dl}}{dt} + C_{dl}\frac{dE}{dt}\right)$$



ADVANTAGES OF DME

- Its surface area is reproducible with single capillary.
- The surface area can be calculated from the weight of the drops.
- Mercury possesses the property of forming amalgams with many metals and therefore lowers their reduction potential.
- High over voltage of hydrogen on mercury makes possible the deposition of ions which are difficult to be reduced on many other metal electrodes.

DISADVANTAGES OF DME

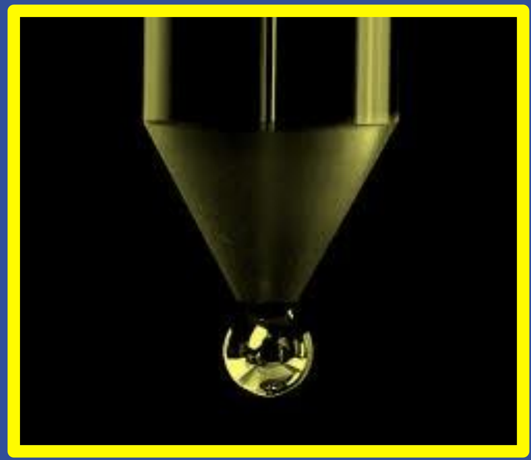
- The area of the microelectrode is constantly changing as the size of the drop changes

- Mercury may be easily oxidized and thus limits the feasible range of electrode

- The capillary may be easily plugged and thus care must be taken to avoid touching the tip of the capillary with any foreign material.

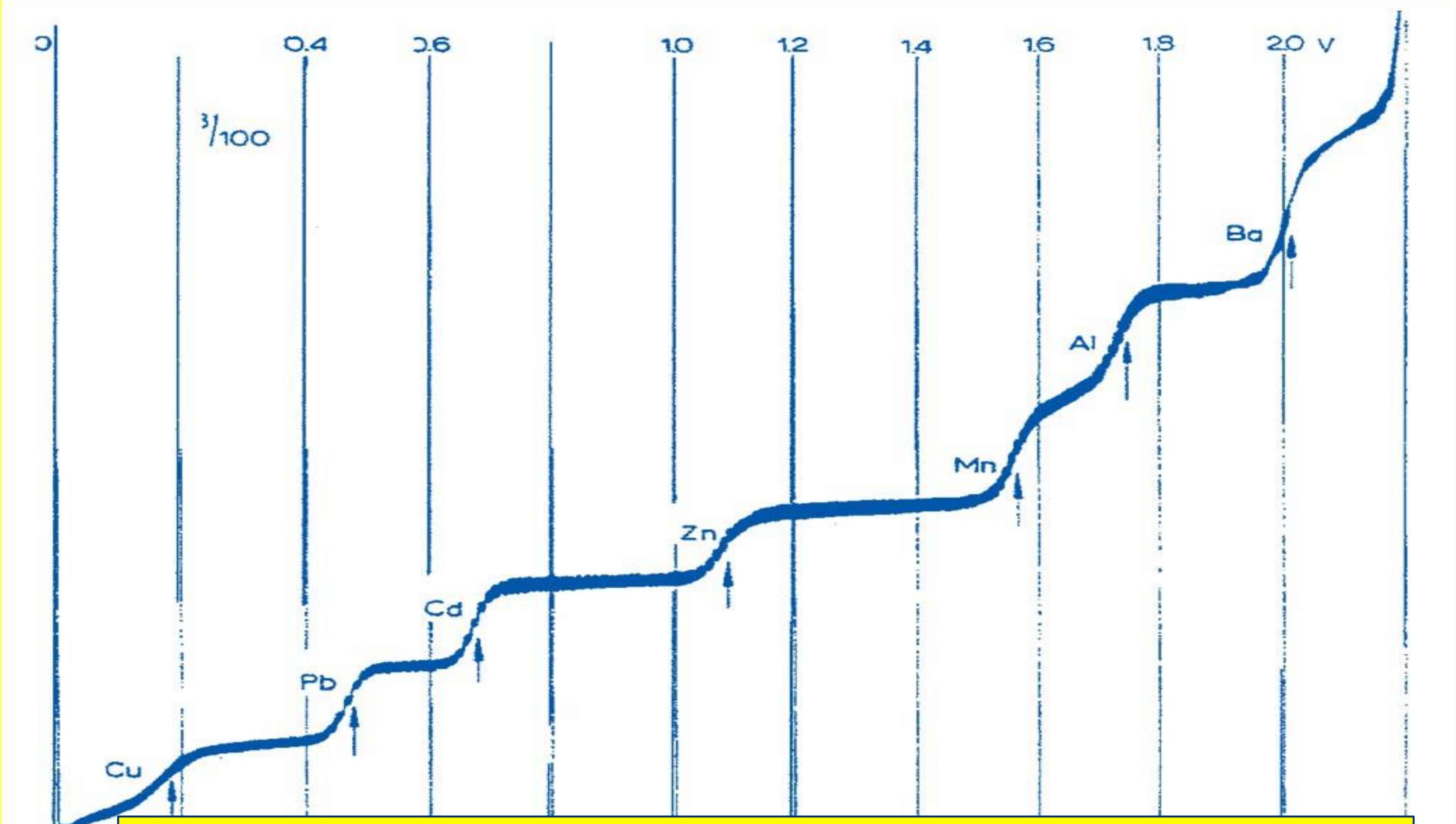
TYPES OF POLAROGRAPHY

- **Differential Pulse Polarography**
- **Pulse Polarography**
- **AC Polarography**



JAROSLAV HEYROVSKÝ

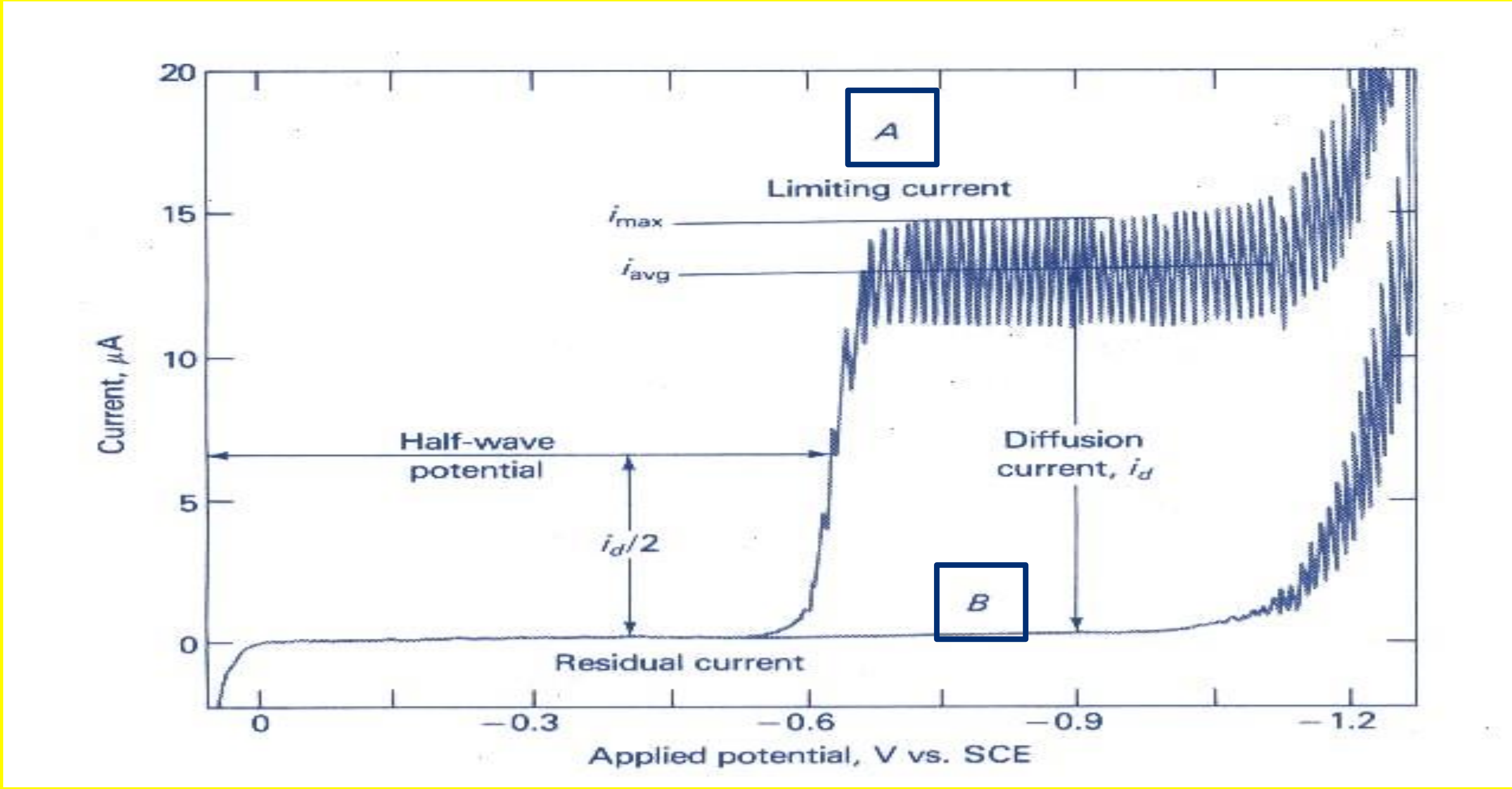
“The trends of polarography”, **Nobel Lecture, December 11, 1959*



Polarographic spectrum showing seven cations in the solution

R. E.	Cu	Pb	Cd	Zn	Mn	Al	Ba
1959, E1/2	0.00	-0.37	-0.62	-1.00	-1.40	-1.64	-1.94
2009, E1/2 SCE = 4.44	4.44	4.07	3.82	3.44	3.04	2.80	2.50

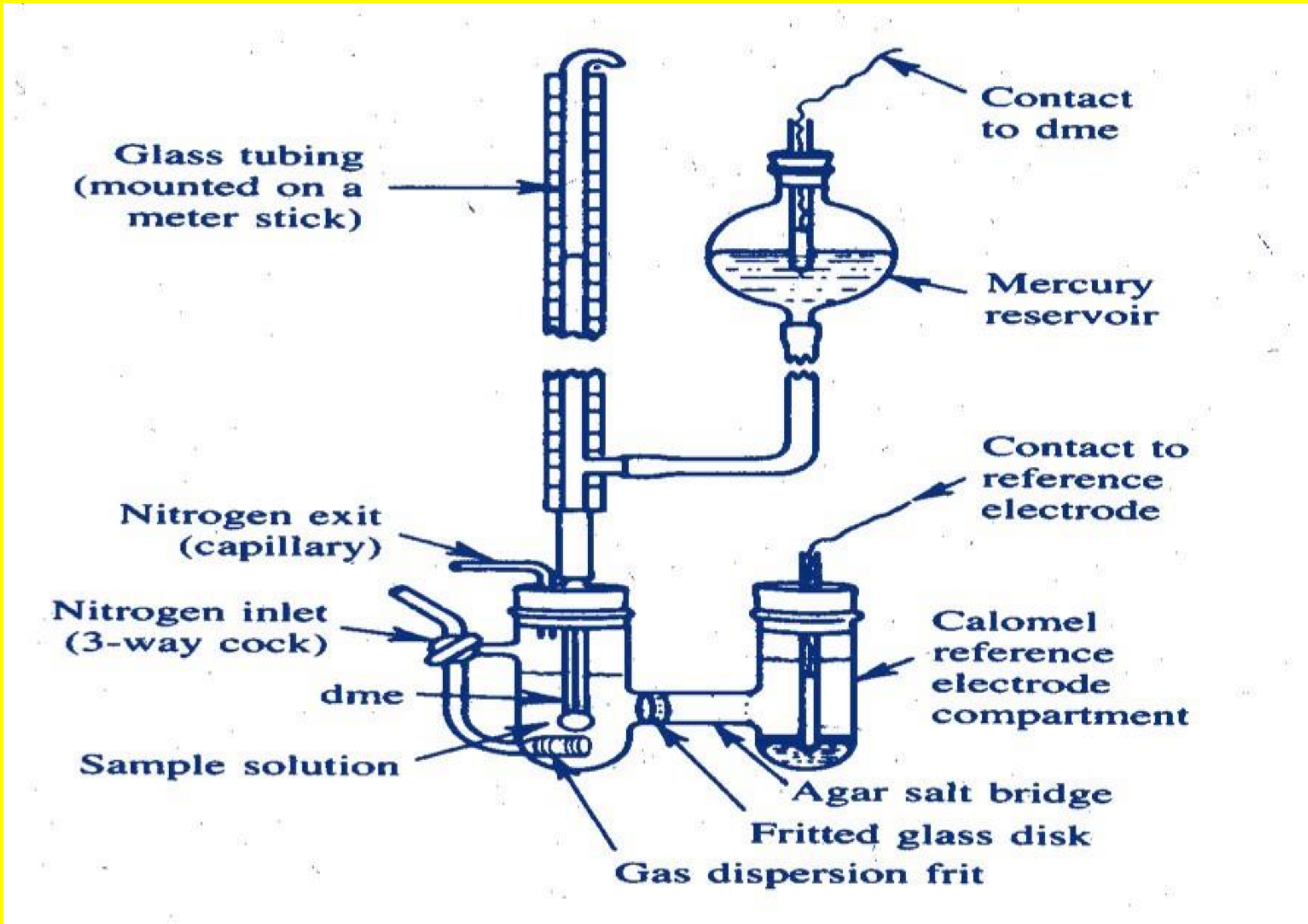
TYPICAL POLAROGRAM



A – $5x10^{-4}$ M Cd^{+2} in 1 M HCl, B – 1 M HCl

- **Residual current, $i_{r,}$ (charging, condenser)**
- **Diffusion current, i_d or $i_{L,}$ (limiting)**
- **Half-wave potential, $E_{½}$**

