POLAROGRAPHY/ VOLTAMMETRY

- *Introduction*
- *Instrumentation, common techniques*
- *Direct Current (DC) polarography*
- *Mercury electrodes (DME, SMDE, HMDE)*
- *Polarographic currents*
- *Tast polarography*
- *Ilkovič equation*
- *Half-wave potential, limited diffusion current*
- *Logarithmic analysis*
- *Current maxima*
- *Brdička reaction*
- *Analytical applications*

POLAROGRAPHY/ VOLTAMMETRY

- *Linear Sweep Voltammetry (LSV)*
- *Cyclic Voltammetry (CV)*
- *Normal Pulse Polarography (NPP) or Voltammetry (NPV)*
- *Differential Pulse Polarography (DPP) or Voltammetry (DPV)*
- *Square Wave (SW) Polarography or Voltammetry*
- *Alternating Current (AC) Polarography or Voltammetry*
- *Elimination Polarography (EP)*
- *Elimination Voltammetry with Linear Scan (EVLS)*

Introduction

Jaroslav Heyrovský

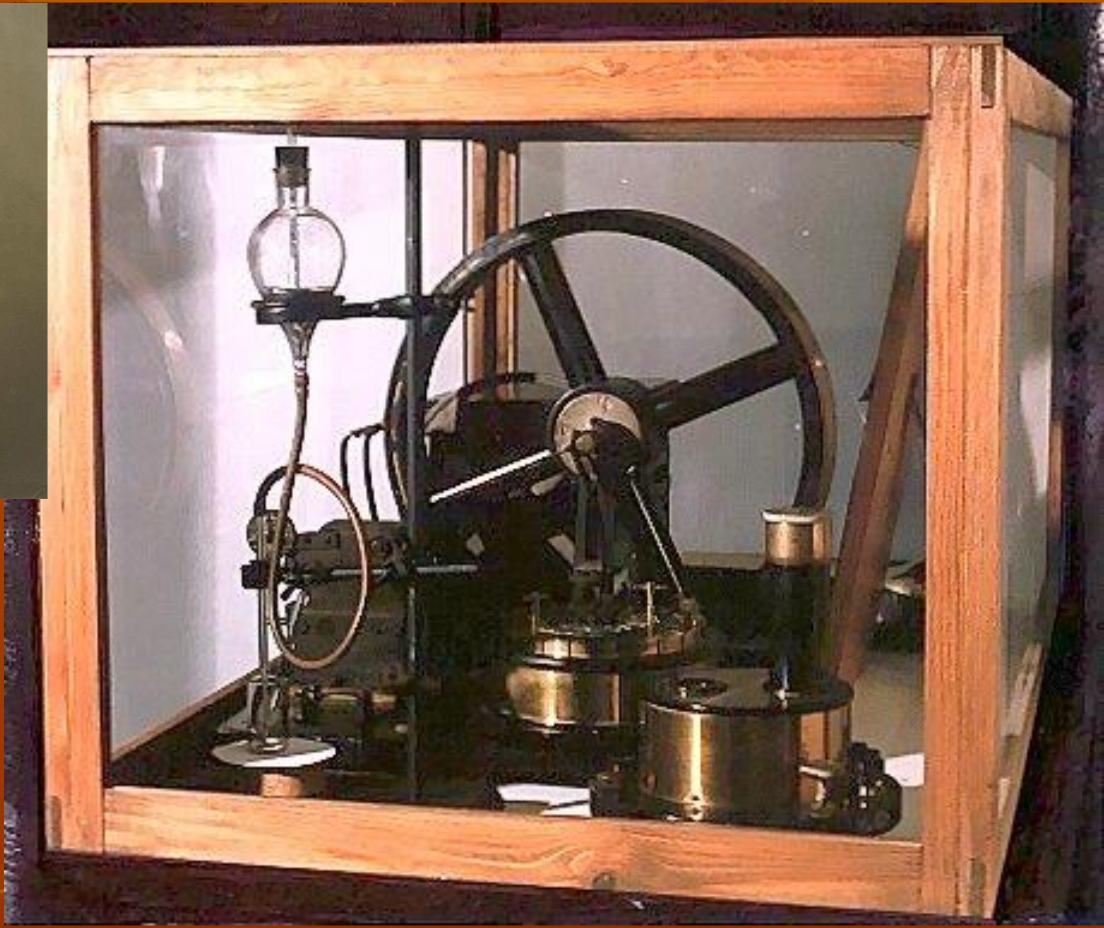
** Dec. 20, 1890, Prague, Bohemia, Austro-Hungarian Empire [now Czech Rep.]*
† March 27, 1967, Prague, Czechoslovakia

J. Heyrovský

Jaroslav Heyrovský was an inventor of the polarographic method, **father of electroanalytical chemistry**, recipient of the Nobel Prize (1959). His contribution to electroanalytical chemistry can not be overestimated. All voltammetry methods used now in electroanalytical chemistry originate from polarography developed by him.

Introduction

Picture of the first polarograph designed by J. Heyrovský and M. Shikata (1924). This instrument is saved in the museum of J. Heyrovský Institute of Physical Chemistry.



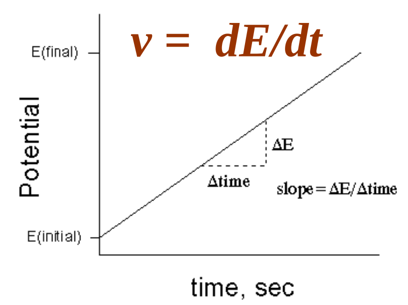
Introduction

- *Polarography is an voltammetric measurement whose response is determined by combined* ***diffusion/convection mass transport.*** *Polarography is a specific type of measurement that falls into the general category of linear-sweep voltammetry where the electrode potential is altered in a linear fashion from* ***the initial potential E_i*** *to* ***the final potential E_λ****. As a* ***linear sweep method*** *controlled by convection/diffusion mass transport, the current vs. potential response of a polarographic experiment has the typical* ***sigmoidal shape.*** *What makes polarography different from other linear sweep voltammetry measurements is that polarography makes use of the dropping mercury electrode (****DME****).*
- *A measure of* ***current as a function of potential*** *when the working electrode is a dropping mercury (or other liquid conductor) electrode and unstirred solutions are used.*

$$I = f(E) \qquad\qquad E = E_i \pm v\, t$$

E – electrode potential, ***v*** – scan rate, ***t*** - time, ***I*** - current

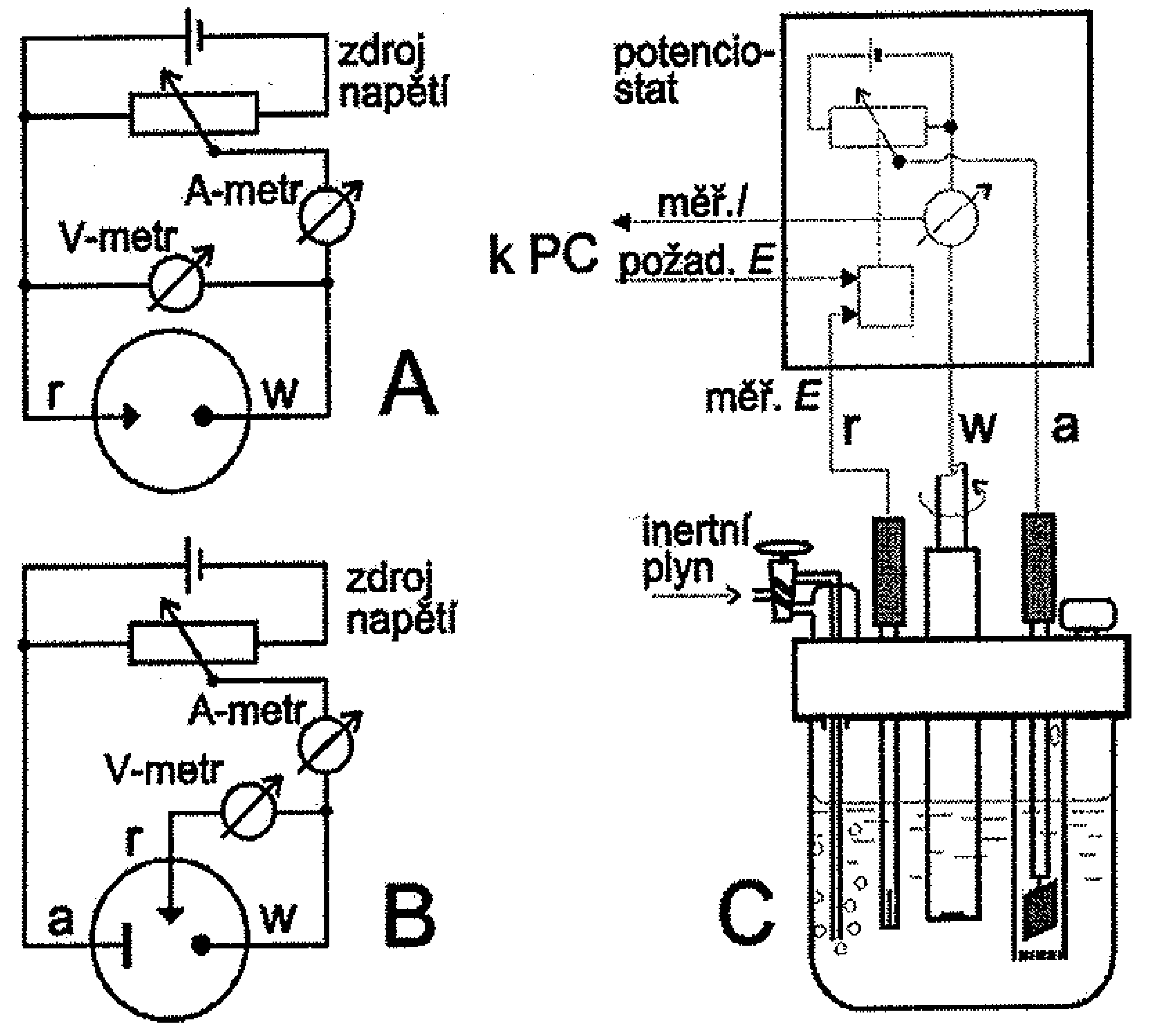
also LSV - Linear Sweep Voltammetry or *CV – Cyclic Voltammetry*