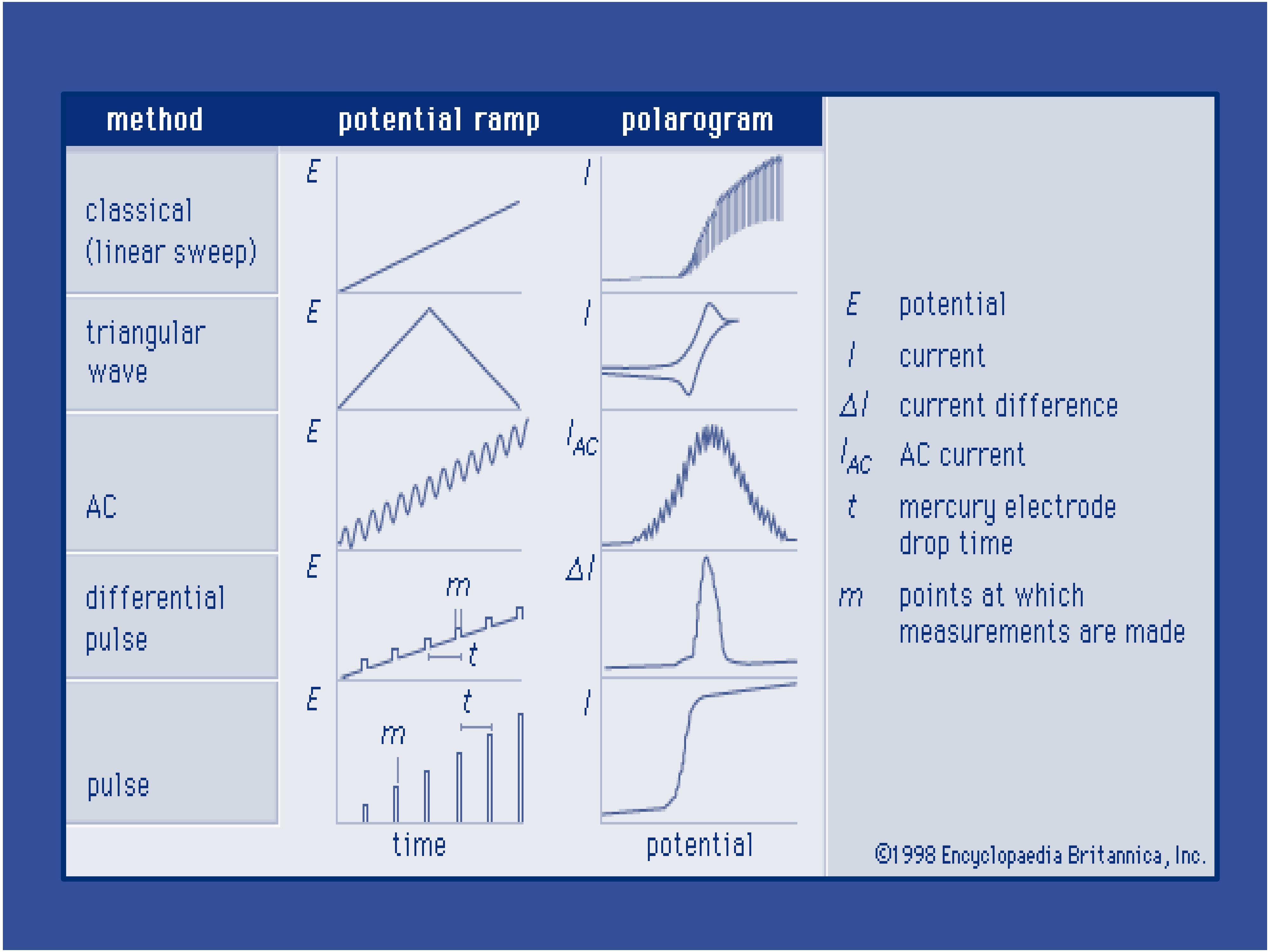
INSTRUMENTATION



DIFFERENTIAL PULSE POLAROGRAPHY

- **Differential pulse polarography is a polarographic technique that use a series of discrete potential steps rather than a linear potential ramp to obtained the experimental polarogram**

- **The differential current is plotted vs. the average potential to obtain the differential pulse polarogram,**



method
potential ramp
polarogram
classical (linear sweep)
triangular wave
AC
differential pulse
pulse
E
I
I_{AC}
ΔI
m
t
time
potential
E potential
I current
ΔI current difference
I_{AC} AC current
t mercury electrode drop time
m points at which measurements are made
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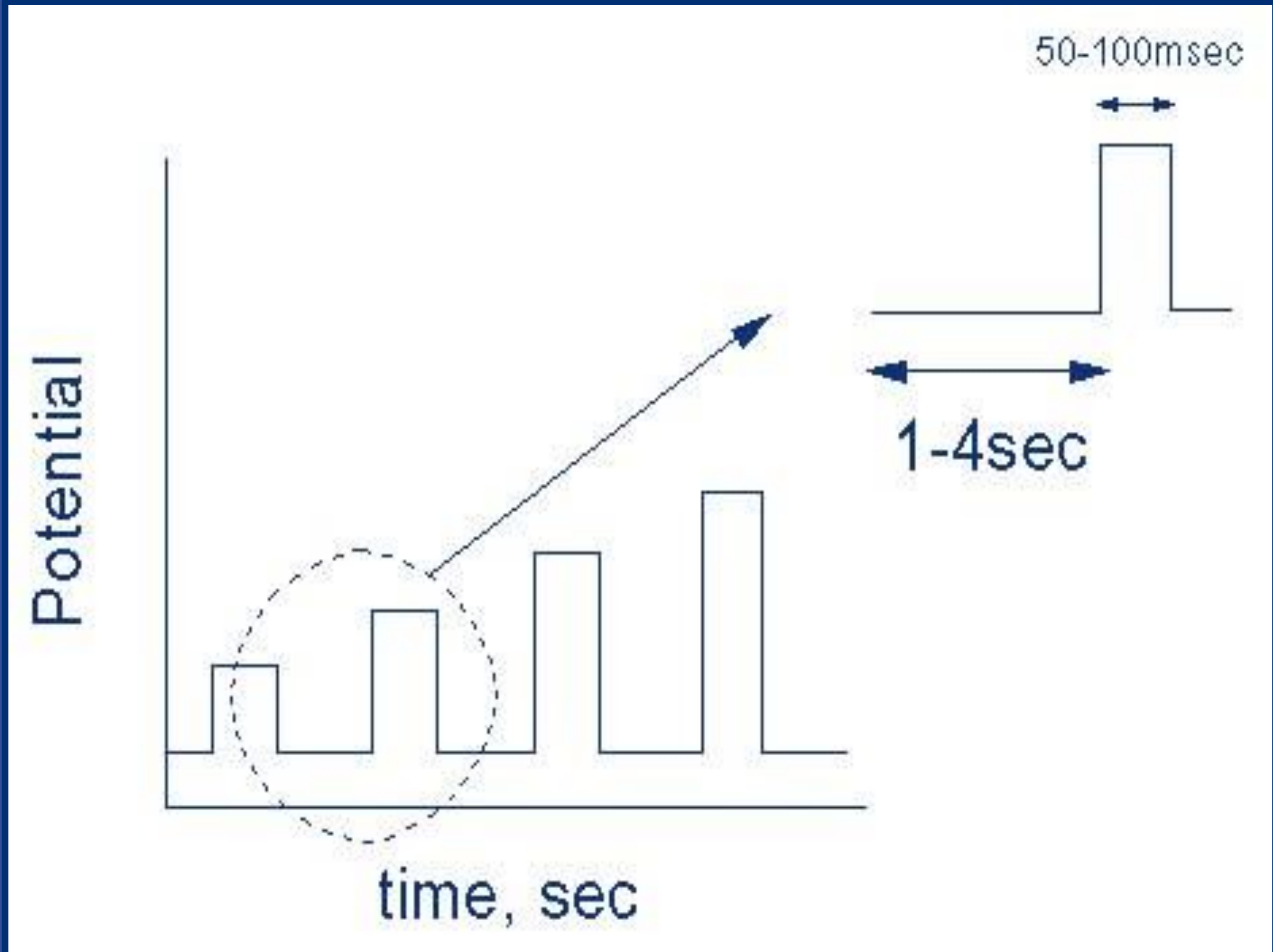
NORMAL PULSE POLAROGRAPHY

- **In normal pulse polarography (NPP) each step begins at the same value and the amplitude of each step increases in small increments.**

- **When Hg drop is dislodged from the capillary the potential is returned to initial value in preparation for a new step**


50-100msec
1-4sec
Potential
time, sec

RECORDING POLAROGRAPHS

- This type of Polarography records current-voltage curve automatically.

PROCEDURE

- The applied voltage is increased at a steady controlled rate by means of a constant speed motor
- Simultaneously the chart paper is moved at steady rate.
- The recording pen move in accordance with the current passing through the cell

FACTORS AFFECTING LIMITING CURRENT

- **Kinetic current**
- **Residual current**
- **Diffusion current**
- **Migration current**

- **RESIDUAL CURRENT:**

RESIDUAL CURRENT = Faradic Current + Condenser current

- **MIGRATION CURRENT:**

The electro active material reaches the surface of electrode by two processes

- The first involves the migration of charge particles in the electrical fields caused by the potential difference existing between the electrode surface and the solution.
- The second involves the diffusion of particles.

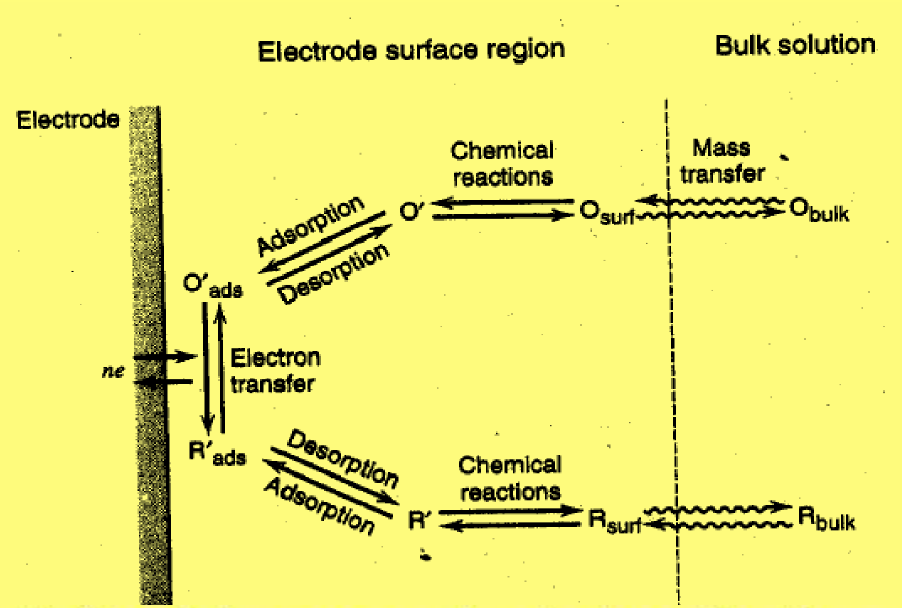
- **DIFFUSION CURRENT:**

  Diffusion current is directly proportional to the concentration of the electro active material.

- **KINETIC CURRENT:**

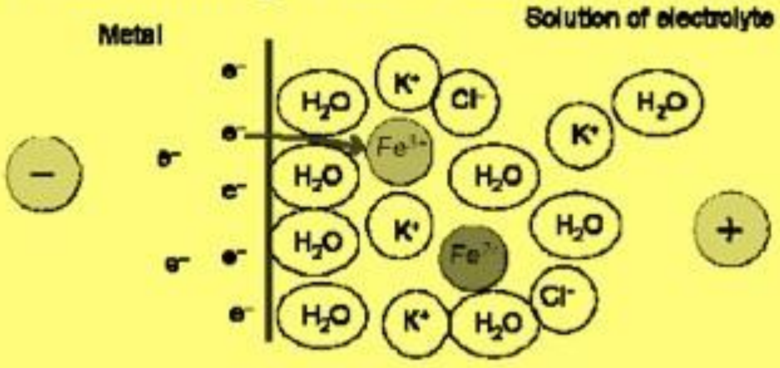
  The limited current may be affected by the rate of non electrode reaction called kinetic current.

Steps in an electron transfer event



- O must be successfully transported from bulk solution (mass transport)
- O must adsorb *transiently* onto electrode surface (non-faradaic)
- CT must occur between electrode and O (faradaic)
- R must desorb from electrode surface (non-faradaic)
- R must be transported away from electrode surface back into bulk solution (mass transport)

A faradaic process leads to reduction or oxidation of species present at the interface.



$$i_f = nFAk \cdot C_{Fe^{3+}}$$

$$i_f = \frac{dQ}{dt} = nF\frac{dN}{dt}$$

APPLICATIONS OF POLAROGRAPHY

INORGANIC COMPOUNDS:

Polarography can be used for estimation of cation and anions.

DETERMINATION OF TRACE ELEMENTS:

Polarography can be used for determination of trace elements

e.g CO, Al, Cu, Ni, etc

APPLICATION TO ORGANIC COMPOUND:

For quantitative identification of compounds and for quantitative analysis of mixtures.

DETERMINATION OF DISSOLVED OXYGEN:

The determination of dissolved oxygen in aqueous solution or organic solvents can be carried out successfully with the help of polarography.

DETERMINATION OF PLANT CONTENTS:

A polarographic analysis of content of essential oils.

STUDIES OF COMPLEXES:

Polarography is powerful tool for study of composition of complexes

if the sample metal ion and

complex of that metal ion in the

same oxidation state.

APPLICATION TO PARMACEUTICALS:

- Oxidation process of medicines like epinephrine and nor-epinephrine.
- The use of A.C. polarography has proved advantageous in the analysis of tetracycline.

ANALYSIS OF BIOLOGICAL SYSTEMS:

The possibility of being able to determine vitamins, alkaloids, hormones, terpenoid substances, and natural coloring substances has made polarography useful in analysis of biological systems

DETERMINTION OF PESTICIDE AND HERBICIDE:

Polarography is also used for the determination of pesticides or herbicides residues in foods.

VOLTAMMETRY

- **The measurement of variations in current produced by variations of the potential applied to a working electrode.**

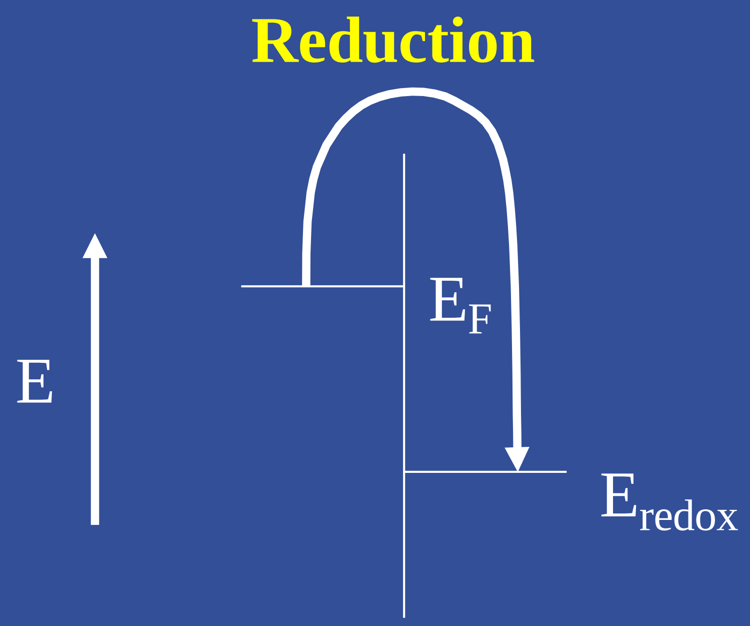
Polarography

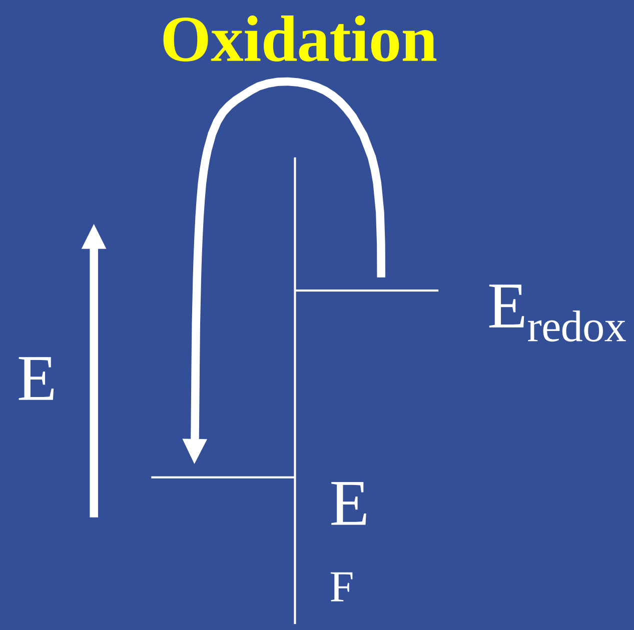
- **Heyrovsky (1922): first Voltammetry experiments using a dropping mercury working electrode**

- **In Voltammetry, once the applied potential is sufficiently negative, electron transfer occurs between the electrode and the electroactive species:**

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

WHY ELECTRONS TRANSFER





- Net flow of electrons from M to solute
- E_f more negative than E_{redox}
- more cathodic
- more reducing

- Net flow of electrons from solute to M
- E_f more positive than E_{redox}
- more anodic
- more oxidizing

MASS TRANSFER

- **Migration – movement of a charged particle in a potential field.**

- **Diffusion – movement due to a concentration gradient.**

  If electrochemical reaction depletes (or produces) some species at the electrode surface, then a concentration gradient develops and the electroactive species will tend to diffuse from the bulk solution to the electrode (or from the electrode out into the bulk solution).

- **Convection – mass transfer due to stirring.**

  Achieved by some form of mechanical movement of the solution or the electrode i.e., stir solution, rotate or vibrate electrode.

  Difficult to get perfect reproducibility with stirring, better to move the electrode.

  Convection is considerably more efficient than diffusion or migration higher currents for a given concentration therefore, greater analytical sensitivity

NERNST-PLANCK EQUATION

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} + \frac{-z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

Diffusion — Migration — Convection

$J_i(x)$ = flux of species i at distance x from electrode (mole/cm^2 s)
D_i = diffusion coefficient (cm^2/s)
$\partial C_i(x)/\partial x$ = concentration gradient at distance x from electrode
$\partial \phi(x)/\partial x$ = potential gradient at distance x from electrode
$v(x)$ = velocity at which species i moves (cm/s)

DIFFUSION

Fick's 1st Law

$$J = -D \frac{\partial C(x,t)}{\partial x}$$

I = nFAJ

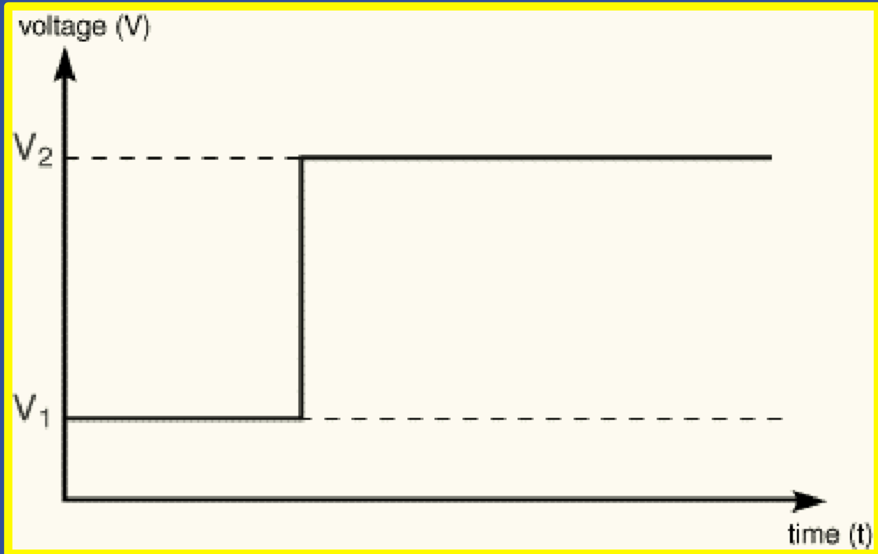
$$C(x,0) = C$$

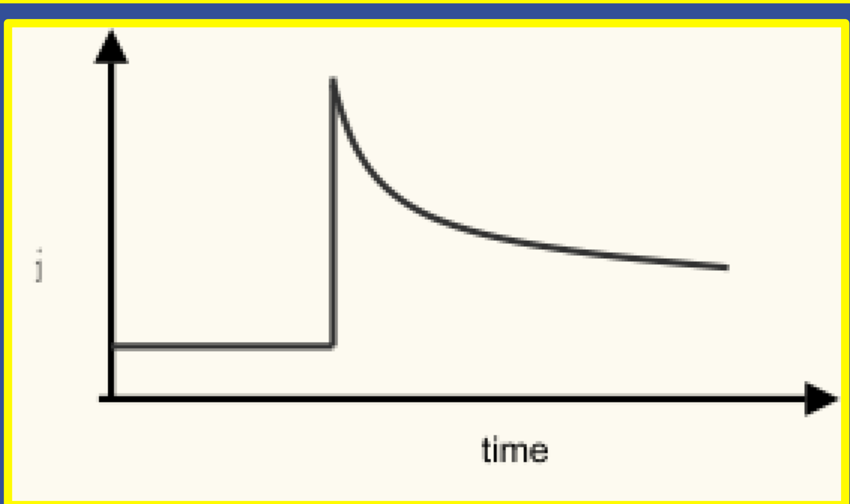
$$C(0,t) = 0$$

$$C(\infty,t) = C$$

Solving Fick's Law for particular applications
like electrochemistry involves establishing Initial Conditions and Boundary Conditions

CHRONOAMPEROMETRY

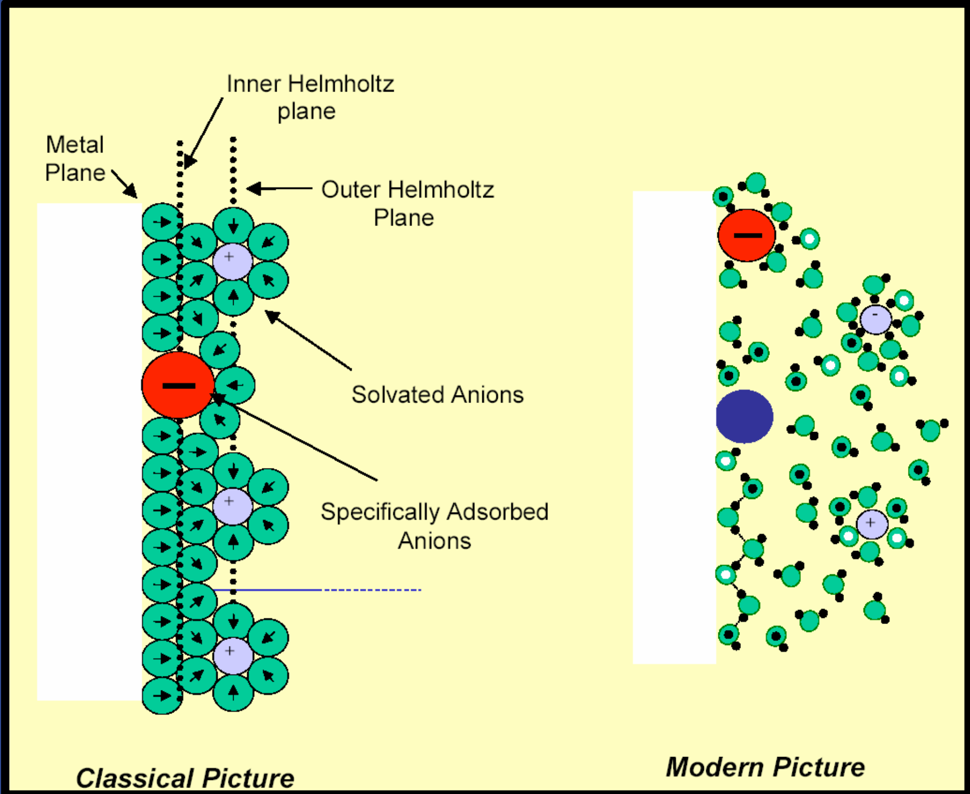




$$I = nFA\,c_o \sqrt{\frac{D}{\pi t}}$$

The Cottrell equation

DOUBLE LAYER



$$i_{nf} = \frac{dQ}{dt} = A\frac{d(C_{dl} \cdot E)}{dt} = A\left(E\frac{dC_{dl}}{dt} + C_{dl}\frac{dE}{dt}\right)$$

Nernst-Planck Equation

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} + \frac{-z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