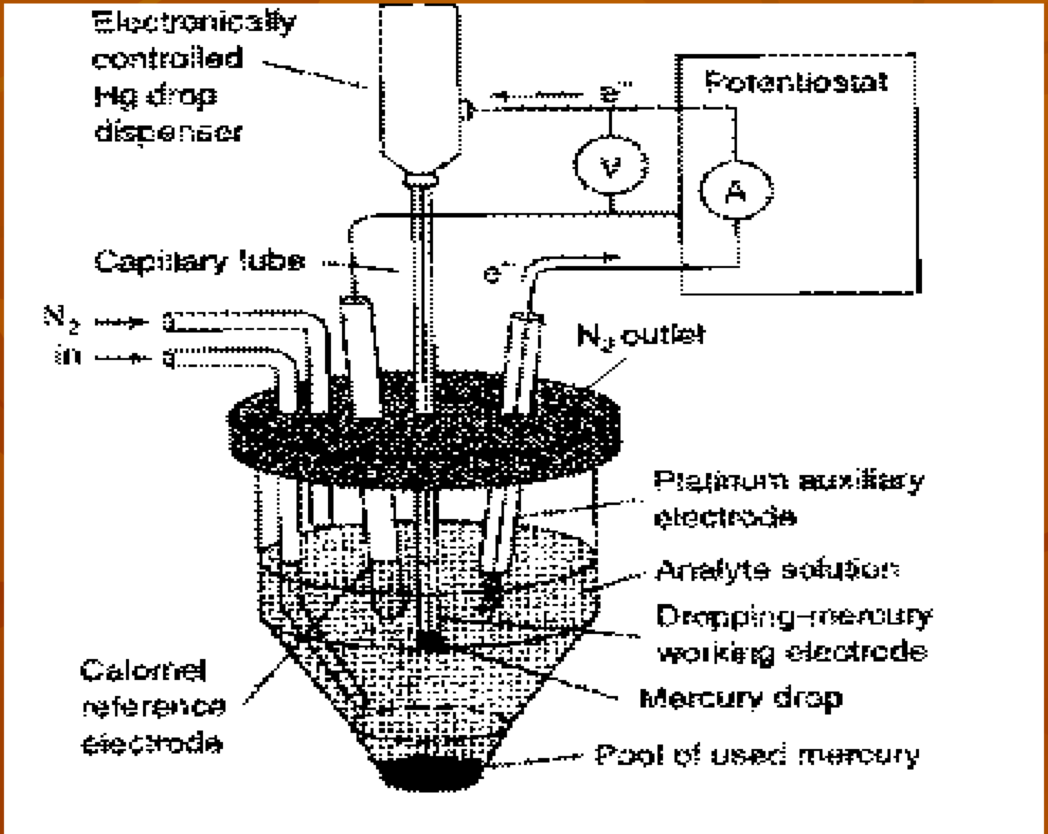
Instrumentation, common techniques

Two-electrode set

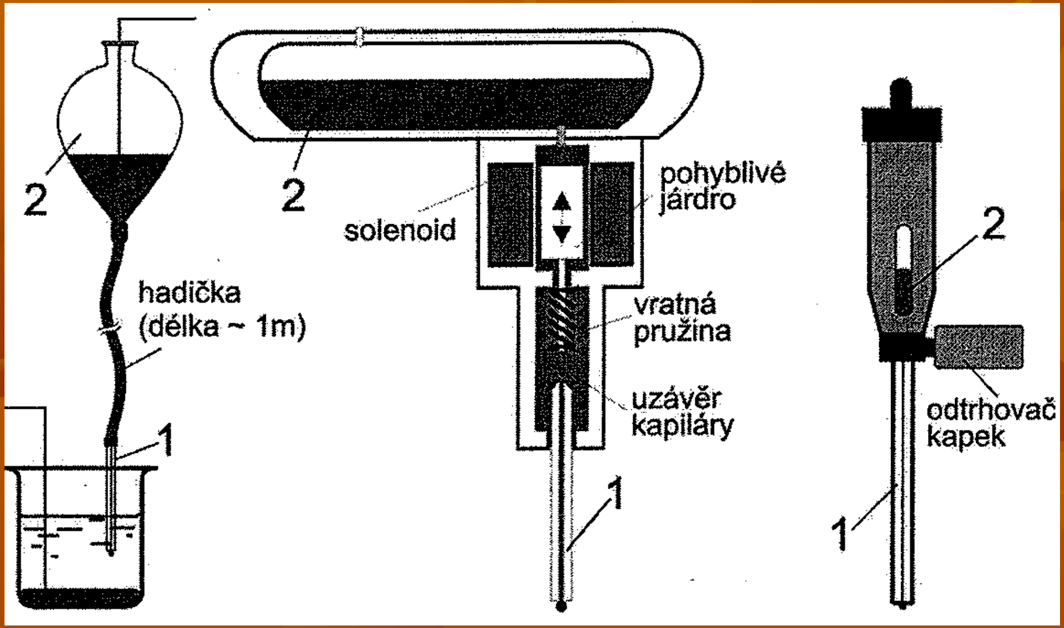
Three-electrode set



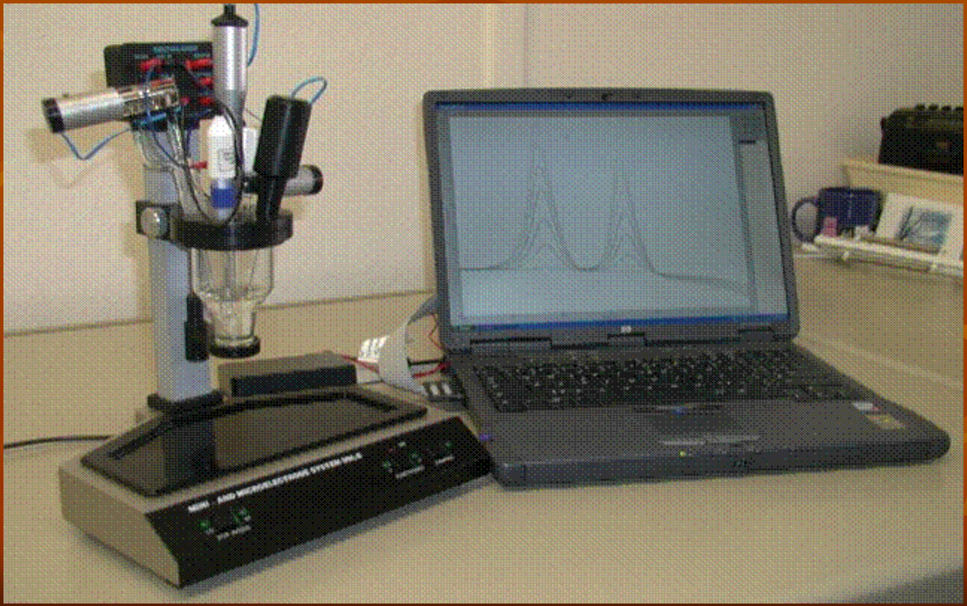
Instrumentation, common techniques



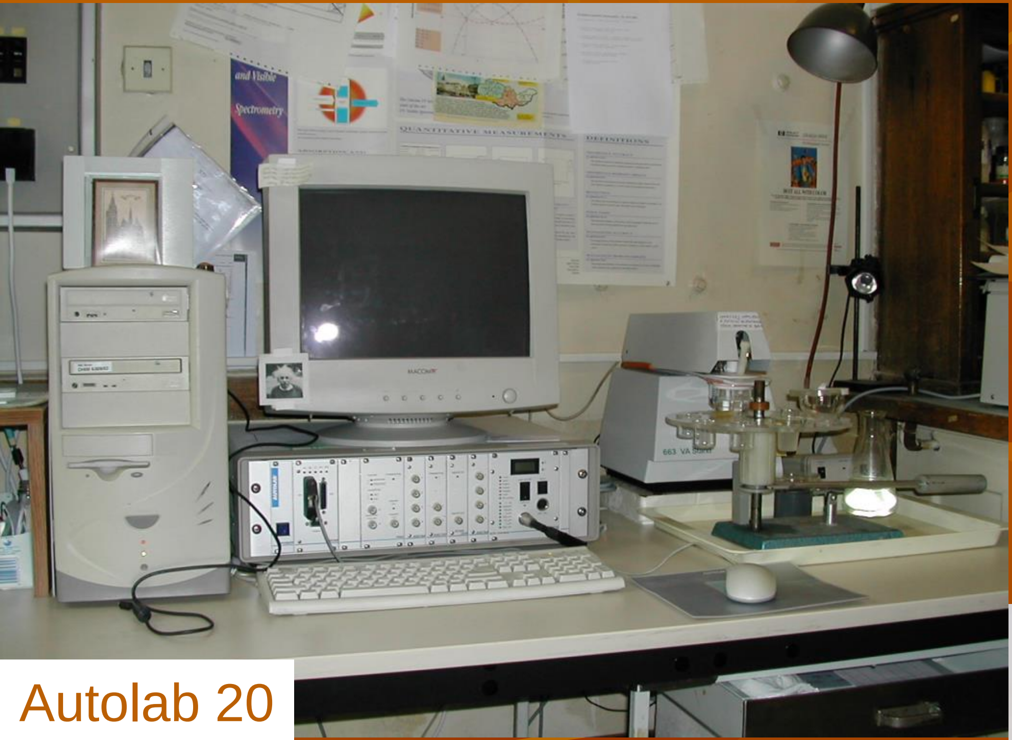
Instrumentation, common techniques



EcoTribo Polarograph
Polaro Sensors - Eco Trend
Prague, Czech Republic



Instrumentation, common techniques



Autolab 20

Electrochemical analyzer AUTOLAB

Autolab
Ecochemie
Utrecht
The Netherlands

VA-Stand 663
Metrohm
Zurich
Switzerland

Autolab 30

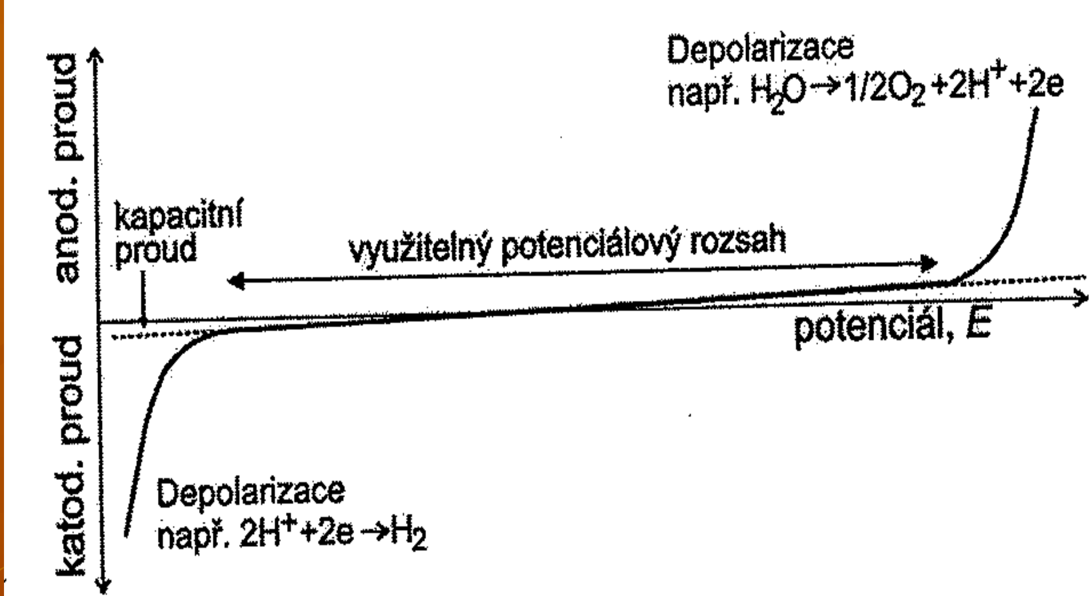
Mercury electrodes (DME, SMDE, HMDE)

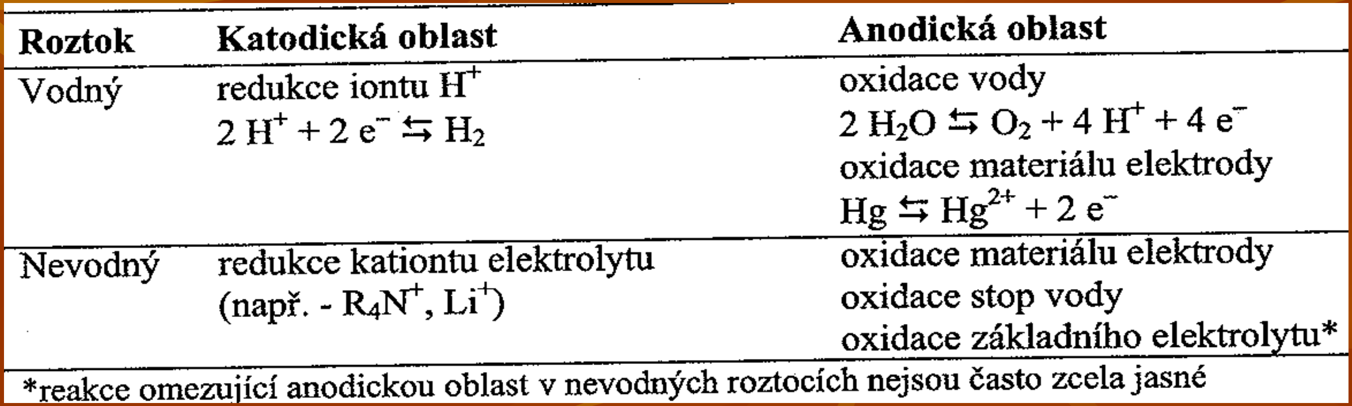
Dropping Mercury Electrode - DME
Static Mercury Drop Electrode - SMDE
Hanging Mercury Drop Electrode - HMDE

Despite its toxicity, the metallic mercury has been used as an electrode material for decades and is the original material for polarography.

- its liquid state at ambient temperature, renewable surface
- high purity material availability,
- high conductivity,
- inertness chemically at low potentials (because of its high overvoltage potential for hydrogen evolution)
- formation of amalgams with numerous metals
- microelectrodes (Hg drop diameter smaller than a millimeter).

Instrumentation, common techniques



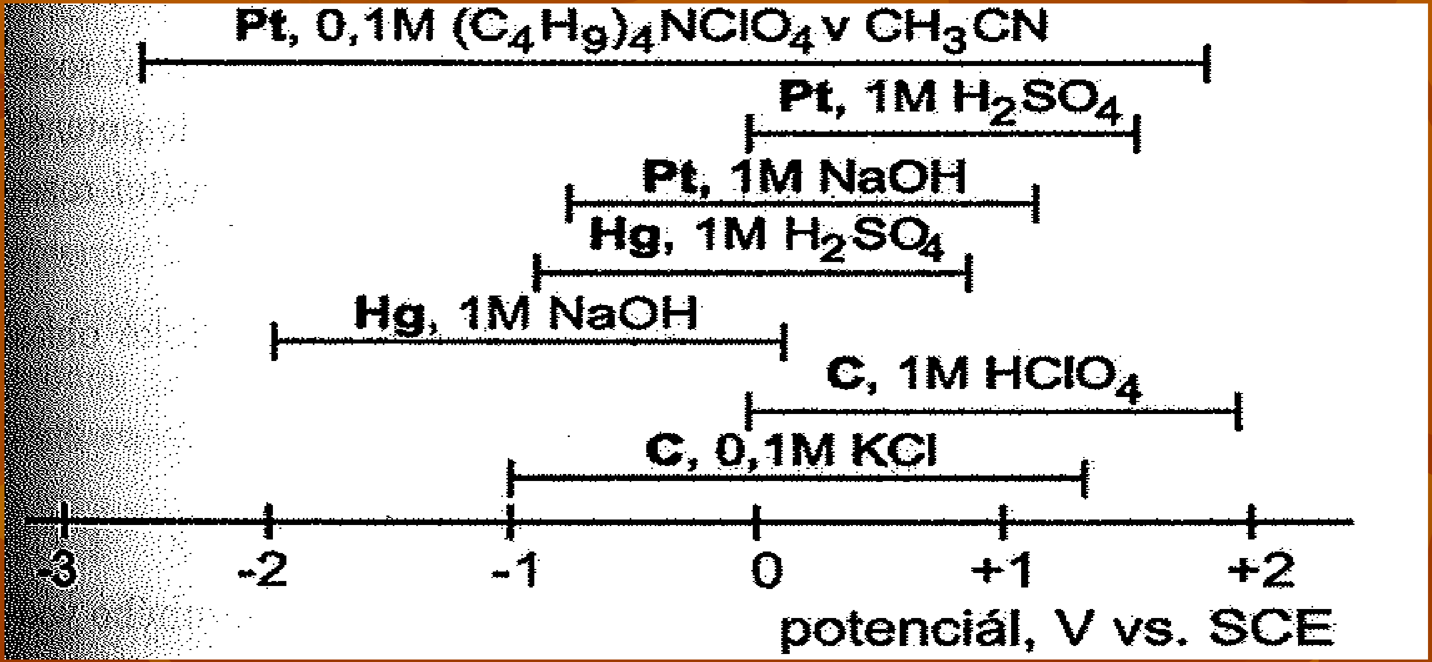


Roztok	Katodická oblast	Anodická oblast
Vodný	redukce iontu H^+ $2\,H^+ + 2\,e^- \leftrightharpoons H_2$	oxidace vody $2\,H_2O \leftrightharpoons O_2 + 4\,H^+ + 4\,e^-$ oxidace materiálu elektrody $Hg \leftrightharpoons Hg^{2+} + 2\,e^-$
Nevodný	redukce kationtu elektrolytu (např. - R_4N^+, Li^+)	oxidace materiálu elektrody oxidace stop vody oxidace základního elektrolytu*