Diffusion Migration Convection

$J_i(x)$ = flux of species i at distance x from electrode (mole/cm^2 s)
D_i = diffusion coefficient (cm^2/s)
$\partial C_i(x)/\partial x$ = concentration gradient at distance x from electrode
$\partial \phi(x)/\partial x$ = potential gradient at distance x from electrode
$v(x)$ = velocity at which species i moves (cm/s)

Diffusion

Fick’s 1st Law

$$J = -D \frac{\partial C(x,t)}{\partial x}$$

$$I = nFAJ$$

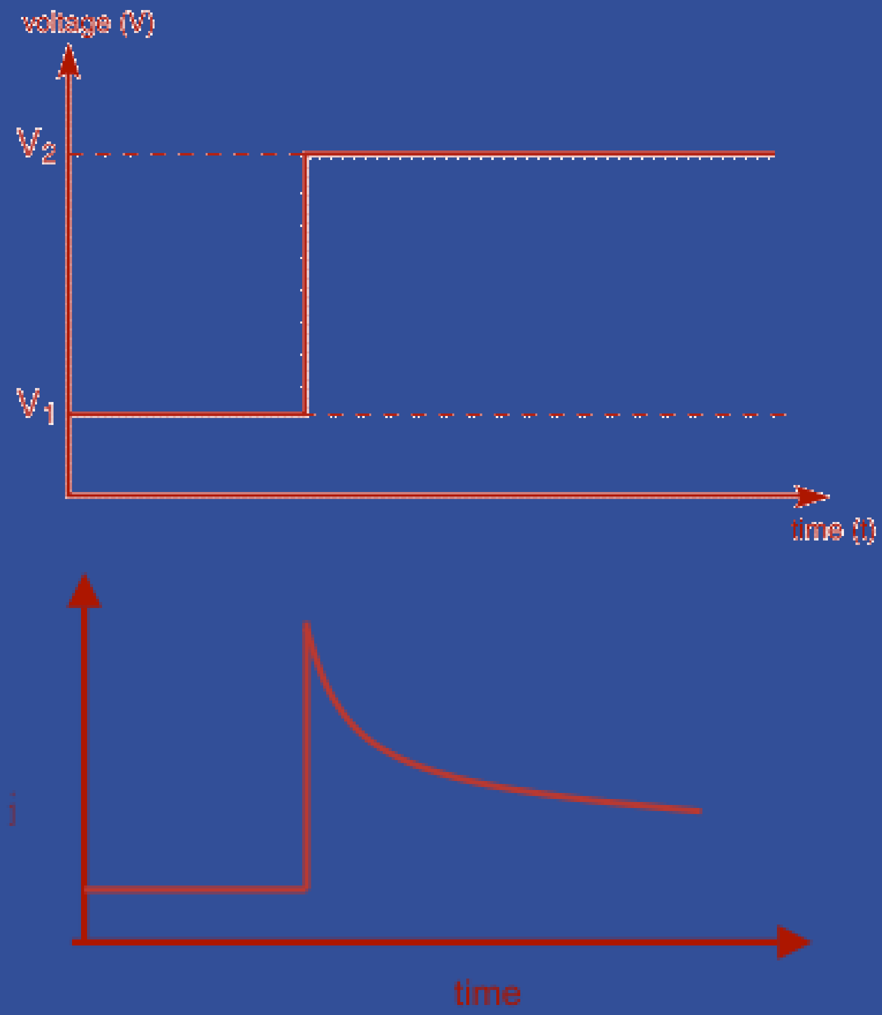
$$C(x,0) = C$$

$$C(0,t) = 0$$

$$C(\infty,t) = C$$

Solving Fick’s Laws for particular applications like electrochemistry involves establishing Initial Conditions and Boundary Conditions

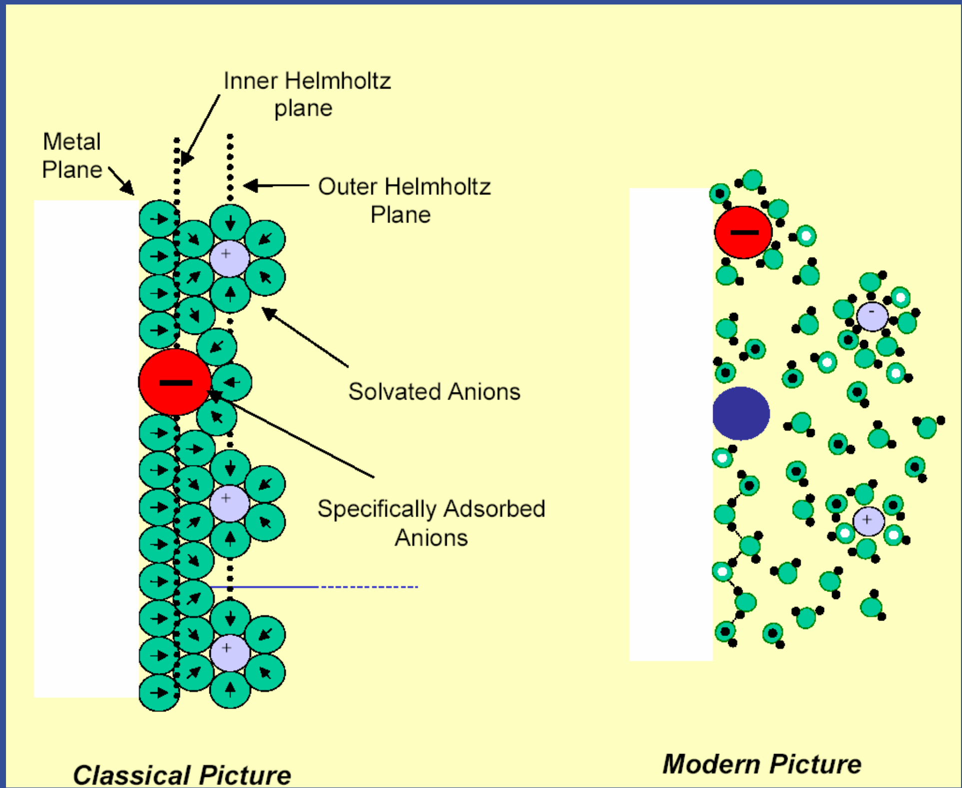
Simplest Experiment
Chronoamperometry



$$I = nFA\,c_o\sqrt{\frac{D}{\pi t}}$$

The Cottrell equation

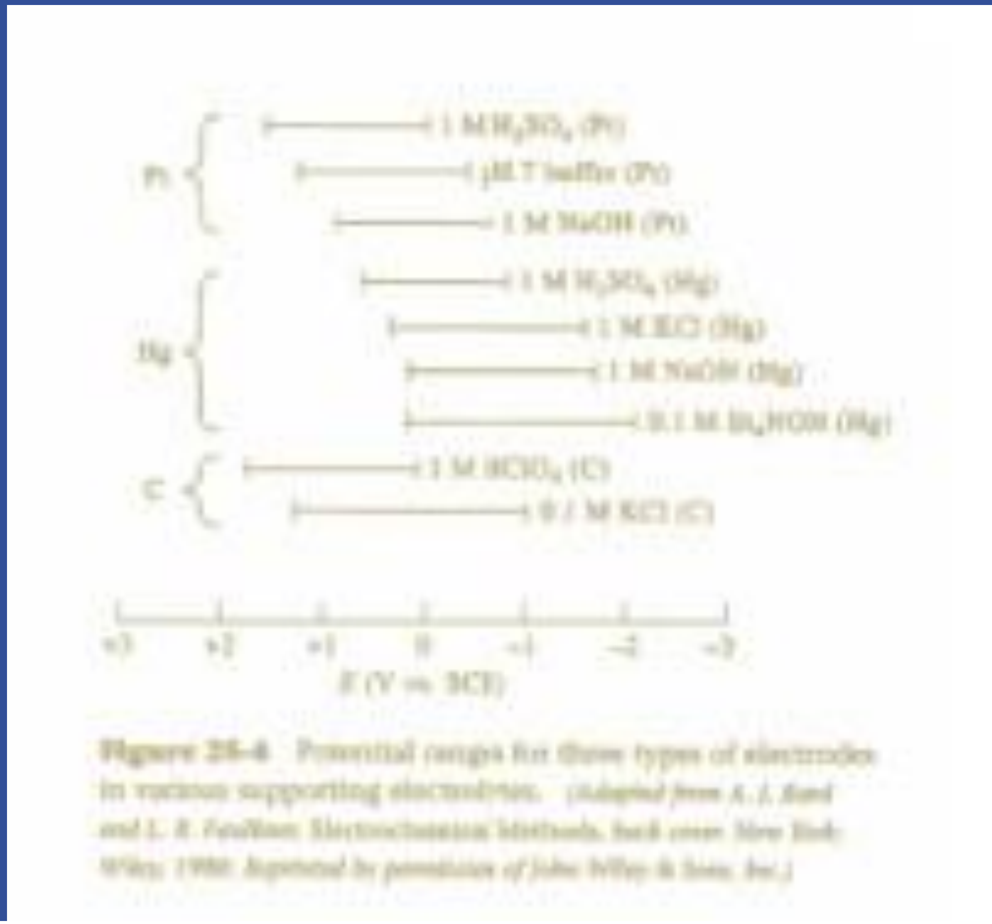
Recall-Double layer



$$i_{nf} = \frac{dQ}{dt} = A\frac{d(C_{dl} \cdot E)}{dt} = A\left(E\frac{dC_{dl}}{dt} + C_{dl}\frac{dE}{dt}\right)$$

Working electrode choice

- Depends upon potential window desired
  - Overpotential
  - Stability of material
  - Conductivity
  - contamination



The polarogram

<u>points a to b</u>

I = E/R

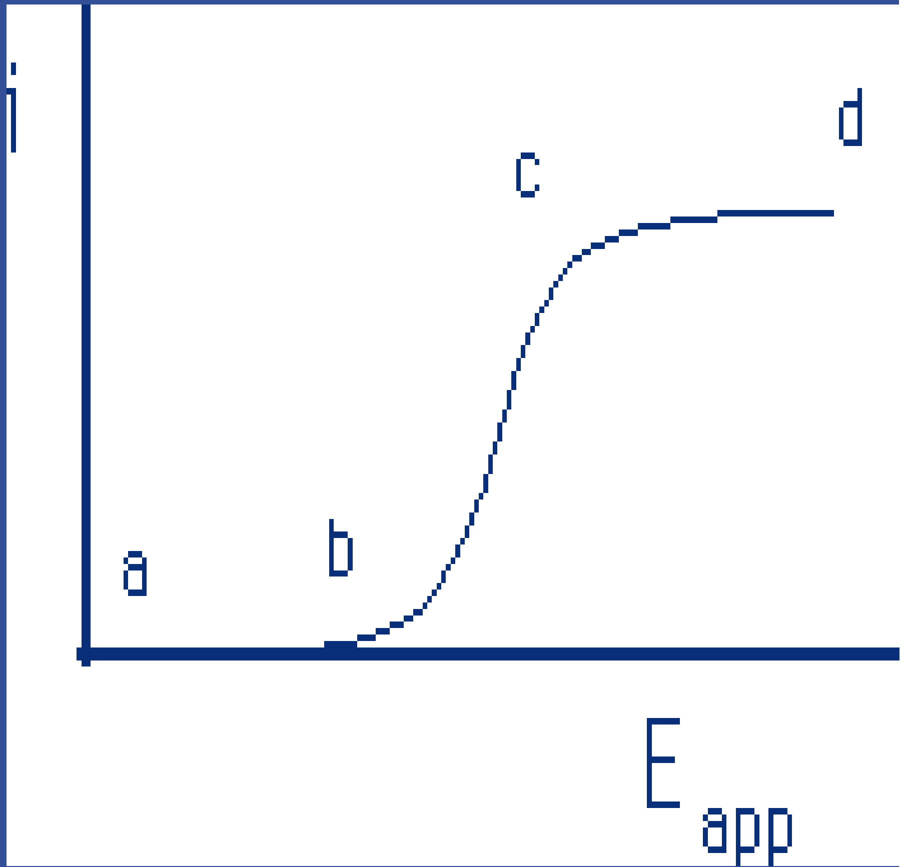
<u>points b to c</u>

electron transfer to the electroactive species.