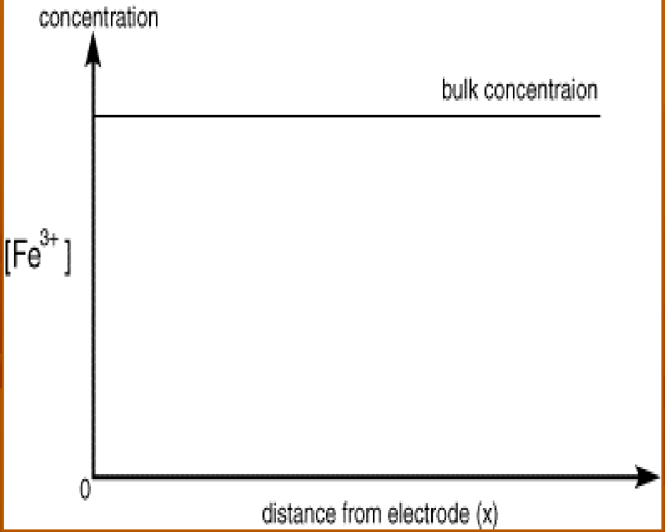
*reakce omezující anodickou oblast v nevodných roztocích nejsou často zcela jasné

Instrumentation, common techniques

Potential windows for different electrodes

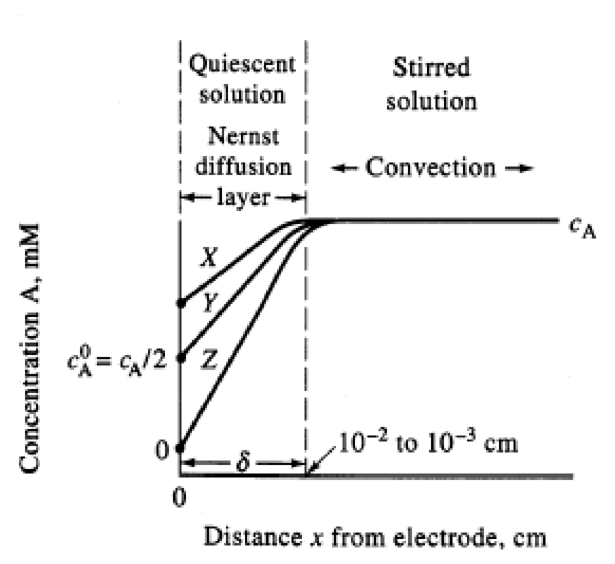


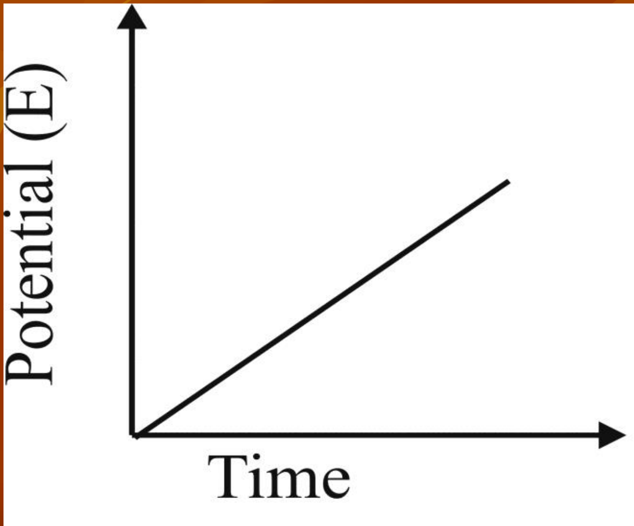
Direct Current (DC) polarography

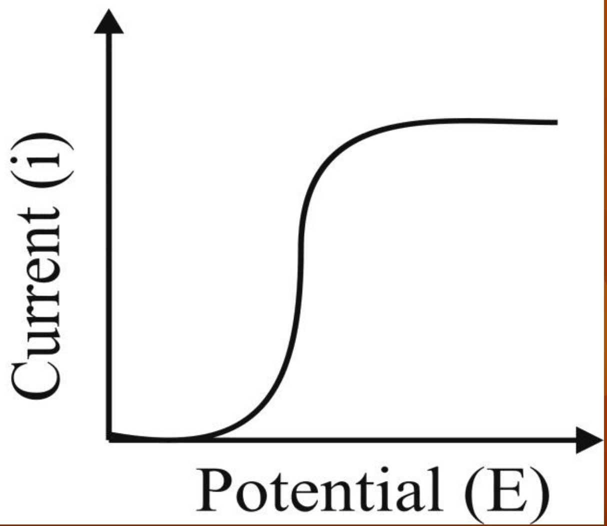


Apply

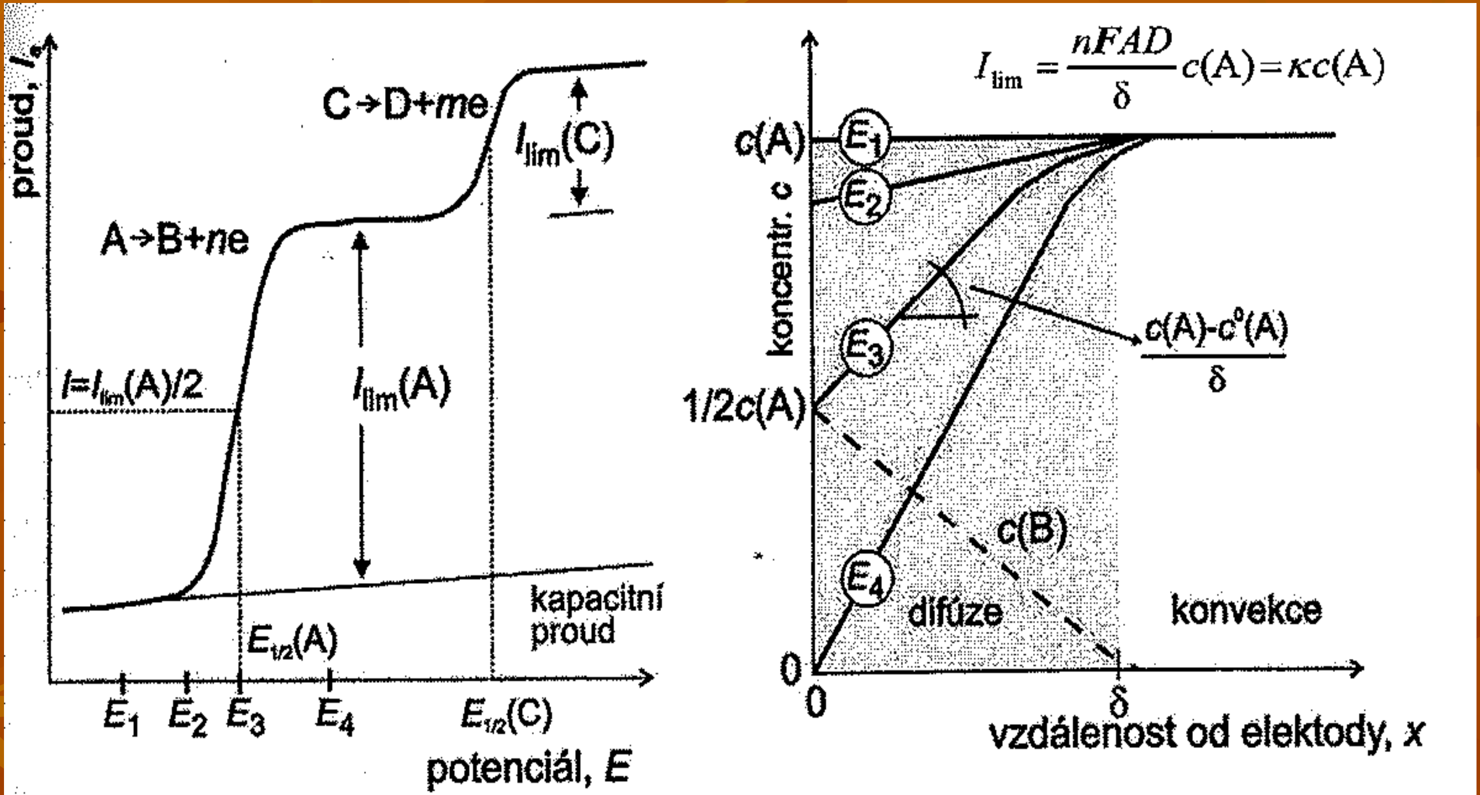
Potential
E << E^o




Apply Linear Potential with Time

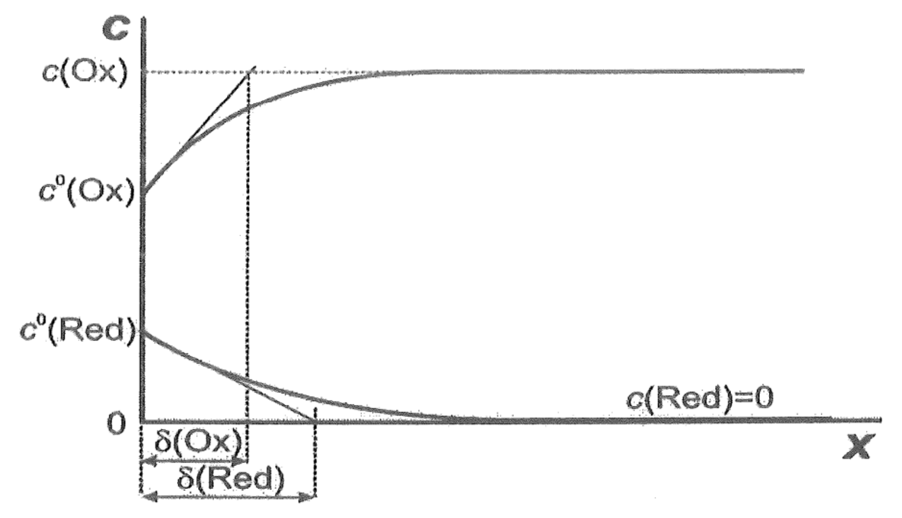

Observed Current Changes with Applied Potential

Direct Current (DC) polarography



Stacionary transport

$$j_{\mathrm{d}} = -D\frac{\partial c}{\partial x}$$



$$\frac{\partial c(\mathrm{Ox})}{\partial x} = -\frac{c(\mathrm{Ox}) - c^0(\mathrm{Ox})}{\delta(\mathrm{Ox})} \qquad \frac{\partial c(\mathrm{Red})}{\partial x} = -\frac{c^0(\mathrm{Red})}{\delta(\mathrm{Red})}$$

$$i = \frac{\mathrm{d}Q}{\mathrm{d}t} = jnF$$

$\mathrm{Ox} + n\mathrm{e} = \mathrm{Red}$

$$i = -nFD(\mathrm{Ox})\frac{c(\mathrm{Ox}) - c^0(\mathrm{Ox})}{\delta(\mathrm{Ox})} = nFD(\mathrm{Red})\frac{c^0(\mathrm{Red})}{\delta(\mathrm{Red})}$$

$$\kappa_{\mathrm{Ox}} = \frac{nFD(\mathrm{Ox})}{\delta(\mathrm{Ox})} \quad \text{a} \quad \kappa_{\mathrm{Red}} = \frac{nFD(\mathrm{Red})}{\delta(\mathrm{Red})}$$

κ - diffusion current constants

Stacionary transport

κ - diffusion current constants

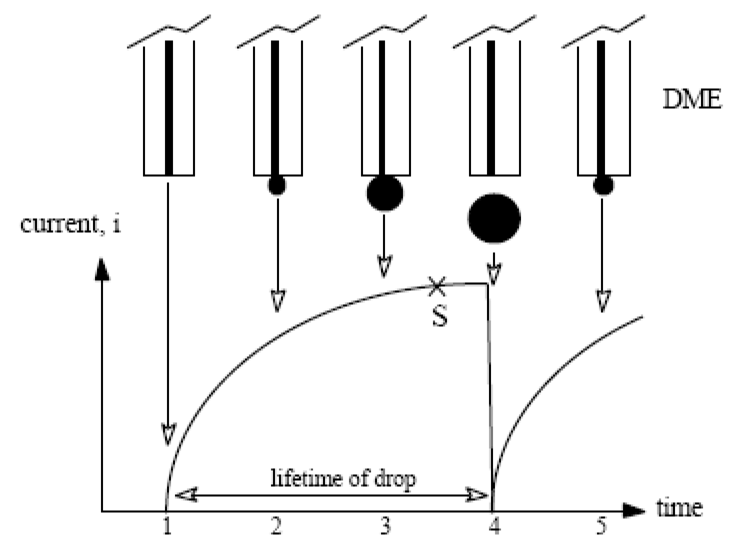
$$i = -\kappa(\mathrm{Ox})\left(c(\mathrm{Ox}) - c^{0}(\mathrm{Ox})\right) = \kappa(\mathrm{Red})c^{0}(\mathrm{Red})$$

$$i_{\mathrm{lim}} = -\kappa(\mathrm{Ox})\, c(\mathrm{Ox})$$

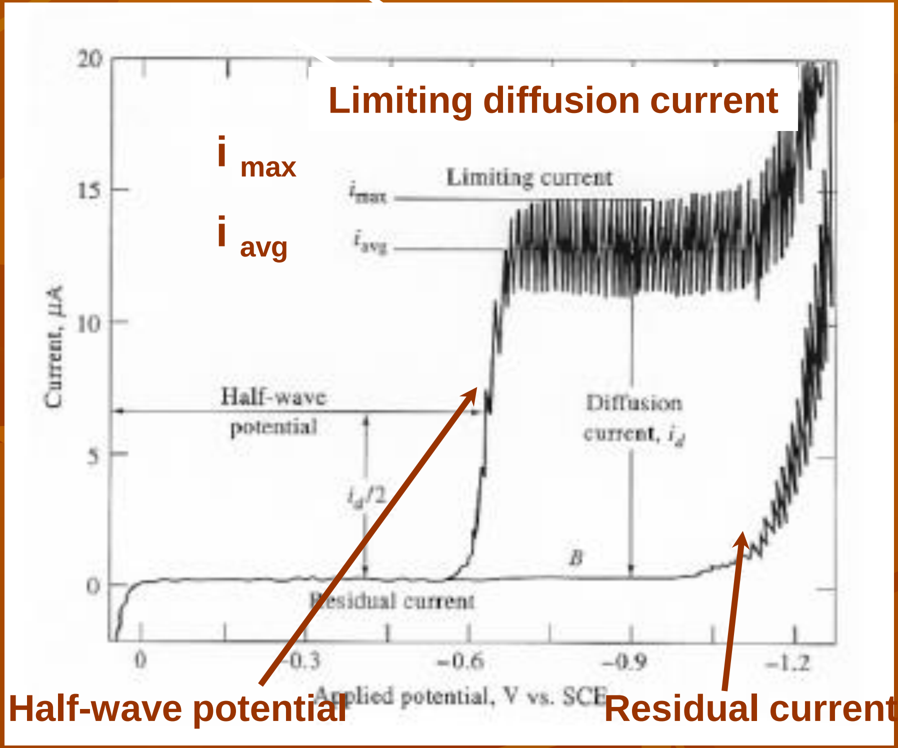
$$-\left(\frac{i_{\mathrm{lim}} - i}{i}\right)\frac{\kappa(\mathrm{Red})}{\kappa(\mathrm{Ox})} = -\left\{\exp\left[\frac{nF}{RT}\left(E - E_{\mathrm{c}}^{\mathrm{o}}\right)\right] + \frac{\kappa(\mathrm{Red})}{nFk'}\exp\left[\frac{\alpha nF}{RT}\left(E - E_{\mathrm{c}}^{\mathrm{o}}\right)\right]\right\}$$

$$E = E_{\mathrm{c}}^{\mathrm{o}} + \frac{RT}{nF}\ln\frac{\kappa(\mathrm{Red})}{\kappa(\mathrm{Ox})} + \frac{RT}{nF}\ln\frac{i_{\mathrm{lim}} - i}{i}$$

Half-wave potential, limited diffusion current



$Mn^{+} + ne^{-} + Hg = M(Hg)$ amalgam



Limiting diffusion current

i_{max}

i_{avg}

Half-wave potential

Residual current

a) ½ wave potential ($E_{½}$) characteristic of M^{n+} (E)
b) height of either average current maxima (i_{avg})
   or top current max (i_{max}) is ~ analyte concentration
c) size of i_{max} is governed by
   rate of growth of DME > drop time (**t**, sec)
   rate of mercury flow (**m**, mg/s)
   diffusion coefficient of analyte (**D**, cm^2/s)
   number of electrons in process (***n***)
   analyte concentration (**c**, mol/ml)

Ilkovič equation

$$(i_d)_{max} = 0.706\, n\, D^{1/2}\, m^{2/3}\, t^{1/6}\, c$$

$$(i_d)_{avg} = 0.607\, n\, D^{1/2}\, m^{2/3}\, t^{1/6}\, c$$

Ilkovič equation

A plot of the current vs. potential in a polarography experiment shows the current oscillations corresponding to the drops of Hg falling from the capillary. If one connected the maximum current of each drop, a sigmoidal shape would result. The limiting current (the plateau on the sigmoid), called the diffusion current because diffusion is the principal contribution to the flux of electroactive material at this point of the Hg drop life, is related to analyte concentration by the

Ilkovic equation

$$\boxed{I_{d,} = 0.708\, n\, D^{1/2}\, m^{2/3}\, t^{1/6}\, c}$$

- Where ***D*** is the diffusion coefficient of the analyte in the medium (***cm²/s***), ***n*** is the number of electrons transferred per mole of analyte, ***m*** is the mass flow rate of Hg through the capillary (***mg/sec***), and ***t*** is the drop lifetime in s, and ***c*** is analyte concentration in ***mol/cm³***.

Direct Current (DC) polarography

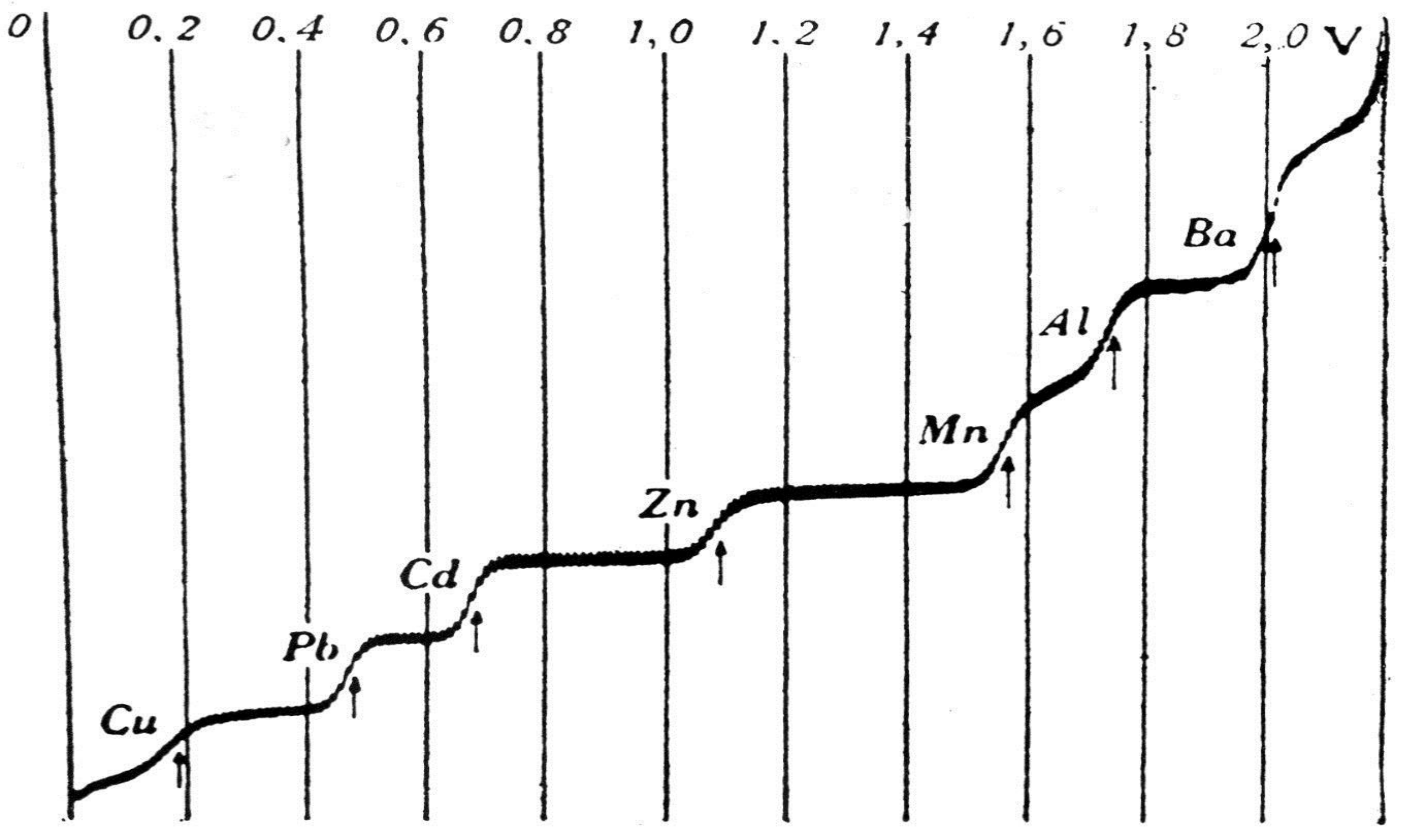
Ilkovič equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + \frac{2x}{3t}\frac{\partial c}{\partial t}$$

$$I = 0{,}732\, nFD^{1/2} m^{2/3} t^{1/6} (c - c^0)$$

$$\bar{I} = 0{,}627\, nFD^{1/2} m^{2/3} t_1^{1/6} (c - c^0)$$

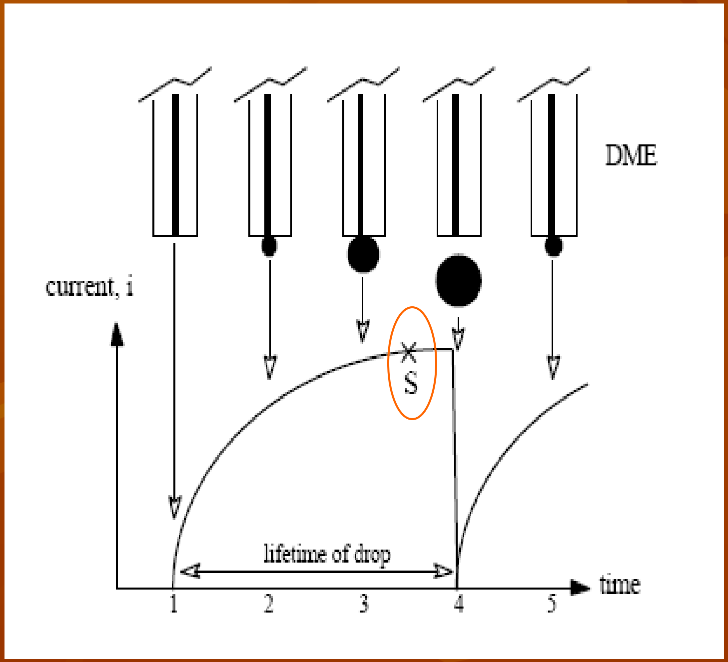
Typical polarographic curves - polarographic spectrum



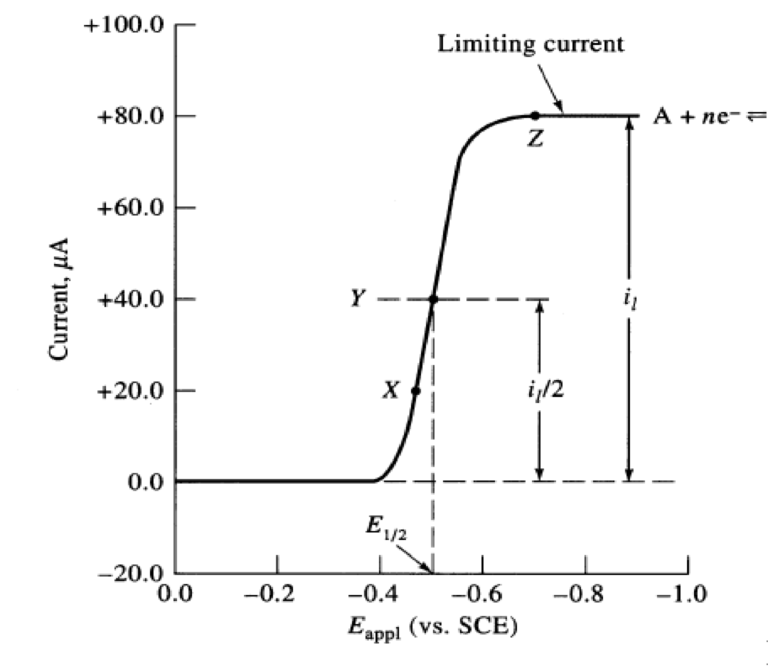
Tast polarography

- One problem with data detection DC polarography is that current varies over lifetime of drop, giving variation on curve
- One simple way to avoid this is to sample only current at particular time of drop life.

Near end of drop = current sampled polarography



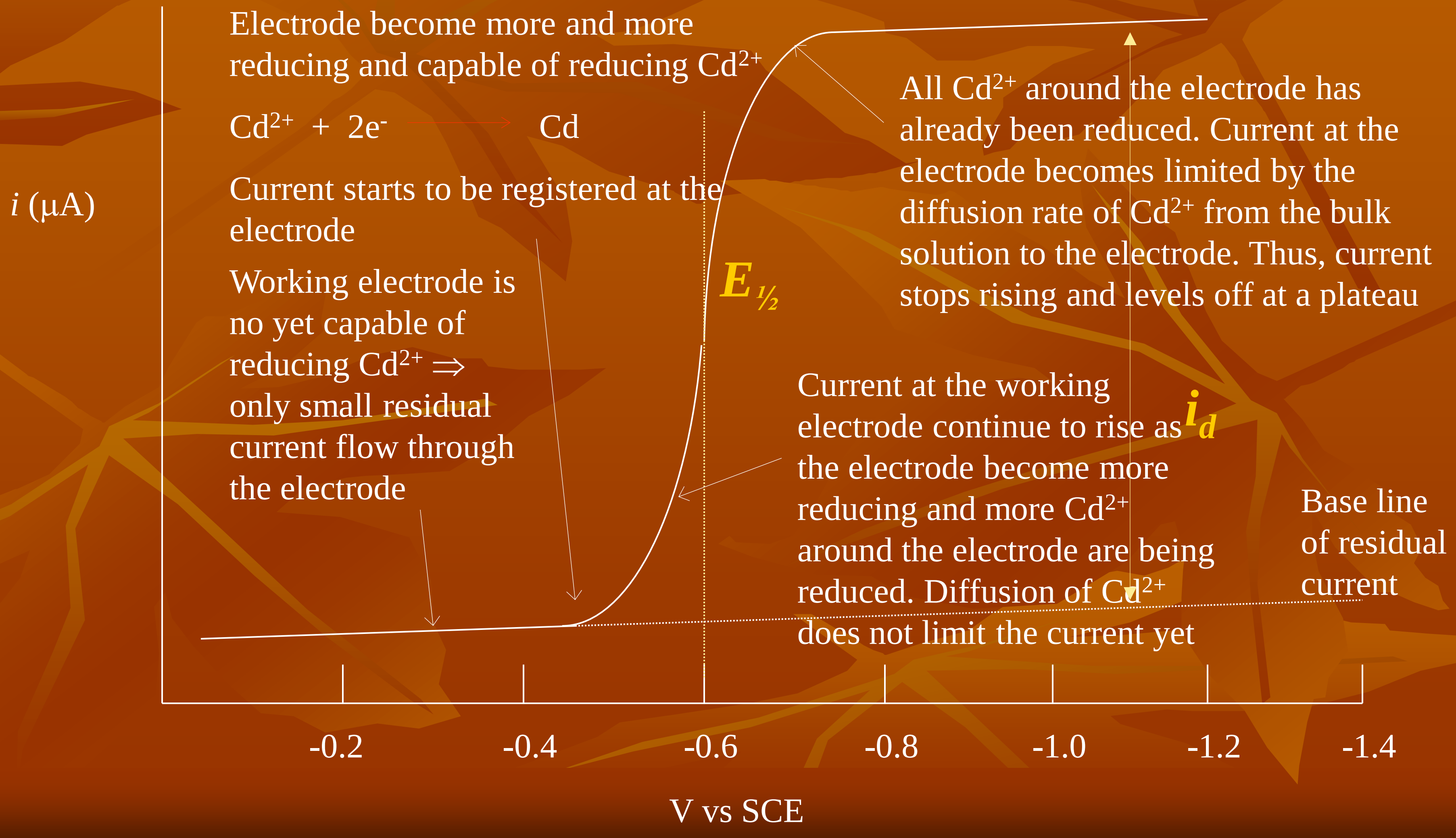
Sample i at same time interval



Easier to determine i_{avg}

Potential applied on the working electrode is usually swept over (i.e. scan) a pre-defined range of applied potential