I(reduction) depends on the no. of molecules reduced/s: this rises as a function of E

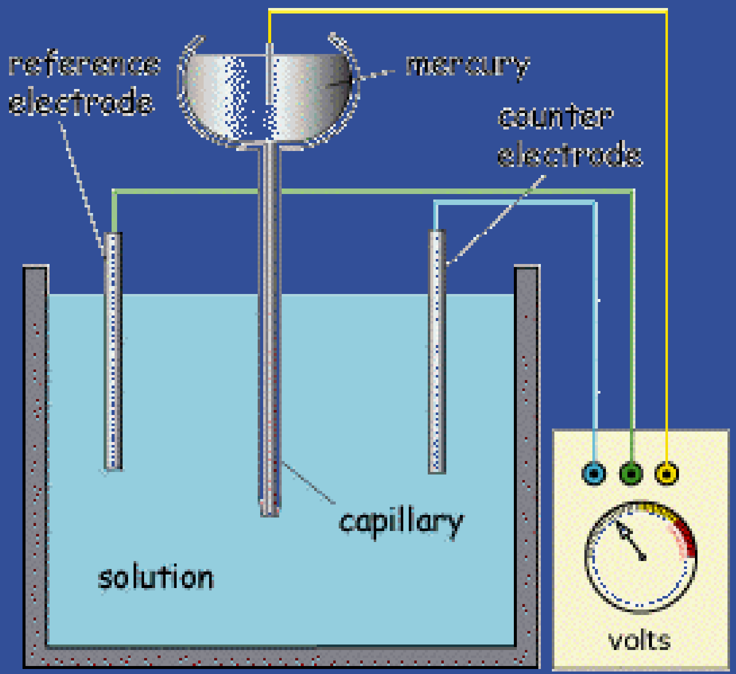
<u>points c to d</u>

when E is sufficiently negative, every molecule that reaches the electrode surface is reduced.



Dropping Mercury Electrode

- Renewable surface
- Potential window expanded for reduction (high overpotential for proton reduction at mercury)



Polarography

$$A = 4\pi(3mt/4\pi d)^{2/3} = 0.85(mt)^{2/3}$$

Density of drop

Mass flow rate of drop

We can substitute this into Cottrell Equation

$$i(t) = nFACD^{1/2}/\ \pi^{1/2}t^{1/2}$$

We also replace D by 7/3D to account for the compression of the diffusion layer by the expanding drop

Giving the Ilkovich Equation:

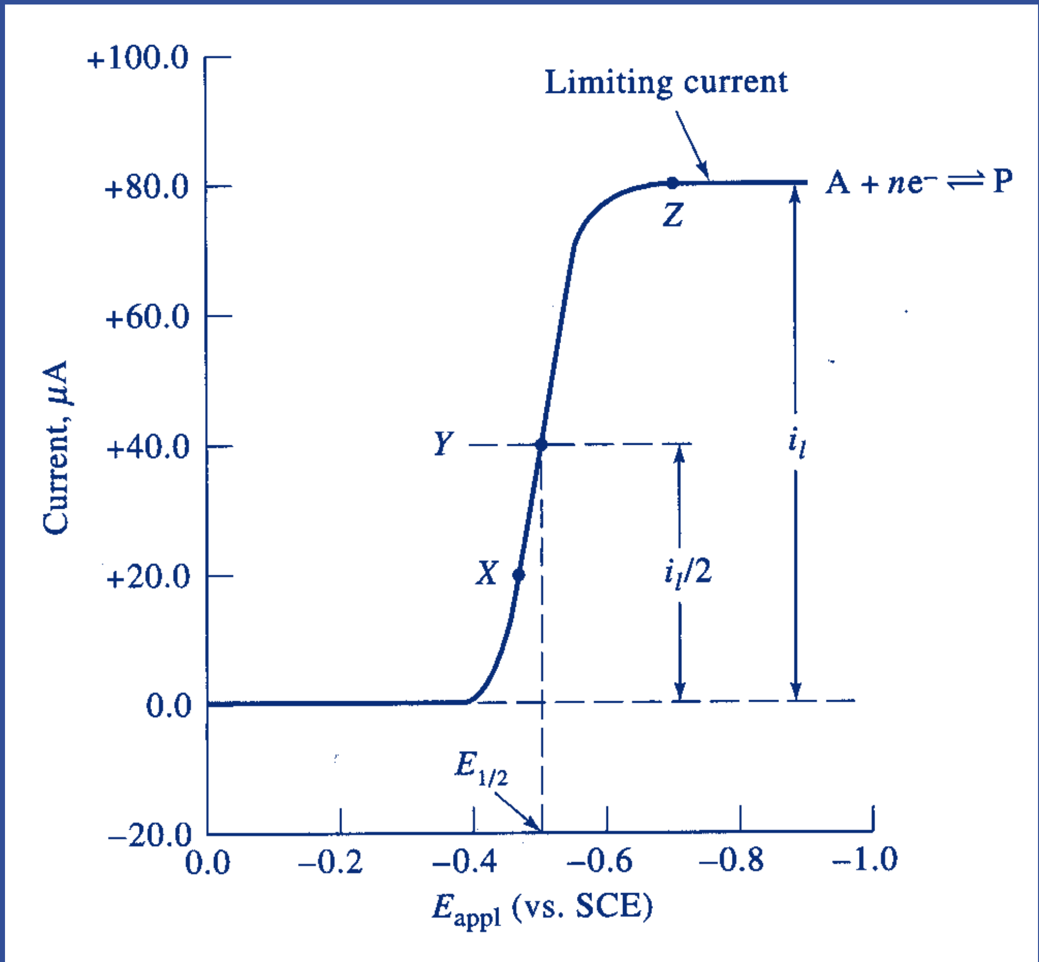
$i_d = 708nD^{1/2}m^{2/3}t^{1/6}C$

I has units of Amps when D is in cm^2s^{-1}, m is in g/s and t is in seconds. C is in mol/cm^3

This expression gives the current at the end of the drop life. The average current is obtained by integrating the current over this time period

$$i_{av} = 607nD^{1/2}m^{2/3}t^{1/6}C$$

Polarograms



$E_{1/2} = E^0 + RT/nF \log (D_R/D_o)^{1/2}$
(reversible couple)

Usually D's are similar so half wave potential is similar to formal potential. Also potential is independent of concentration and can therefore be used as a diagnostic of identity of analytes.

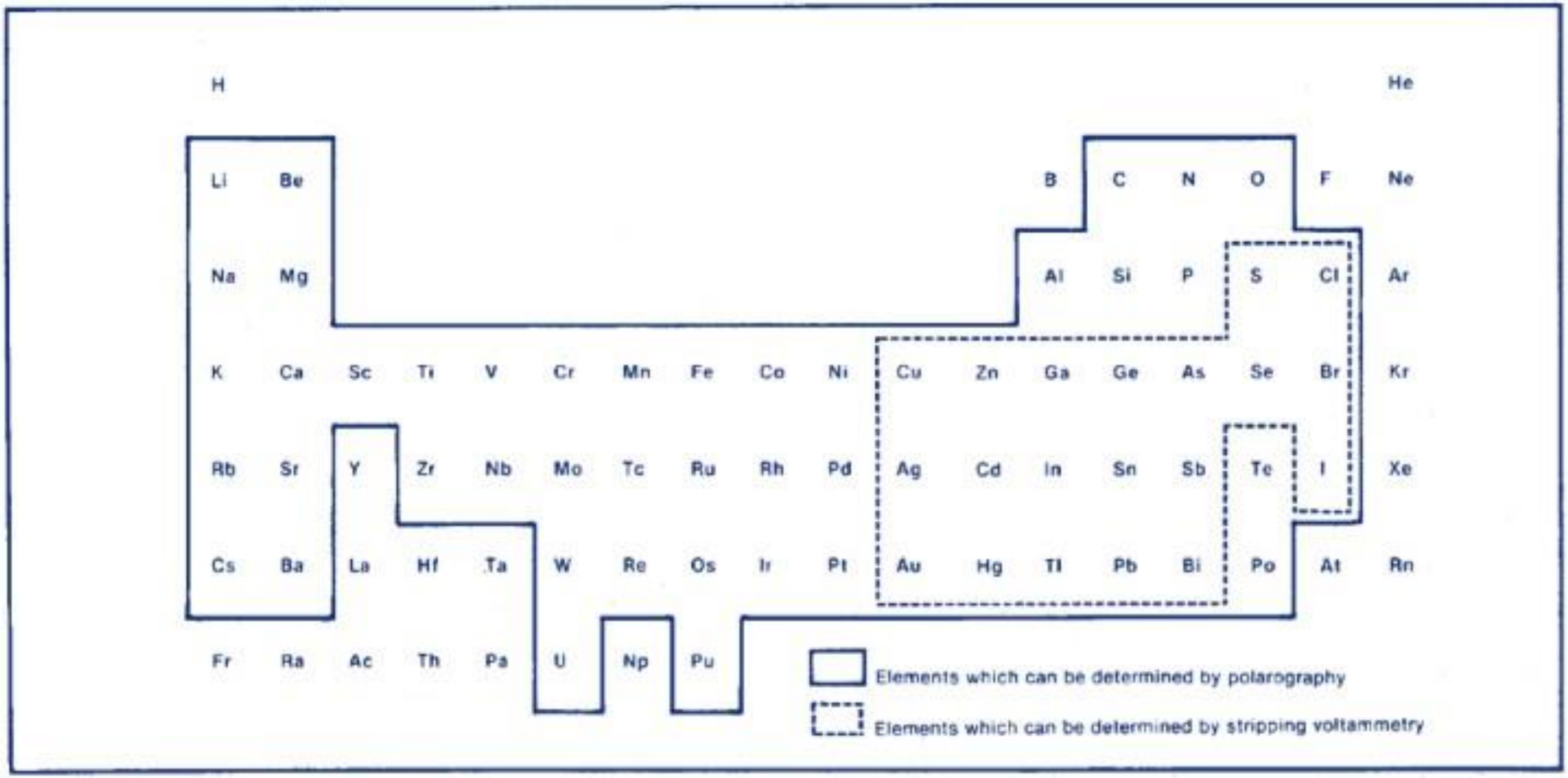
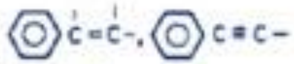
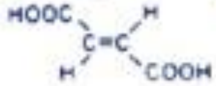


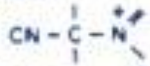
FIGURE 3. Elements which can be determined by voltammetry.

Olefin-conjugated aromatics, e.g. 

Conjugated systems such as: 

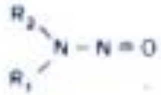
Imines, e.g. $RCH=NH$

Oximes, e.g. $>C=NOH$

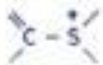
Nitriles, e.g. 

Diazo Compounds, e.g. $-\overset{+}{N}\equiv N$

Diazonium Salts

Nitroso Compounds, e.g. 

Sulfones, e.g. 

Sulfonium Salts, e.g. 

Nitro Compounds

Dienes

Acetylenes

Ketones

Aldehydes

Aromatic Carboxylic Acids

Halides

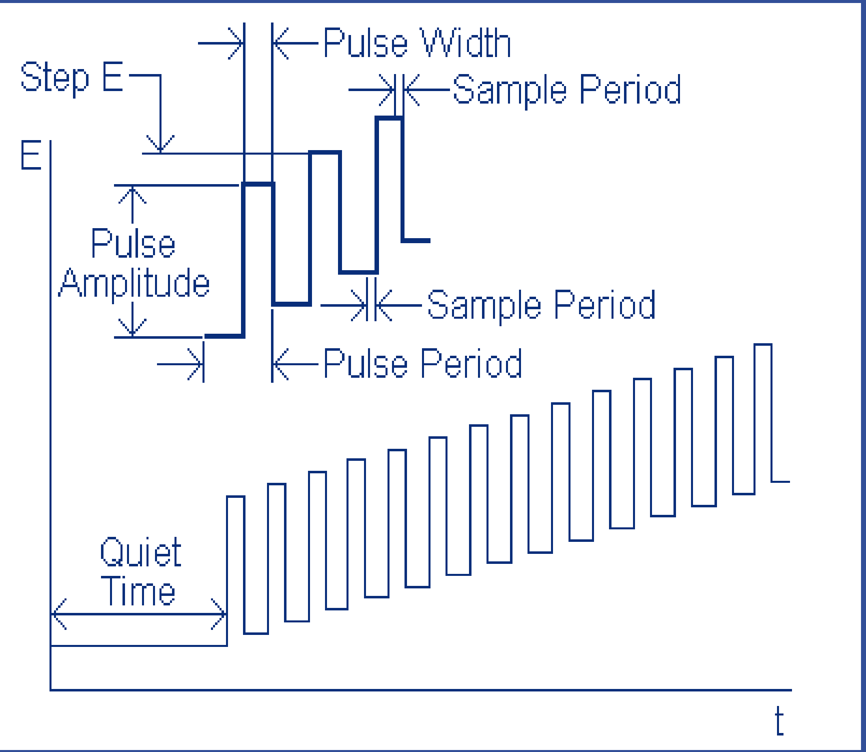
Thiocyanates

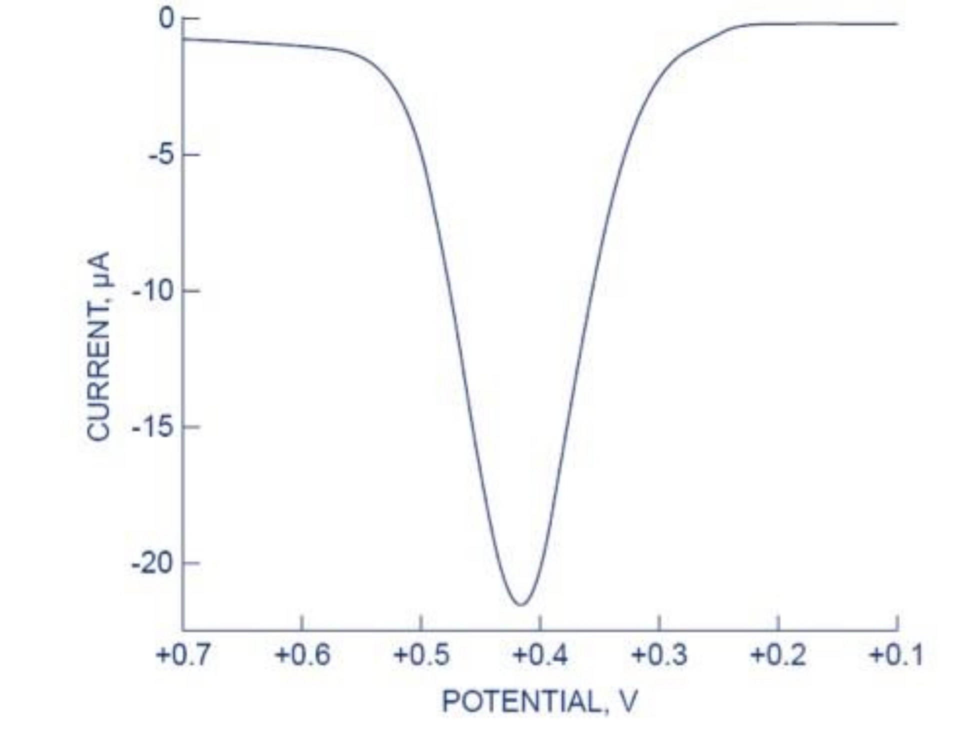
Heterocycles

Organo-metallics

TABLE 4: Polarographic reduction of various functional groups.