0.001 M Cd^{2+} in 0.1 M KNO_3 supporting electrolyte



Electrode become more and more reducing and capable of reducing Cd^{2+}

$Cd^{2+} + 2e^- \rightarrow Cd$

Current starts to be registered at the electrode

Working electrode is no yet capable of reducing Cd^{2+} ⇒ only small residual current flow through the electrode

All Cd^{2+} around the electrode has already been reduced. Current at the electrode becomes limited by the diffusion rate of Cd^{2+} from the bulk solution to the electrode. Thus, current stops rising and levels off at a plateau

Current at the working electrode continue to rise as the electrode become more reducing and more Cd^{2+} around the electrode are being reduced. Diffusion of Cd^{2+} does not limit the current yet

Base line of residual current

Logarithmic analysis

Plot log $(I_d - I)/I$ against potential (E) from your polarogram data

Polarographic Wave Equation

$$E = E_{1/2} + 0.0591/n\,(\log[(I_d - I)/I])$$

when the value of the logarithmic term becomes zero, the above equation becomes $E = E_{1/2}$

n the number of electrons involved in reduction

$$\log[(I_d - I)/I] = n(E - E_{1/2})/\ 0.0591$$

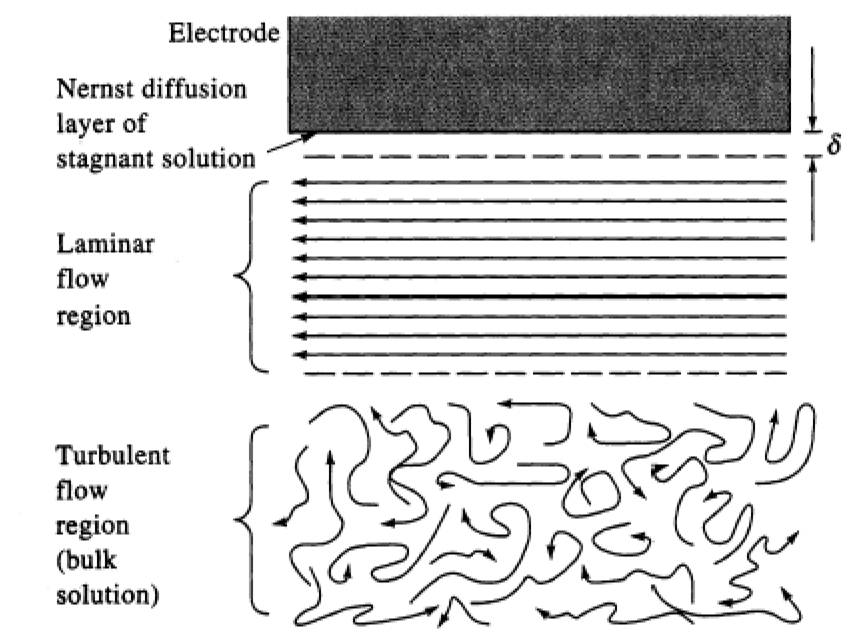
Select about four or five readings on each side of the half-wave potential from the graph of current versus voltage in order to calculate the values of the logarithmic term in the above equation. Indicate on the graph:

1) value of the **slope**,
2) calculated value of **n**,
3) half-wave potential $\mathbf{E_{1/2}}$
4) reversibility.

$$\frac{n}{0.058}(E_{1/2} - E) = \log\frac{i}{i_d - i}$$

Polarographic currents

Current is just measure of rate at which species can be brought to electrode surface



Two methods

Stirred - hydrodynamic voltammetry

Unstirred - polarography (DME)

Three transport mechanisms:

(i) *migration* – movement of ions through solution by electrostatic attraction to charged electrode

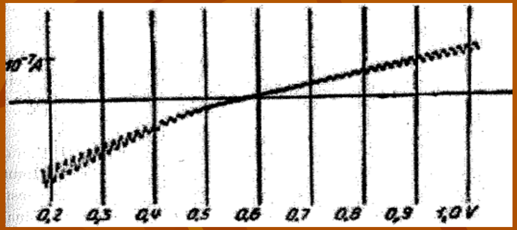
(ii) *convection* – mechanical motion of the solution as a result of stirring or flow

(iii) *diffusion* – motion of a species caused by a concentration gradient

Polarographic currents

Diffusion current: $f(c)$, $f(h^{1/2})$, $f(t^{1/6})$

Capacity, charging current: $f(h)$, $f(E)$, $f(t^{-1/3})$, SE, ECM

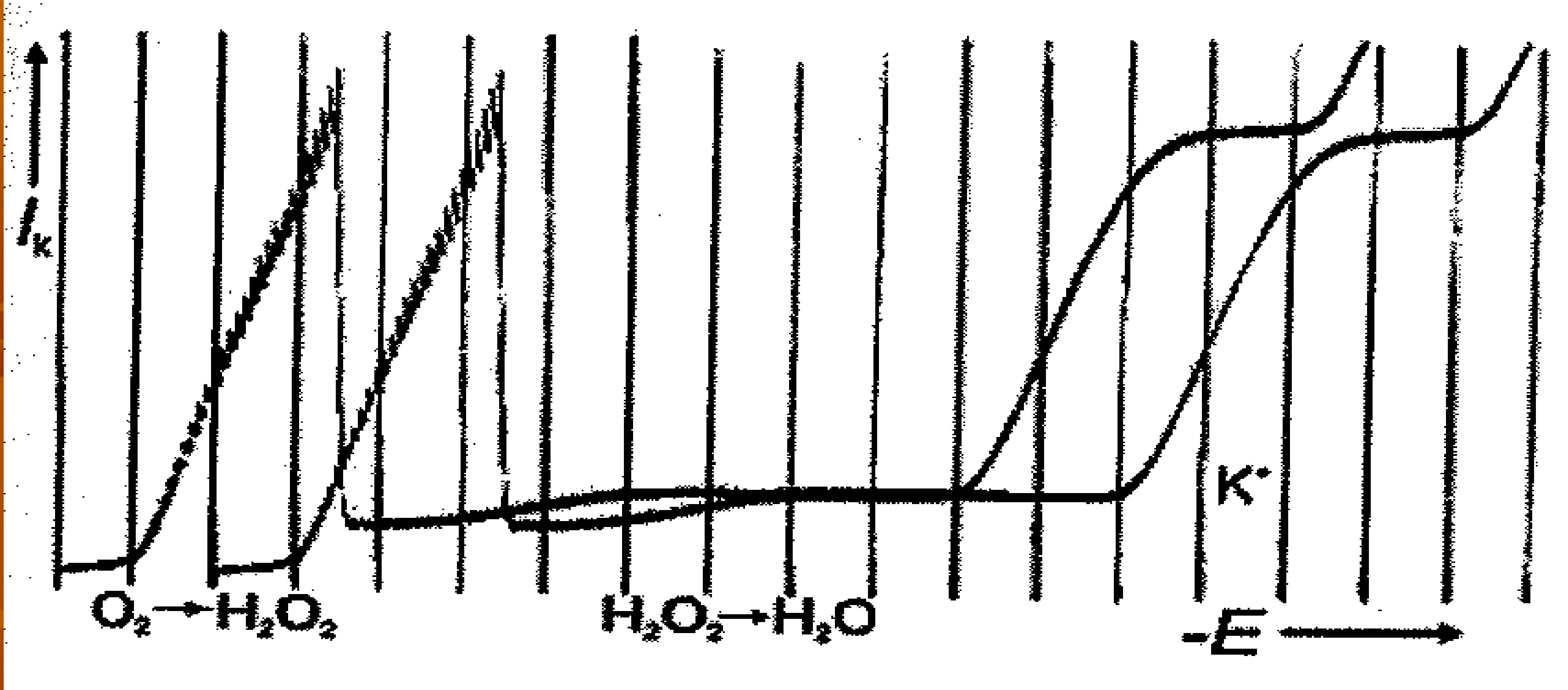


Kinetic or catalytic current : ~~$f(h)$~~, $f(c)$ (I. order) **,**
$f(t^{2/3})$, $f(E)$, SE (pH)**, $f(T)$,**
preceeding, proceednig,following reactions
catalytic currents (Brdička reation)

Adsorption: *adsorption isotherms…………….$I = f(c)$*

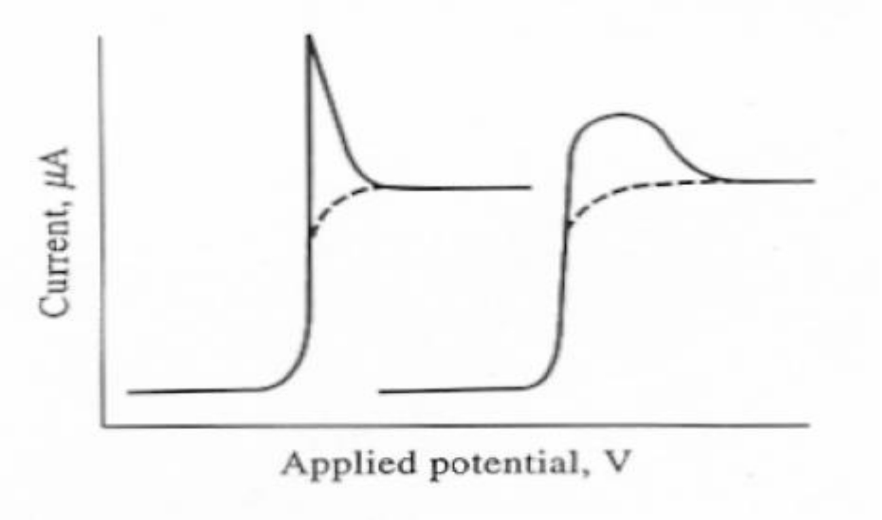
(c……*concentration of analyt*) (*h* ……*height of resorvoir*) (*t*……*time*) (*T*……*temperature*)

Current maxima

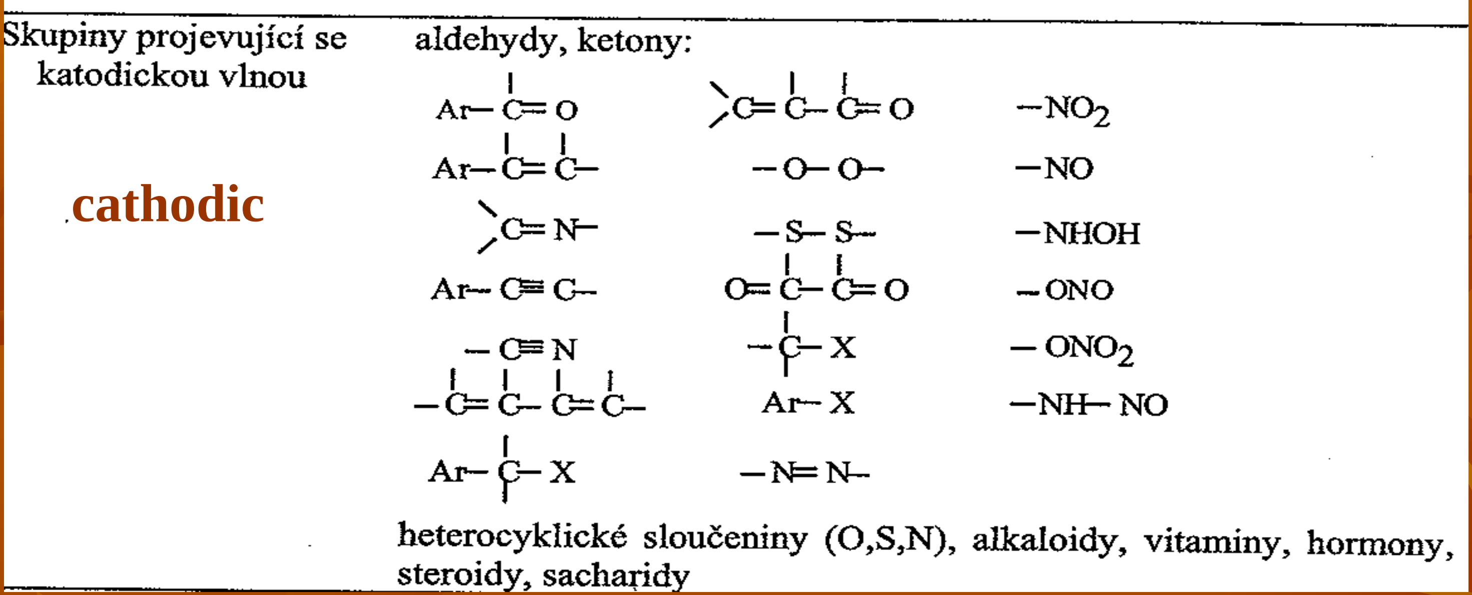


$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2$

$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O$



Analytical applications



Skupiny projevující se katodickou vlnou

cathodic

aldehydy, ketony:

$Ar-C=O$

$Ar-C=C-$

$>C=N-$

$Ar-C\equiv C-$

$-C\equiv N$

$-C=C-C=C-$

$Ar-C-X$

$>C=C-C=O$

$-O-O-$

$-S-S-$

$O=C-C=O$

$-C-X$

$Ar-X$

$-N=N-$

$-NO_2$

$-NO$

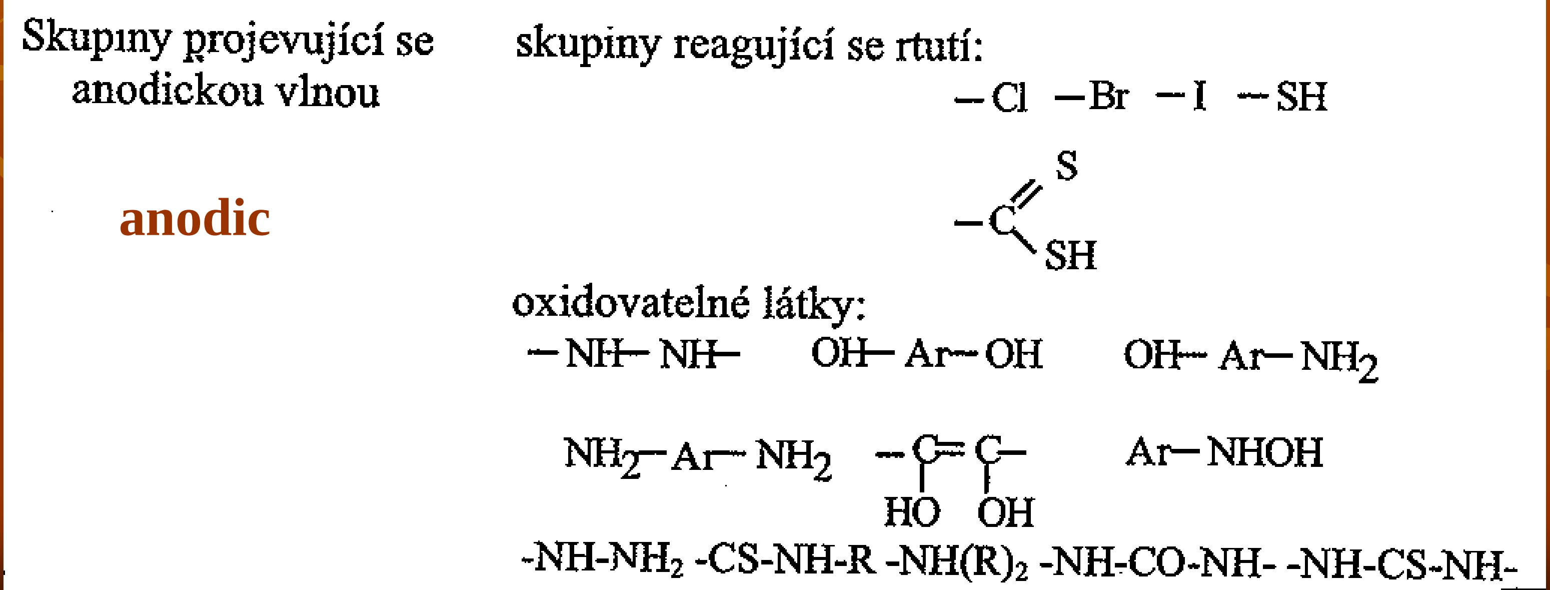
$-NHOH$

$-ONO$

$-ONO_2$

$-NH-NO$

heterocyklické sloučeniny (O,S,N), alkaloidy, vitaminy, hormony, steroidy, sacharidy



Skupiny projevující se anodickou vlnou

anodic

skupiny reagující se rtutí:

$-Cl$ $-Br$ $-I$ $-SH$

$-C(=S)SH$

oxidovatelné látky:

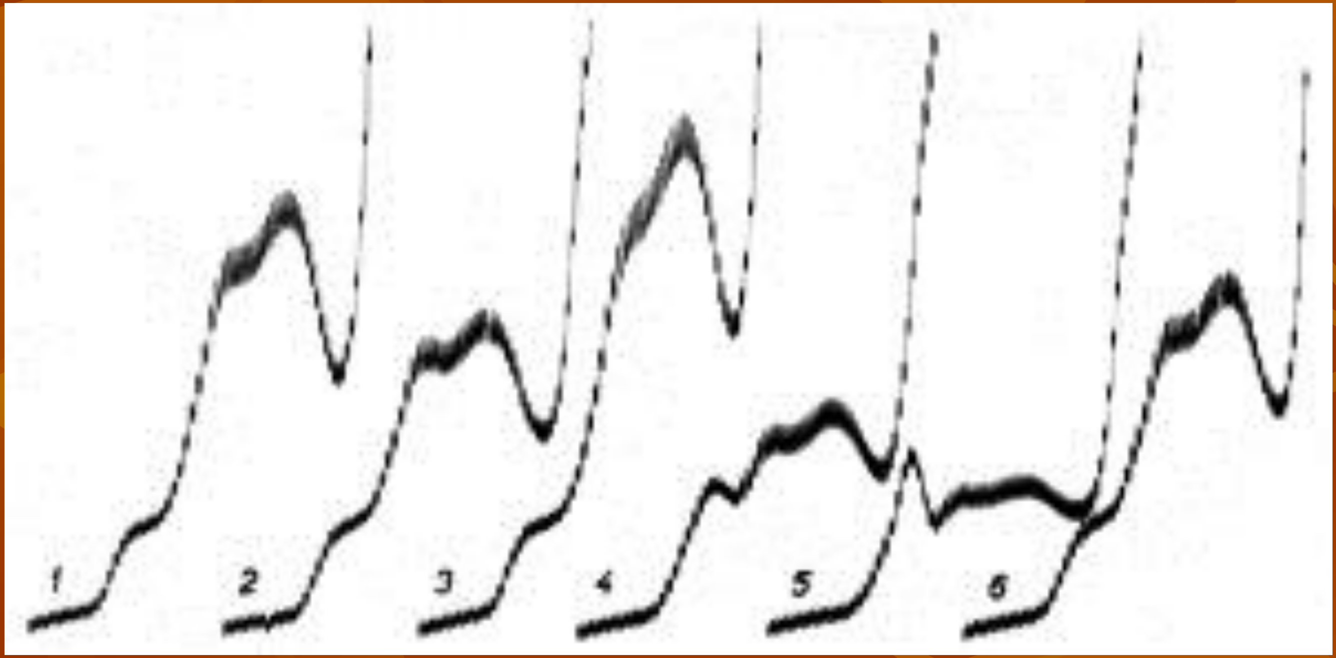
$-NH-NH-$ $OH-Ar-OH$ $OH-Ar-NH_2$

$NH_2-Ar-NH_2$ $-C(HO)=C(OH)-$ $Ar-NHOH$

$-NH-NH_2$ $-CS-NH-R$ $-NH(R)_2$ $-NH-CO-NH-$ $-NH-CS-NH-$

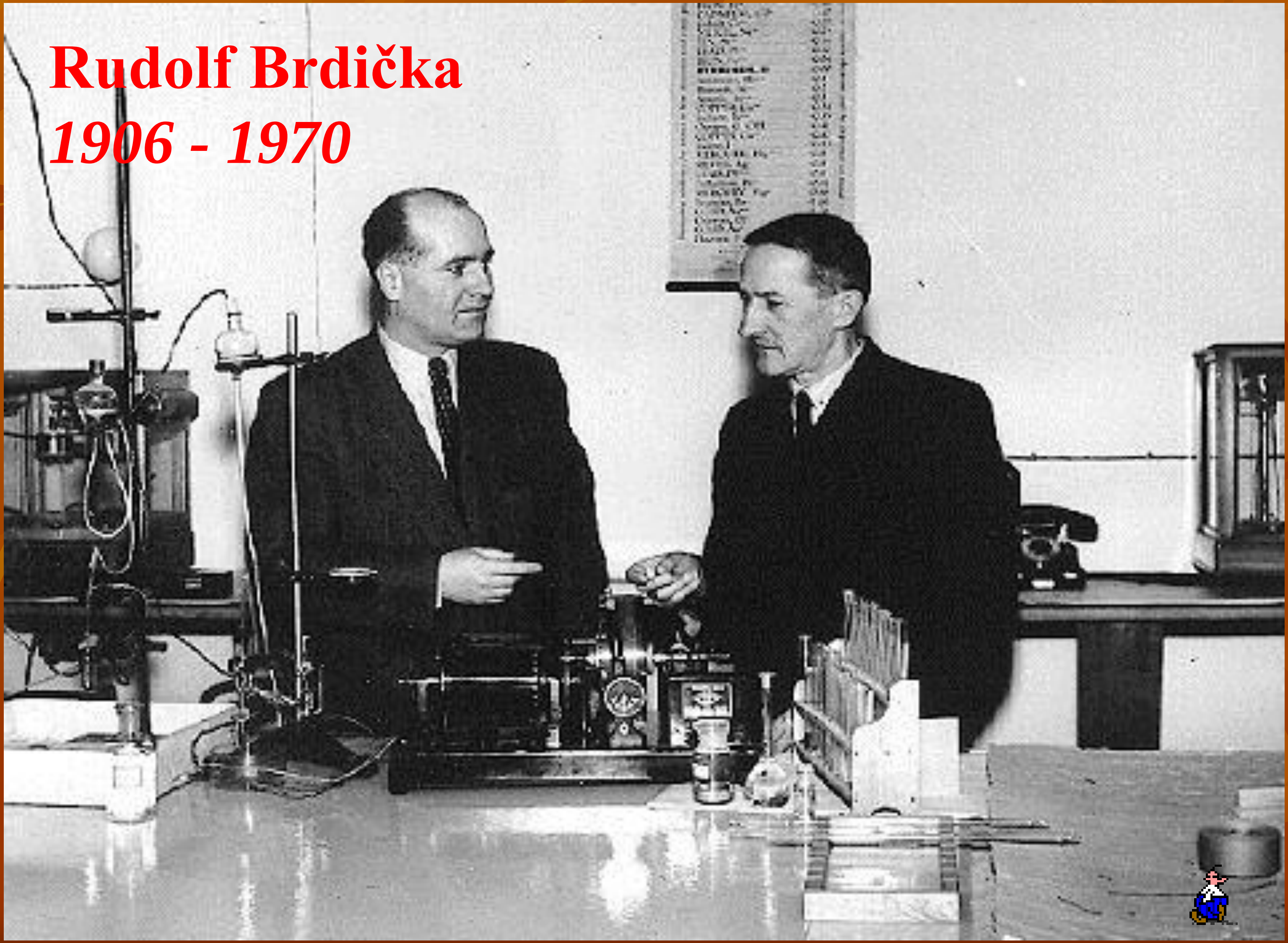
Brdička reaction

Heyrovsks's second assistant, Dr. Rudolf Brdicka, discovered a sensitive catalytic hydrogen-evolution reaction of proteins: in buffer solutions of pH about 9, containing ions of cobalt, proteins yield a prominent catalytic "double-wave"; this polarographic reaction was used in many countries over several decades as a diagnostic tool in treatment of cancer



Polarographic "Brdicka reaction" of blood sera of different patients with following diagnoses: 1) status febrilis 2) tumor hepatis susp 3) ca. ventriculi susp 4) normal serum 5) cirrhosis hepatic 6) atherosclerosis.