Differential pulse voltammetry





DPP

- current measured twice during the lifetime of each drop difference in current is plotted.
- Results in a peak-shaped feature, where the top of the peak corresponds to $E_{1/2}$, and the height gives concentration
- This shape is the **derivative** of the regular DC data.
- DPP has the advantage of sensitive detection limits and discrimination against background currents. Traditionally, metals in the **ppm** range can be determined with DPP.
- Derivative improves contrast (resolution) between overlapping waves

DPP vs DCP

Ep ~ $E_{1/2}$ ($E_p = E_{1/2} \pm \Delta E/2$)

where ΔE=pulse amplitude

$$I_p = \frac{nFAD^{1/2}c}{(\pi t_m)} \frac{1-\sigma}{1+\sigma}$$

$\sigma = \exp[(nF/RT)(\Delta E/2)]$

Resolution depends on ΔE

$W_{1/2} = 3.52RT/nF$ when $\Delta E \rightarrow 0$

Improved response
because charging current
is subtracted and adsorptive
effects are discriminated against.
l.o.d. 10^{-8}M

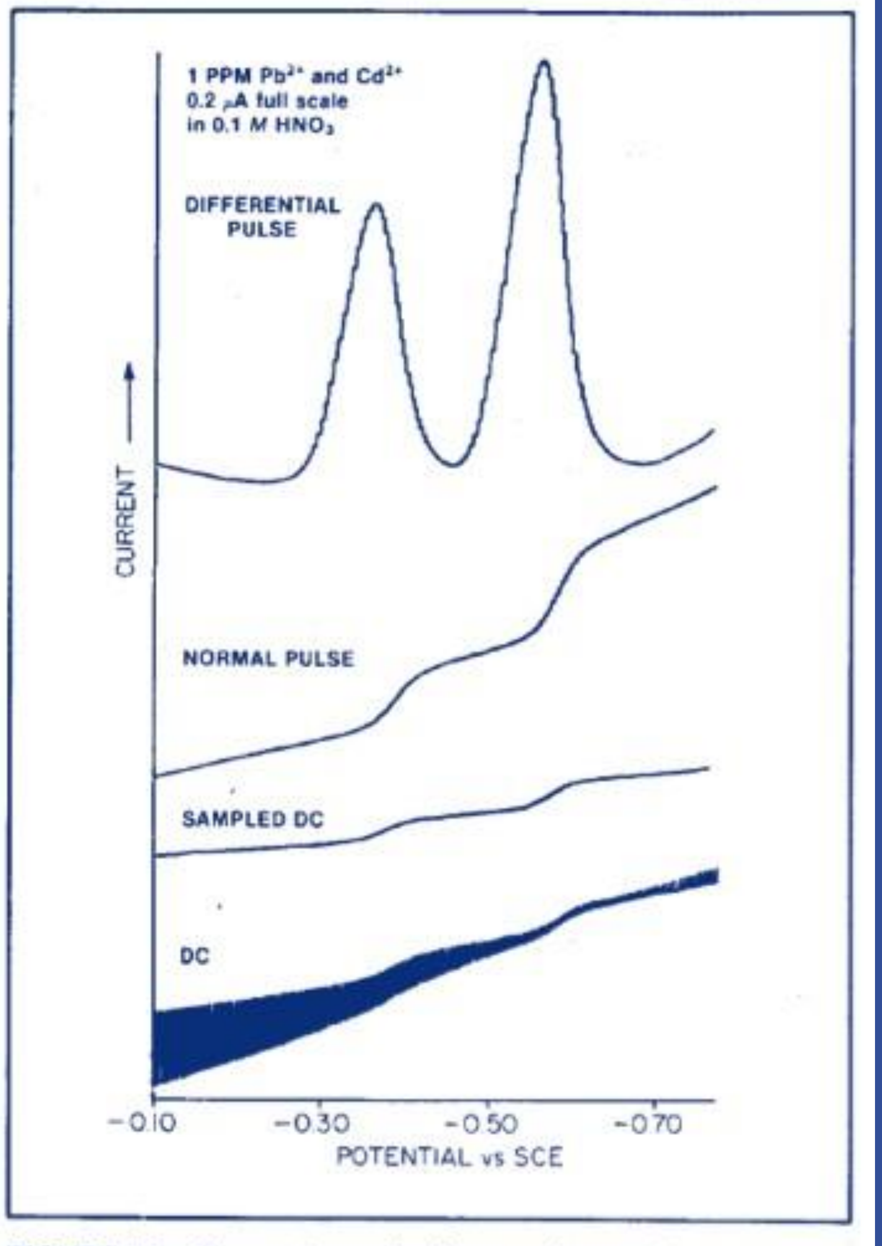


FIGURE 11. Comparison of polarographic modes.

Resolution

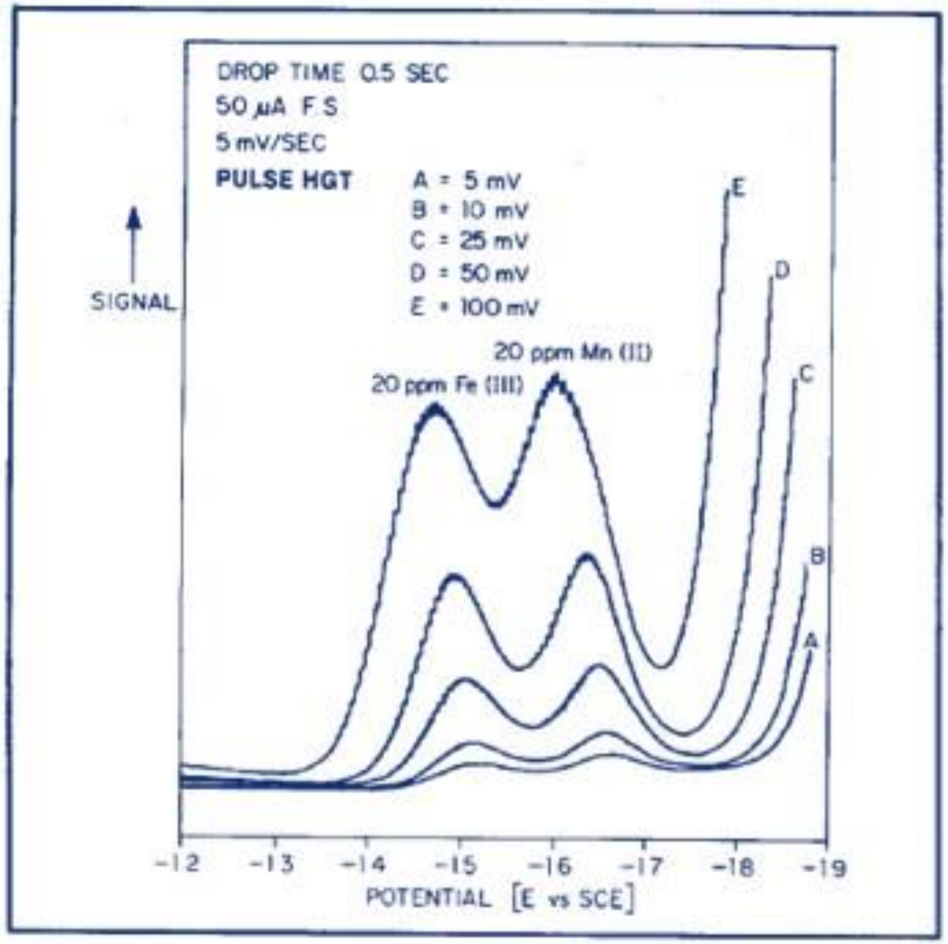
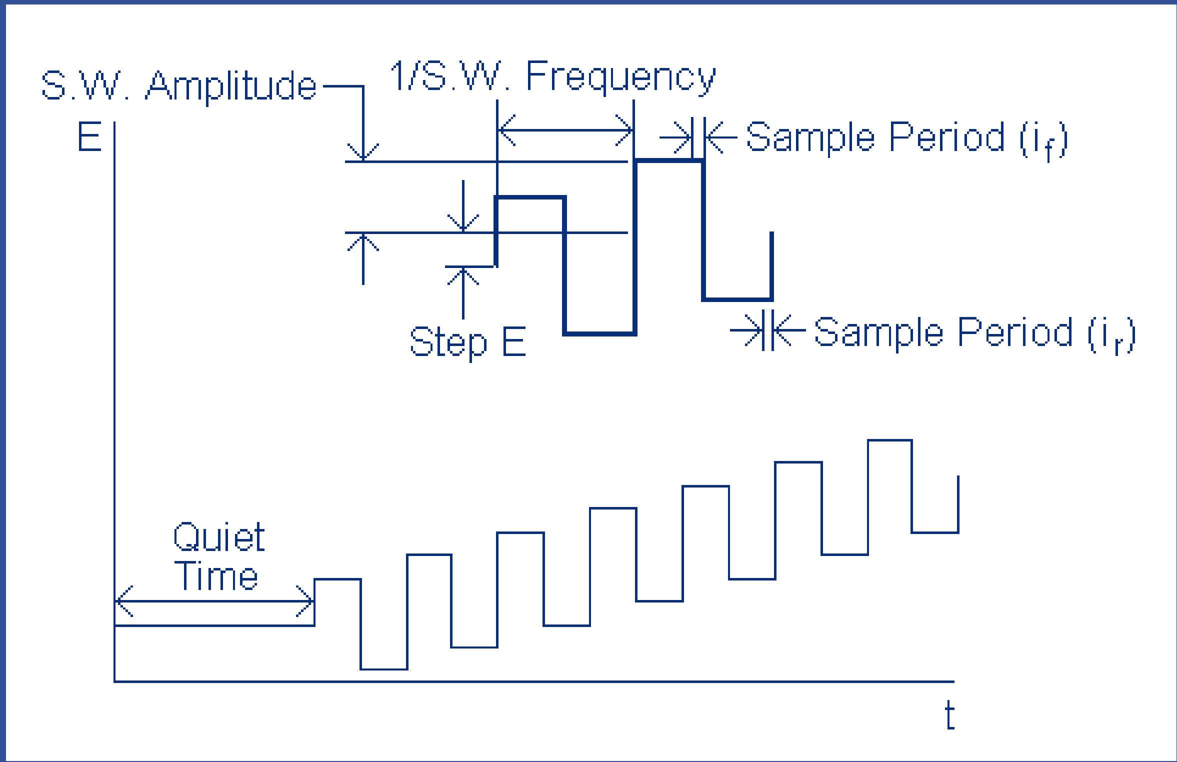


FIGURE 10. Effect of pulse height on peak height and resolution.