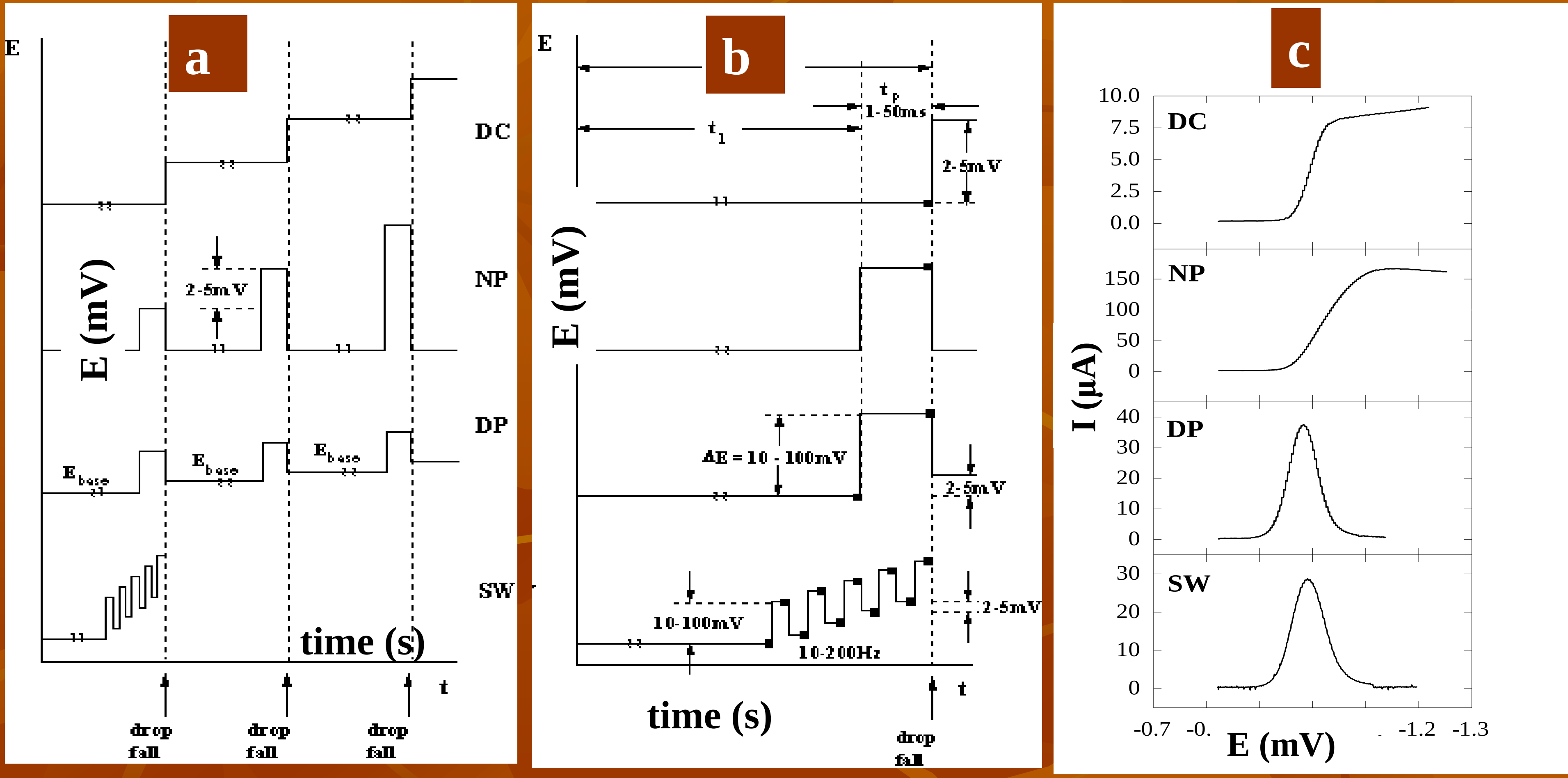
Heyrovsky and Brdicka



Rudolf Brdička

1906 - 1970

Types of voltammetric technics



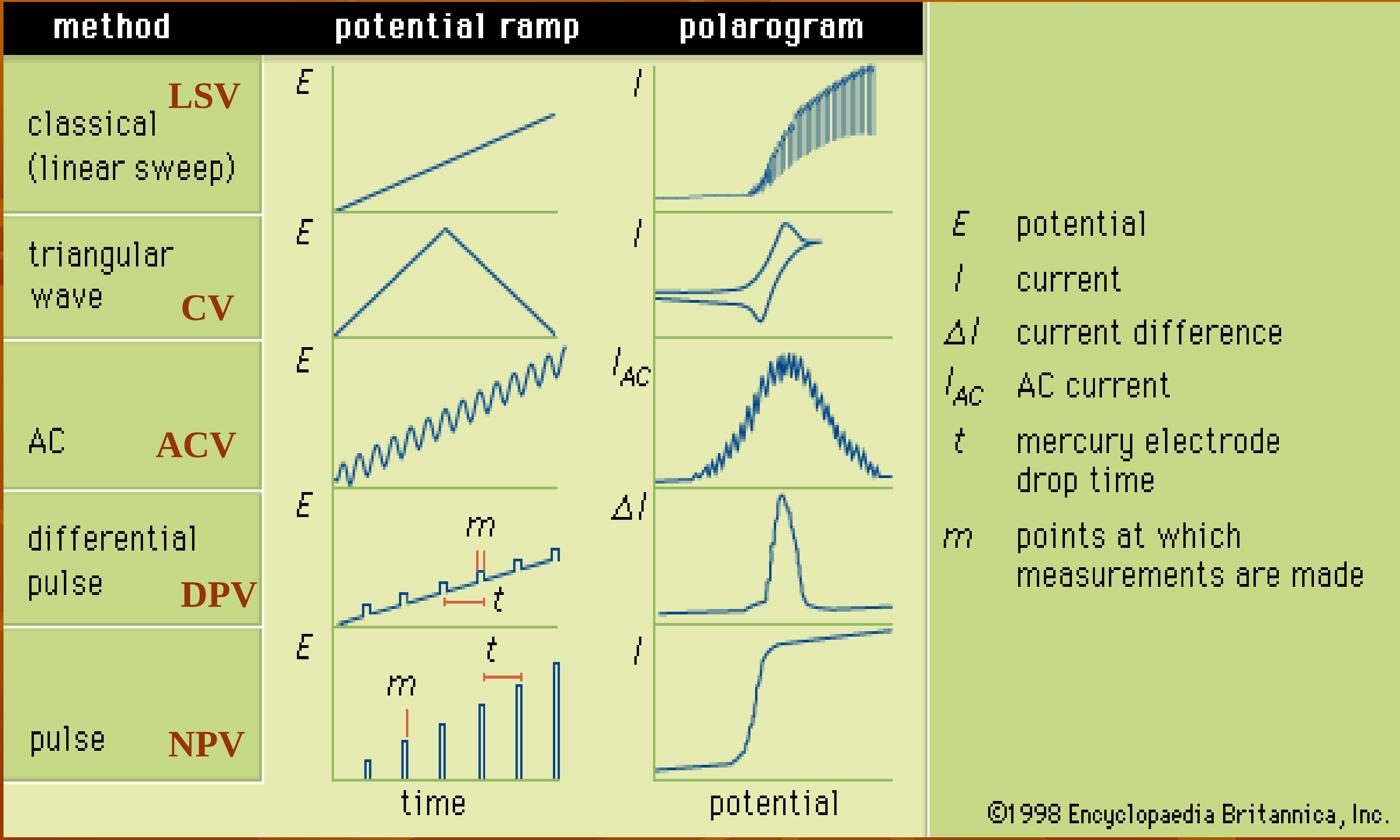
(a) Potential sequences (E-t curves).

(b) Potential sequence on one drop (■ tast).

(c) Current-potential curves for 1 mM Zn^{2+} in 1 M KNO_3.

DC: τ = 2 s; **NP:** τ = 2 s, t_p = 5 ms; **DP:** τ = 2 s, t_p = 5 ms; ΔE_p = 20 mV; **SW:** ΔE_p = 20 mV, f = 100 Hz.

Types of voltammetric technics



method	
classical (linear sweep)	LSV
triangular wave	CV
AC	ACV
differential pulse	DPV
pulse	NPV

E	potential
I	current
ΔI	current difference
I_{AC}	AC current
t	mercury electrode drop time
m	points at which measurements are made

VOLTAMMETRY (LSV, CV)

A) Comparison of Voltammetry to Other Electrochemical Methods

1) Voltammetry: electrochemical method in which information about an analyte is obtained by measuring current (i) as a function of *applied* potential

- only a small amount of sample (analyte) is used

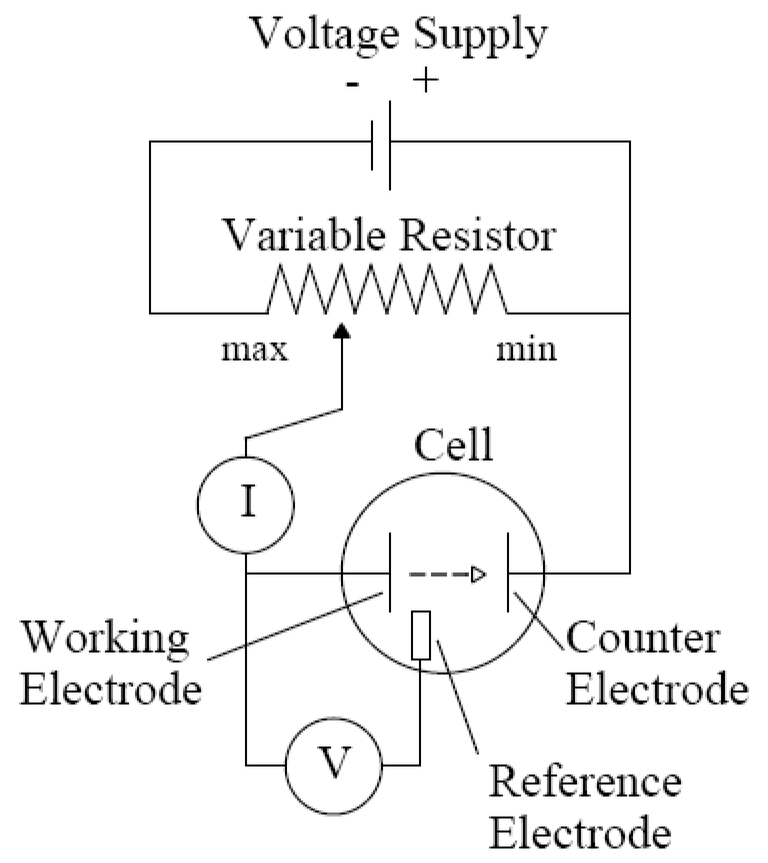
Instrumentation – Three electrodes in solution containing analyte

Working electrode: microelectrode whose potential is varied with time

Reference electrode: potential remains constant (Ag/AgCl electrode or calomel)

Counter electrode: Hg or Pt that completes circuit, conducts e^- from signal source through solution to the working electrode

Supporting electrolyte: excess of nonreactive electrolyte (alkali metal) to conduct current



2) Differences from Other Electrochemical Methods

a) Potentiometry: measure potential of sample or system at or near zero current.

Voltammetry : measure current as a change in potential

b) Coulometry: use up all of analyte in process of measurement at fixed current or potential

Voltammetry: use only small amount of analyte while vary potential

B) Theory of Voltammetry

Excitation Source: potential set by instrument (working electrode)

- establishes concentration of Reduced and Oxidized Species at electrode based on Nernst Equation:

$$E_{electrode} = E^0 - \frac{0.0592}{n} \log \frac{(a_R)^r(a_S)^s \ldots}{(a_P)^p(a_Q)^q \ldots}$$

- reaction at the surface of the electrode

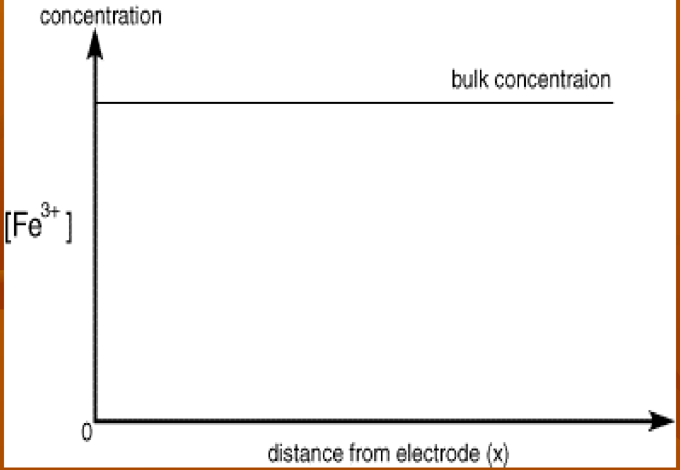
-current generated at electrode by this process is proportional to concentration at surface, which in turn is equal to the bulk concentration

For a planar electrode:

$$\text{measured current } (i) = nFAD_{Ox} \left(\frac{\delta_{CA}}{\delta_x}\right)$$

n = number of electrons in ½ cell reaction, F = Faraday's constant, A = electrode area (cm^2), D = diffusion coefficient (cm^2/s) of Ox (oxidant)

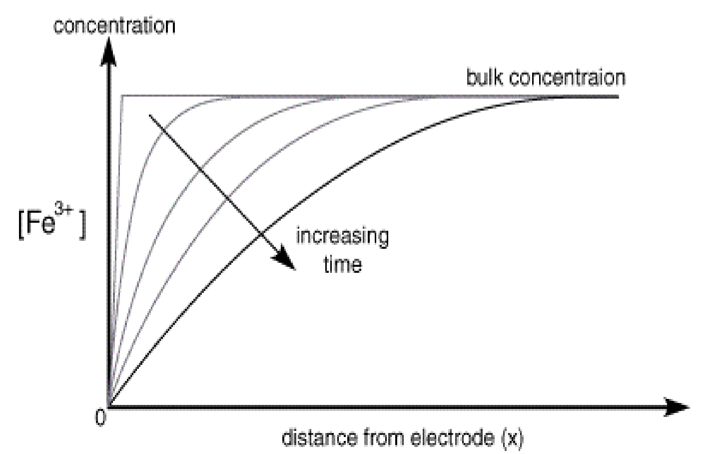
$\frac{\delta_{CA}}{\delta_x}$ = *slope of curve between* $C_{Mox,bulk}$ *and* $C_{Mox,s}$