Square wave voltammetry



SWV

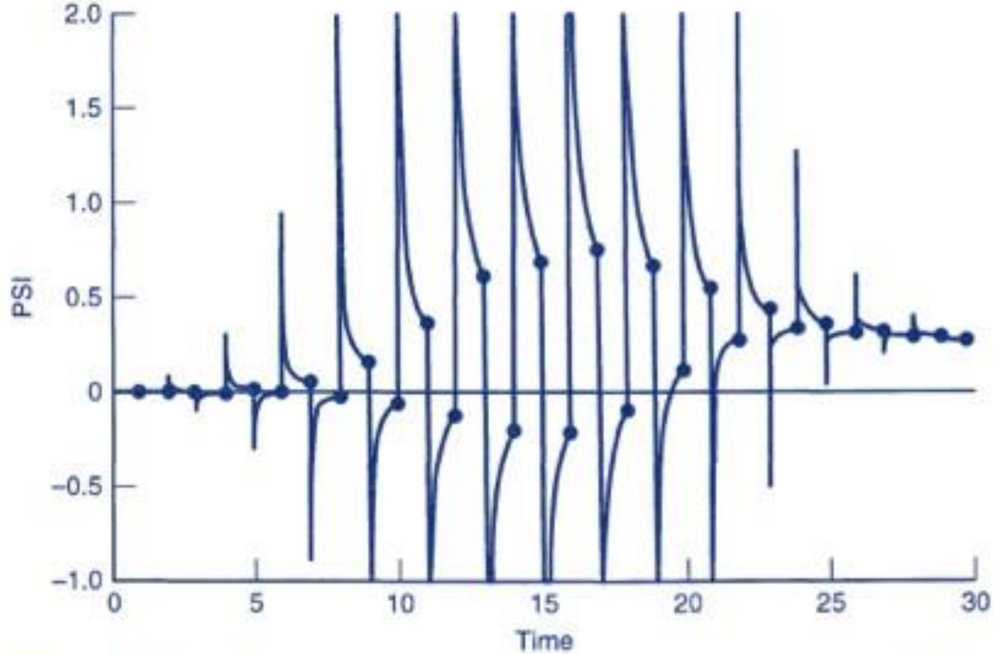


Figure 7.3.14 Dimensionless current response throughout an SWV experiment for the reversible O/R system with R absent from the bulk and with the scan beginning well positive of $E^{0'}$. Cathodic currents are upward. The time axis corresponds to the half-cycle index m, and the staircase potential reaches $E^{0'}$ near m = 15. Sampled currents are shown as points. $n\Delta E_p = 50$ mV and $n\Delta E_s = 30$ mV. [Reprinted from J. Osteryoung and J. J. O'Dea, *Electroanal. Chem.*, **14**, 209 (1986), by courtesy of Marcel Dekker, Inc.]

SWV Response

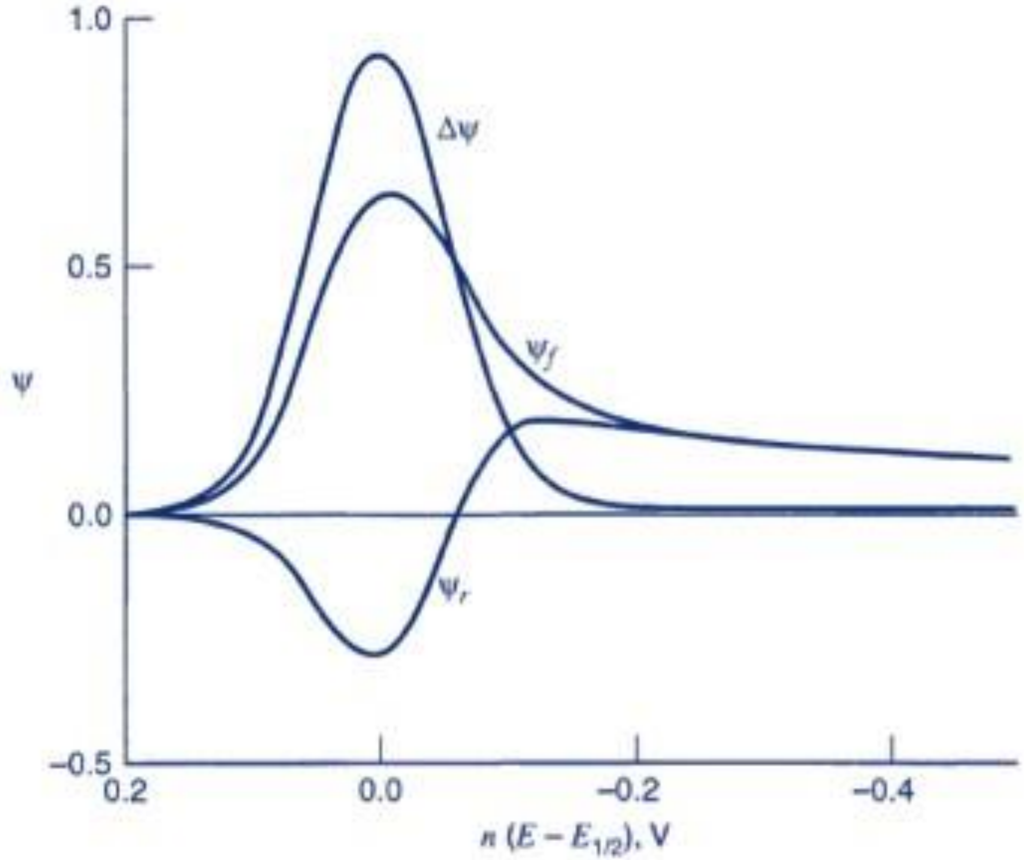


Figure 7.3.15 Dimensionless square wave voltammograms for the reversible O/R case with R absent from the bulk. $n\Delta E_p = 50$ mV and $n\Delta E_s = 10$ mV. Forward currents (ψ_f), reverse currents (ψ_r), and difference currents ($\Delta\psi$) *vs.* a potential axis referred to the "reversible" $E_{1/2} = E^{0'} + (RT/nF)\ln(D_R/D_O)^{1/2}$. Note that $n(E_m - E_{1/2}) = (RT/F)\ln \xi\theta_m$. [Reprinted from J. Osteryoung and J. J. O'Dea, *Electroanal. Chem.*, **14**, 209 (1986), by courtesy of Marcel Dekker, Inc.]

SWV

- advantage of square wave voltammetry is that the entire scan can be performed on a single mercury drop in about 10 seconds, as opposed to about 5 minutes for the techniques described previously. SWV saves time, reduces the amount of mercury used per scan by a factor of 100. If used with a pre-reduction step, detection limits of 1-10 ppb can be achieved, which rivals graphite furnace AA in sensitivity.

- data for SWV similar to DPP
- height and width of the wave depends on the exact combination of experimental parameters (i.e. scan rate and pulse height

Stripping Voltammetry

- **Preconcentration** 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.

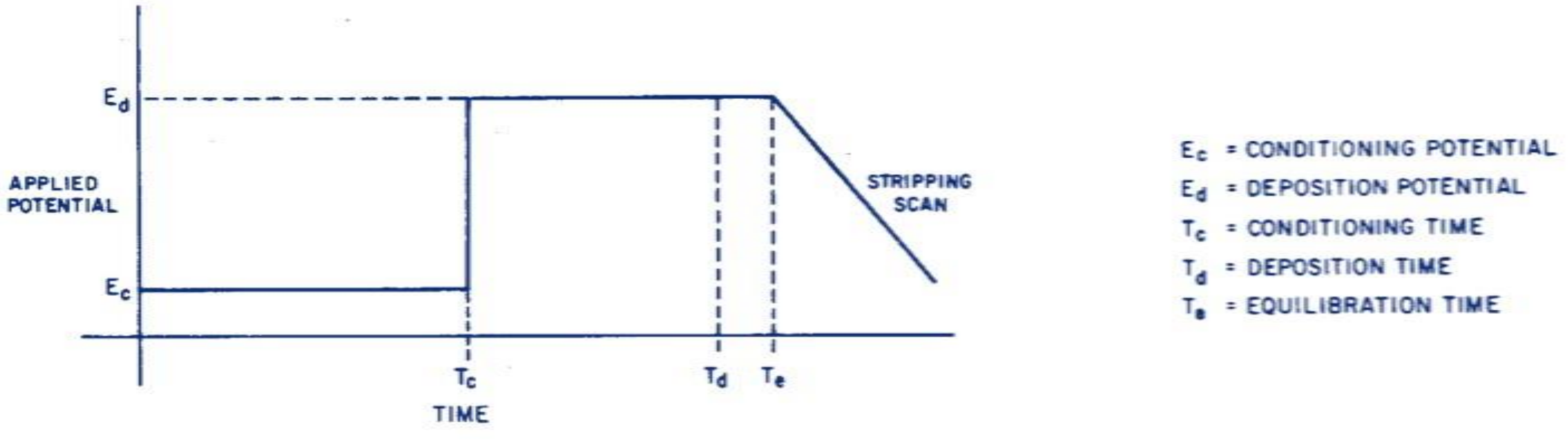


Figure 1 *Potential waveform for stripping voltammetry.*

Deposition potential

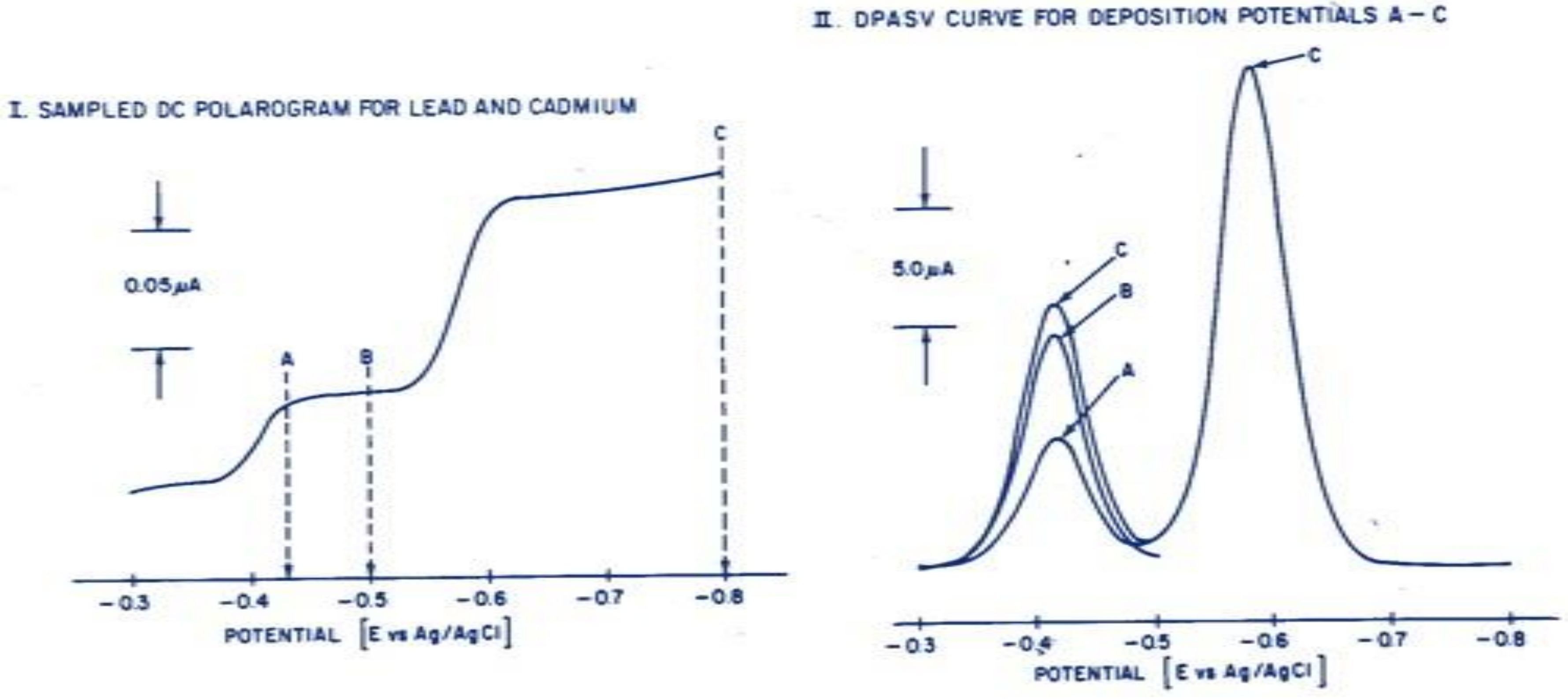


Figure 2 *Effect of deposition potential on stripping voltammogram.*

ASV

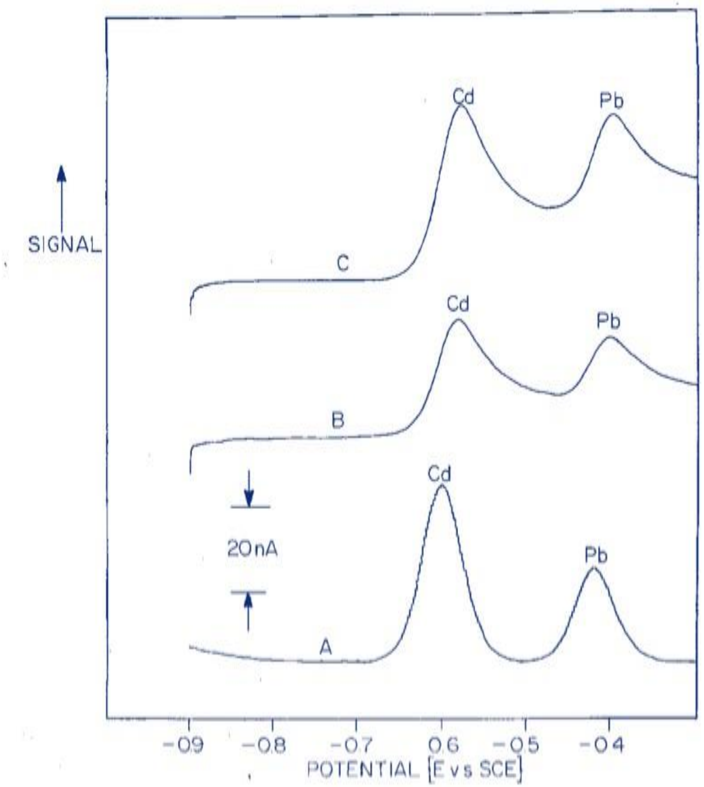


Figure 4 *Comparison of dc and differential pulse anodic stripping voltammetry at an HMDE—5 ppb Cd in 0.1 M acetate buffer (Pb impurity); deposition time: 20 sec; equilibration time: 30 sec. Curve A: Differential pulse—25-mv pulse height, 2-mv/sec scan rate. Curve B: Direct current—20-mv/sec scan rate. Curve C: Direct current—50-mv/sec scan rate.*

Table 1

Metals that can be determined by anodic stripping voltammetry

Antimony	Indium
Arsenic (Ref. 11)	Lead
Bismuth	Mercury[a] (Ref. 20)
Cadmium	Silver[a]
Copper	Thallium
Gallium	Tin
Germanium	Zinc
Gold[a]	

[a]Must be determined on solid electrode, such as glassy carbon or gold.

ASV or CSV

Deposition:	Applied potential more negative than $E_{1/2}$ of M^{n+} $M^{n+} + ne^- \rightarrow M(Hg)$
Stripping:	Scan in the positive direction, peak current is proportional to the concentration of M $M(Hg) \rightarrow M^{n+} + ne^-$

Figure 5 *Anodic stripping voltammetry.*

Deposition:	At a relatively positive potential where Hg^+ ions can be produced $Hg \rightarrow Hg^+ + e^-$ then $2\,Hg^+ + 2X^- \rightarrow Hg_2X_2$ (insoluble film)
Stripping:	Scan in the negative direction, peak current is proportional to the concentration of X^- $Hg_2X_2 + 2e^- \rightarrow 2Hg + 2X^-$

Figure 6 *Cathodic stripping voltammetry.*

Table 2

Species that can be determined by cathodic stripping voltammetry

Arsenic (Ref. 12)	Sulfide
Chloride	Mercaptans (RSH)
Bromide	Thiocyanate (SCN)
Iodide	Thio compounds
Selenium (IV)	

Adsorptive Stripping Voltammetry

- Use a chelating ligand that adsorbs to the WE.
- Can detect by redox process ***of metal or ligand.***

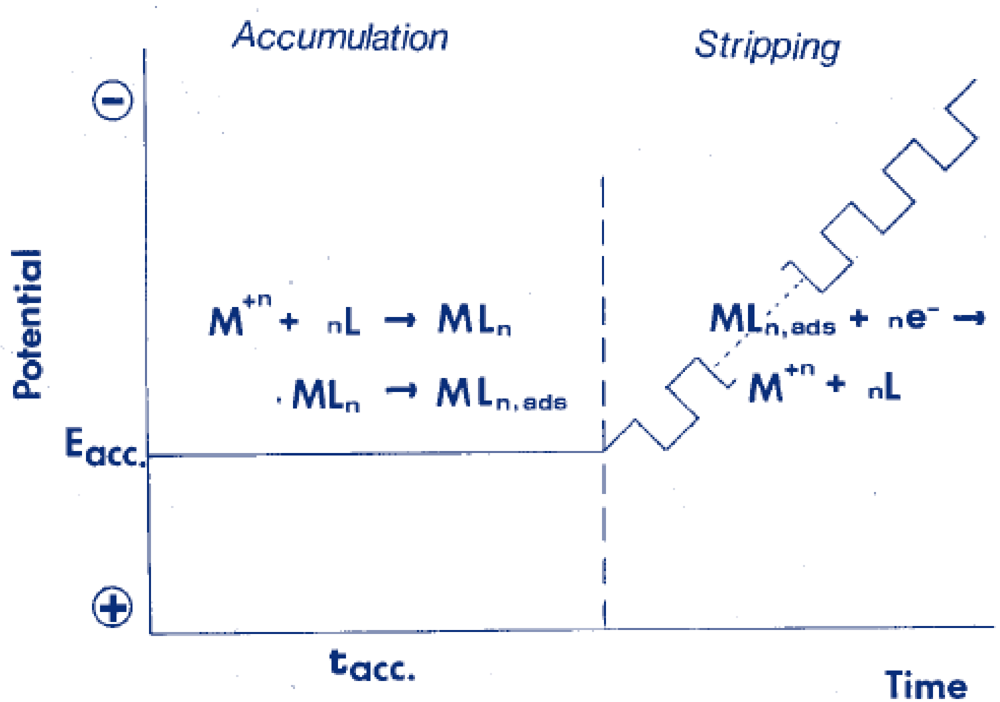


Figure 2 *Steps in the adsorptive stripping measurement of a metal ion (M^{+n}) based on the formation, accumulation, and reduction of its surface-active complex.*

Table 1

Adsorptive stripping measurements of organic compounds

Analyte	Working electrode	Electrolyte	Detection limit	Ref.
Heme	Hanging mercury drop	60% ethanol/H_2O	$1 \times 10^{-9} M$	9
Chlorpromazine and other phenothiazines	Impregnated graphite, Carbon paste	Phosphate buffer	$5 \times 10^{-9} M$	16,20,21
Adriamycin	Carbon paste	Acetate buffer	$1 \times 10^{-8} M$	18
Butylated hydroxyanisole	Carbon paste	Phosphate buffer	$2 \times 10^{-8} M$	31
Phenanthrenequinone	Carbon paste	0.1 M $HClO_4$	$1 \times 10^{-9} M$	32
Riboflavin	Static mercury drop	0.001 M NaOH	$2.5 \times 10^{-11} M$	2
Bilirubin	Static mercury drop	Sodium acetate	$5 \times 10^{-10} M$	25
Codeine, cocaine, and papaverine	Static mercury drop	NaOH	$1 \times 10^{-8} M$	10
Dopamine	Platinum	Ethanol	$5 \times 10^{-8} M$	26,27
Diazepam and nitrazepam	Static mercury drop	Acetate buffer	$5 \times 10^{-9} M$	19
Cimetidine	Static mercury drop	0.1 M HCl	$4 \times 10^{-9} M$	11
Digoxin and digitoxin	Static mercury drop	0.005 M NaOH	$2 \times 10^{-10} M$	23
Progesterone and testosterone	Static mercury drop	0.005 M NaOH	$2 \times 10^{-10} M$	22
Nitro group—containing pesticides	Static mercury drop	Britton-Robinson buffer	$5 \times 10^{-10} M$	29
Thiourea	Static mercury drop	0.1 M $NaClO_4$	$2 \times 10^{-11} M$	3
Trichlorobiphenyl	Static mercury drop	0.2 M KF	$4 \times 10^{-8} M$	30
Monensin	Static mercury drop	0.2 M KF	$1 \times 10^{-7} M$	24
Poly(ethylene glycols)	Static mercury drop	0.5 M Na_2SO_4	$5 \times 10^{-8} M$	5
DNA	Static mercury drop	0.5 M Mcllavine buffer	$1 \times 10^{-5} M$	28

Table 2

Adsorptive stripping of metal ions via the adsorption of metal complexes

Analyte	Ligand	Working electrode	Detection limit	Ref.
Uranium	Pyrocatechol	Static mercury drop	$2 \times 10^{-9} M$	37
Nickel	Dimethylglyoxime	Static mercury drop	$4 \times 10^{-10} M$	33,34
	Bipyridine	Static mercury drop	$2 \times 10^{-8} M$	35
Lanthanum, cerium, and praseodymium	Cresolphthalexon	Static mercury drop	$2 \times 10^{-10} M$	40
Cobalt	Dimethylgloxime	Static mercury drop	$1 \times 10^{-10} M$	36
Vanadium	Catechol	Static mercury drop	$1 \times 10^{-10} M$	38
Copper	Catechol	Static mercury drop	$1 \times 10^{-11} M$	39
Iron	Catechol, 1-amine-2-naph-tol-4-sulfonic acid	Static mercury drop	$6 \times 10^{-10} M$	41
Aluminum	Solochrome Violet RS	Static mercury drop	$5 \times 10^{-9} M$	52

Multi-Element

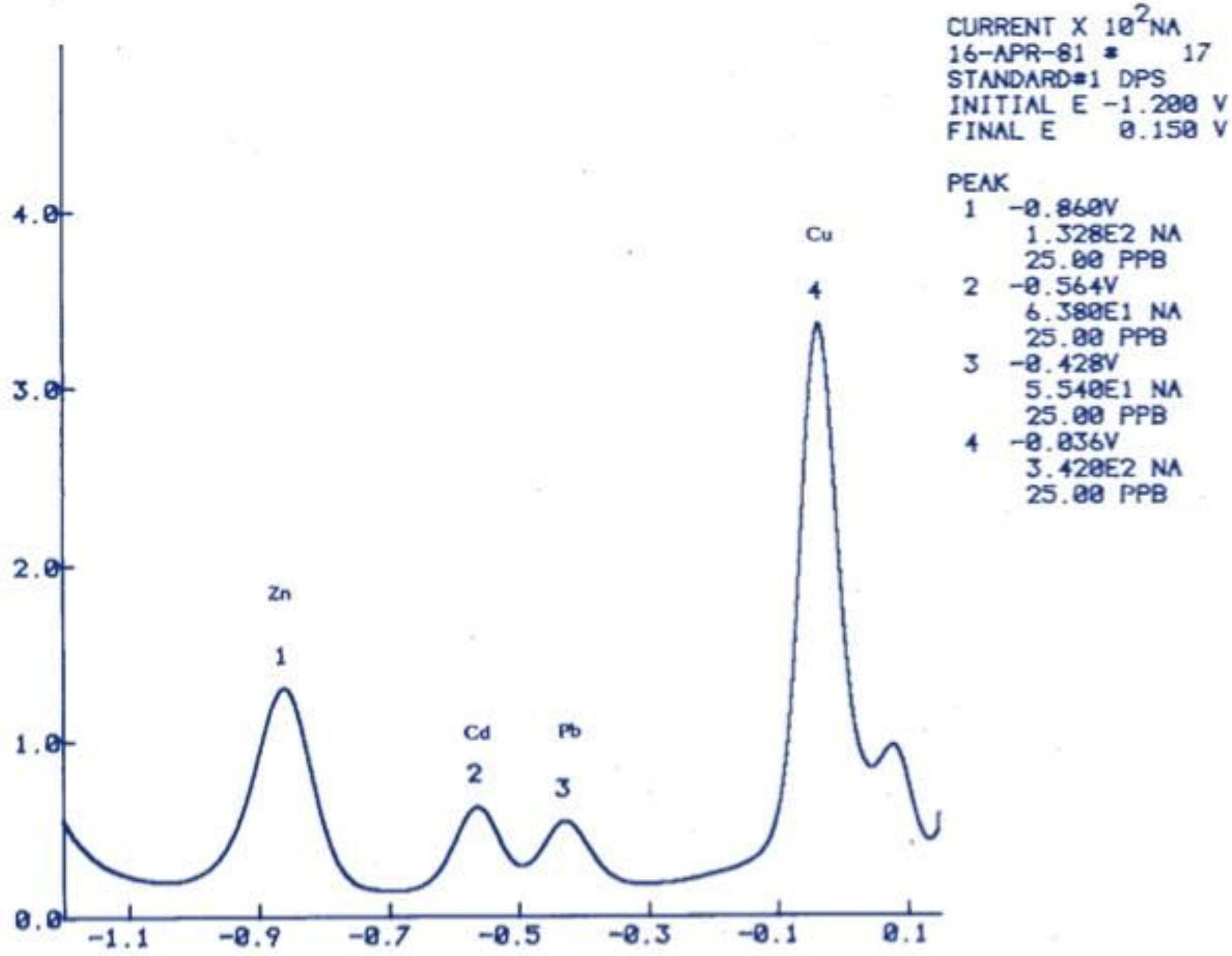


Figure 7 *Differential-pulse anodic stripping voltammogram of 25 ppb zinc, cadmium, lead, and copper.*

Standard Addition

$$C_x = \frac{i_1 v C_s}{i_2 v + (i_2 - i_1) V} \qquad (1)$$

where

i_1	= sample peak height
i_2	= standard addition peak height
v	= volume of standard solution added
V	= volume of original sample
C_s	= concentration of standard solution
C_x	= concentration of original sample

If the volume of added standard v is small compared to the volume of the original sample V, Eq. (1) simplifies to:

$$C_x = \frac{i_1 v C_s}{(i_2 - i_1) V} \qquad (2)$$

Use of a 10-mL sample and a 10- to 100-µL micropipet for the standard addition allows the valid use of Eq. (2).