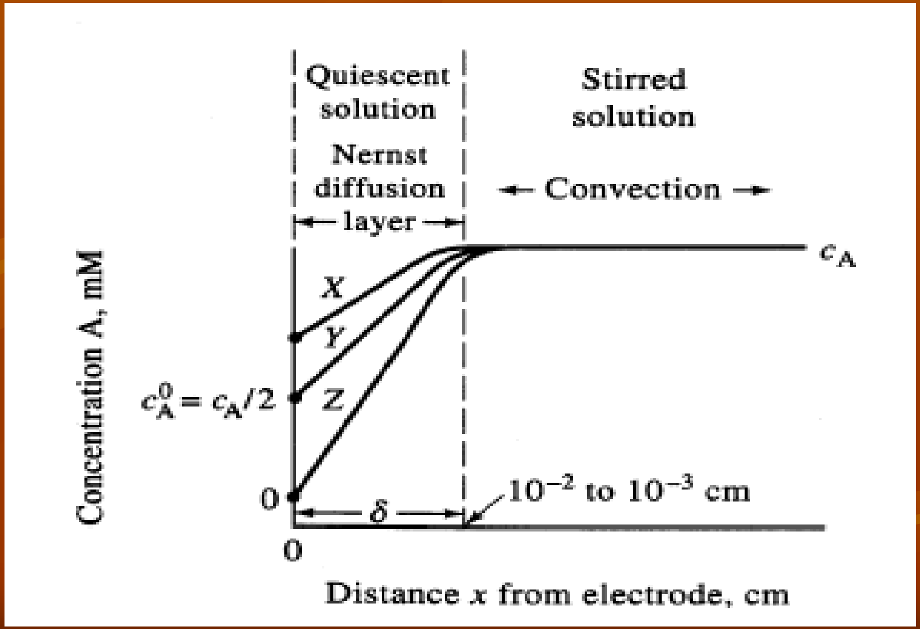


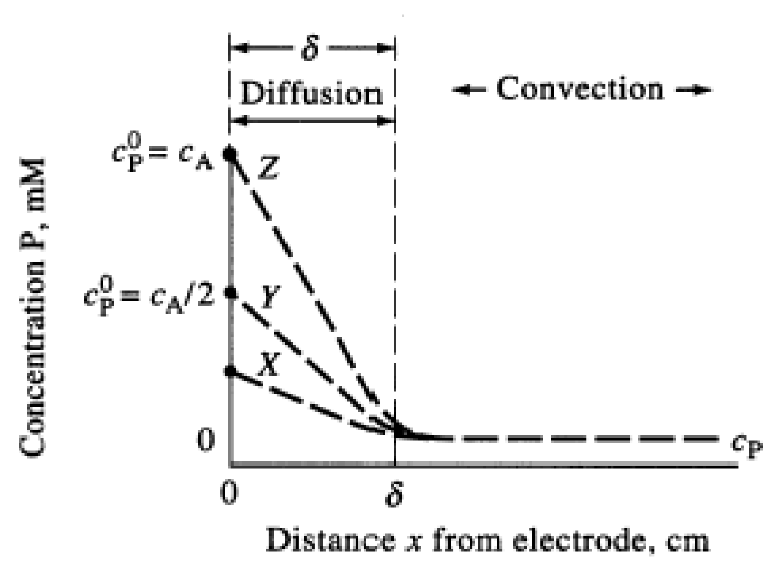
$Fe^{3+} + e^{-} = Fe^{2+}$

Apply

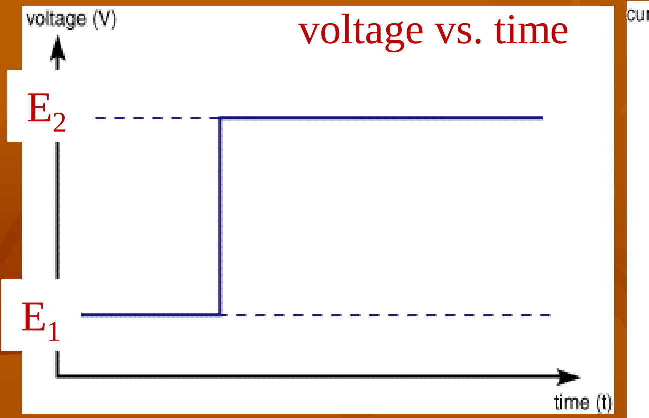
Potential

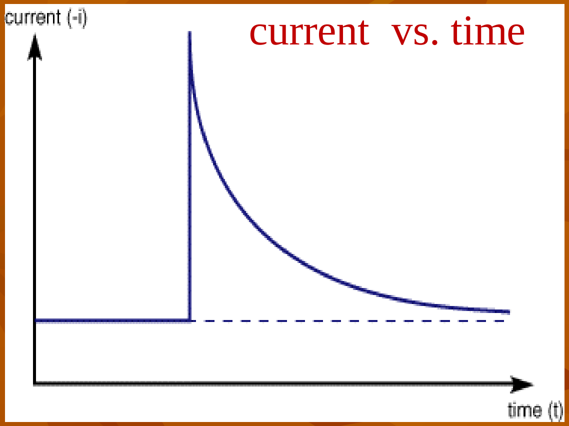


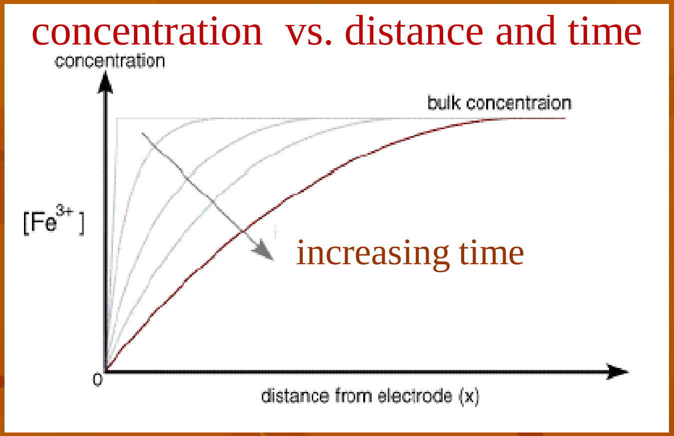




Linear SweepVoltammetry (LSV)

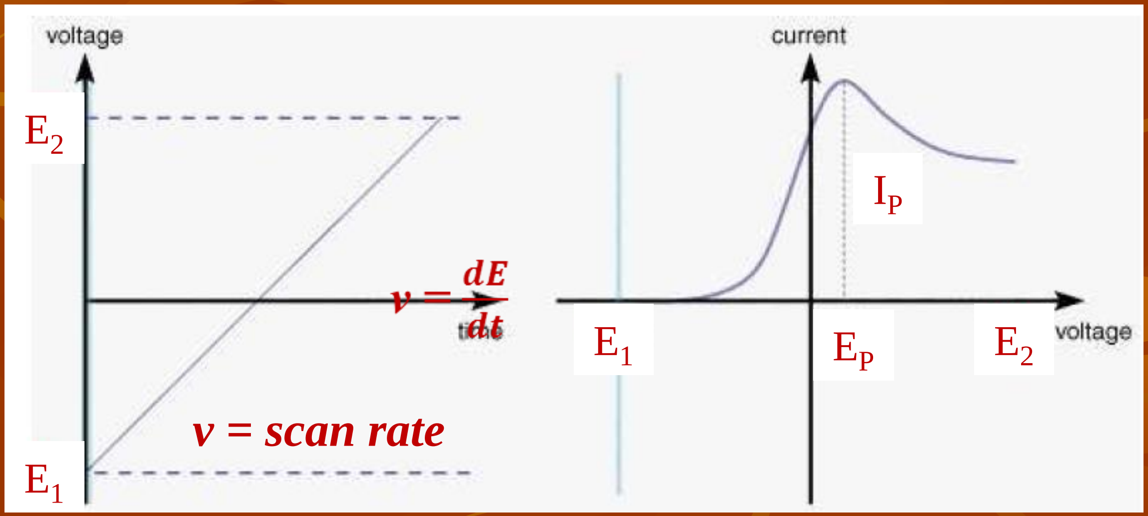




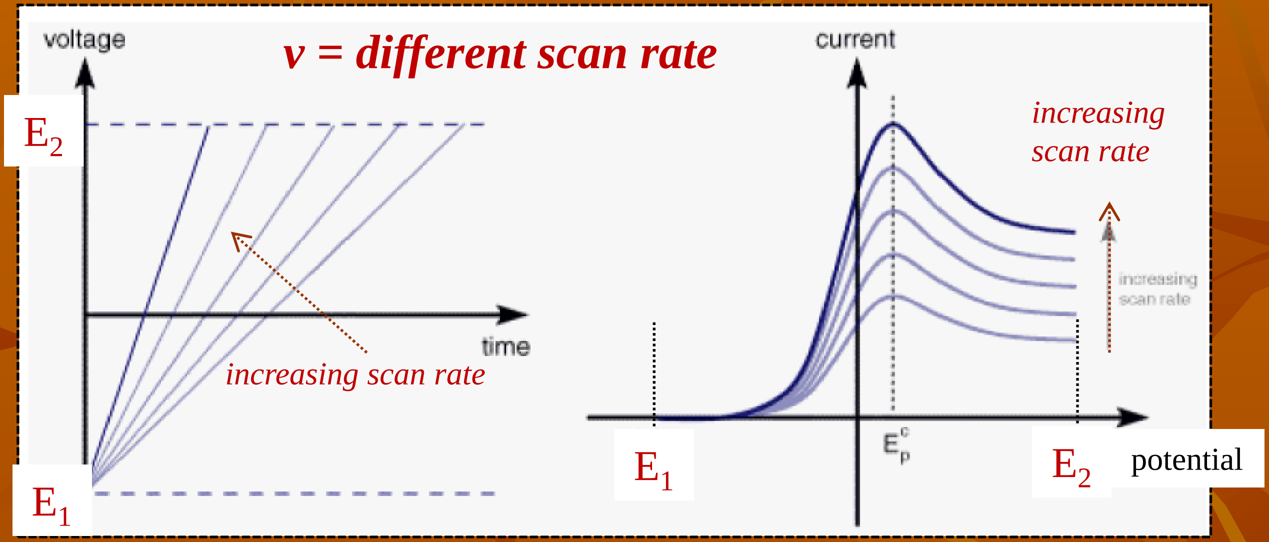


chrono - time

Potential step voltammetry: voltage vs time, current versus voltage, and concentration versus distance from the electrode plotted for several times.



Linear Sweep Voltammetry (LSV)



Randles – Sevcik equation

$$I_p = 2.69.10^5\ n^{3/2} A\ D^{1/2}\ c^0_{Ox}\ v^{1/2}$$

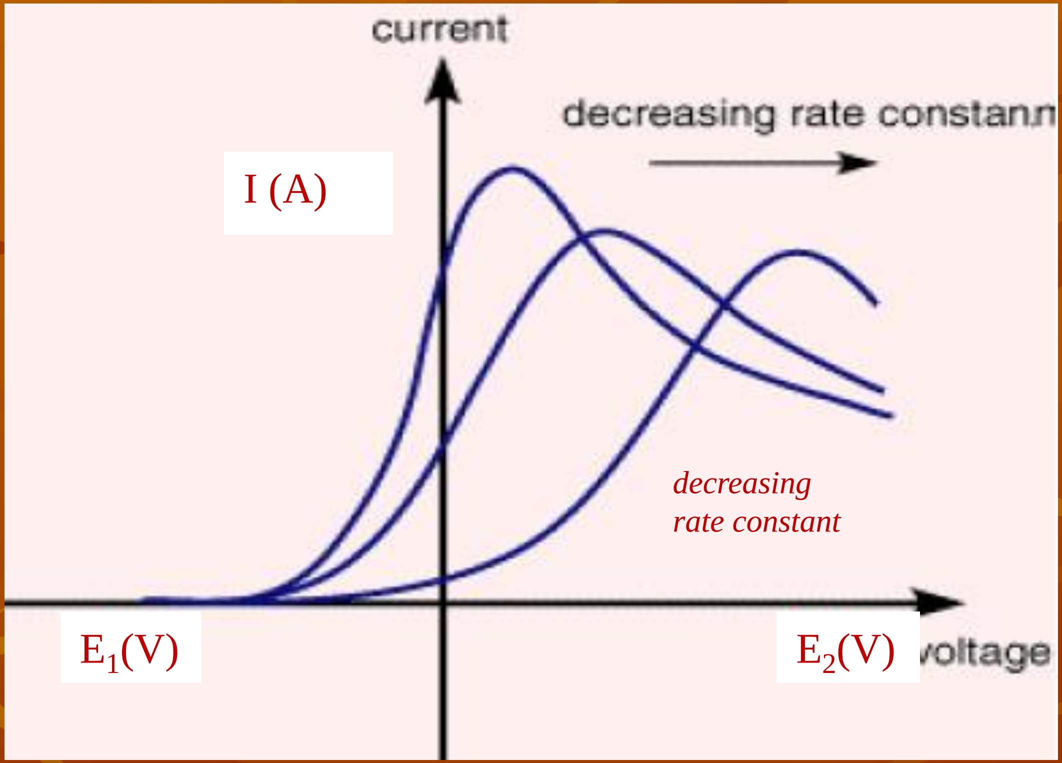
I_p (A) A (cm^2), D ($cm^2.s^{-1}$), v ($V.s^{-1}$), c_{ox} (mol.cm^{-3})

diffusion - rds

Delahay equation

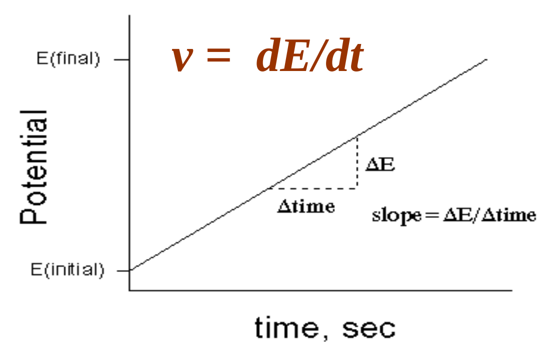
$$I_p = 2.99.10^5\ n(\alpha n_a)^{1/2} A\ D^{1/2}\ c^0_{Ox}\ v^{1/2}$$

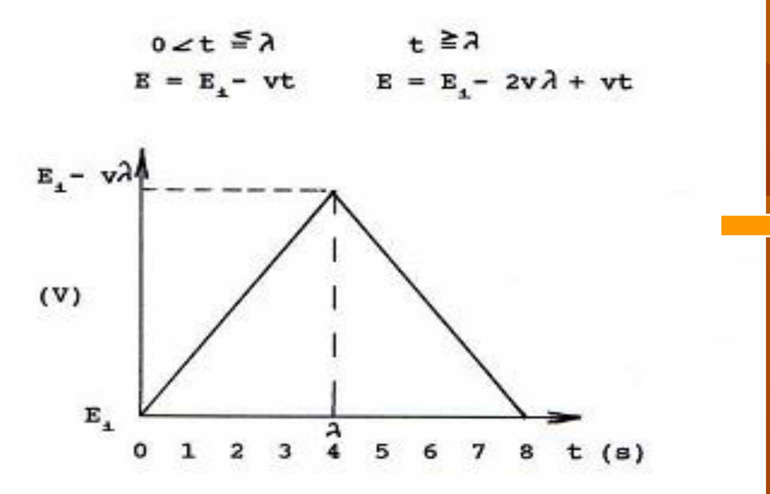
Linear SweepVoltammetry (LSV)

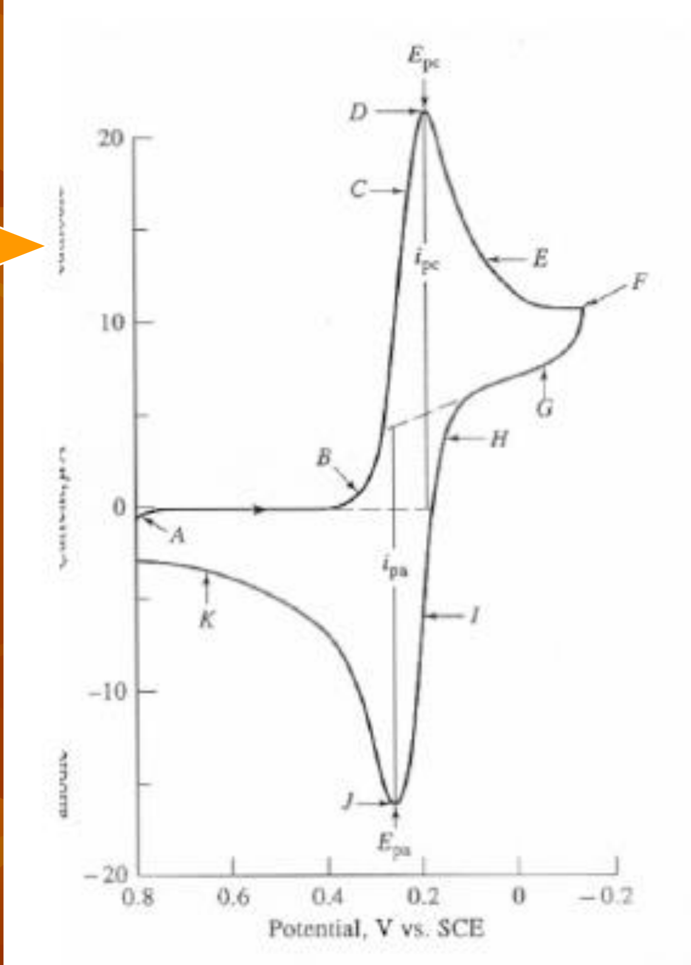


Cyclic Voltammetry (CV)

1) Method used to look at mechanisms of redox reactions in solution
2) Looks at i vs. E response of small, stationary electrode in unstirred solution using triangular waveform for excitation







Cyclic voltammogram

Randles – Sevcik equation

$$I_p = 2.69 .\, 10^5 \; n^{3/2} A \; D^{1/2} \; c_{Ox}^0 \; v^{1/2}$$

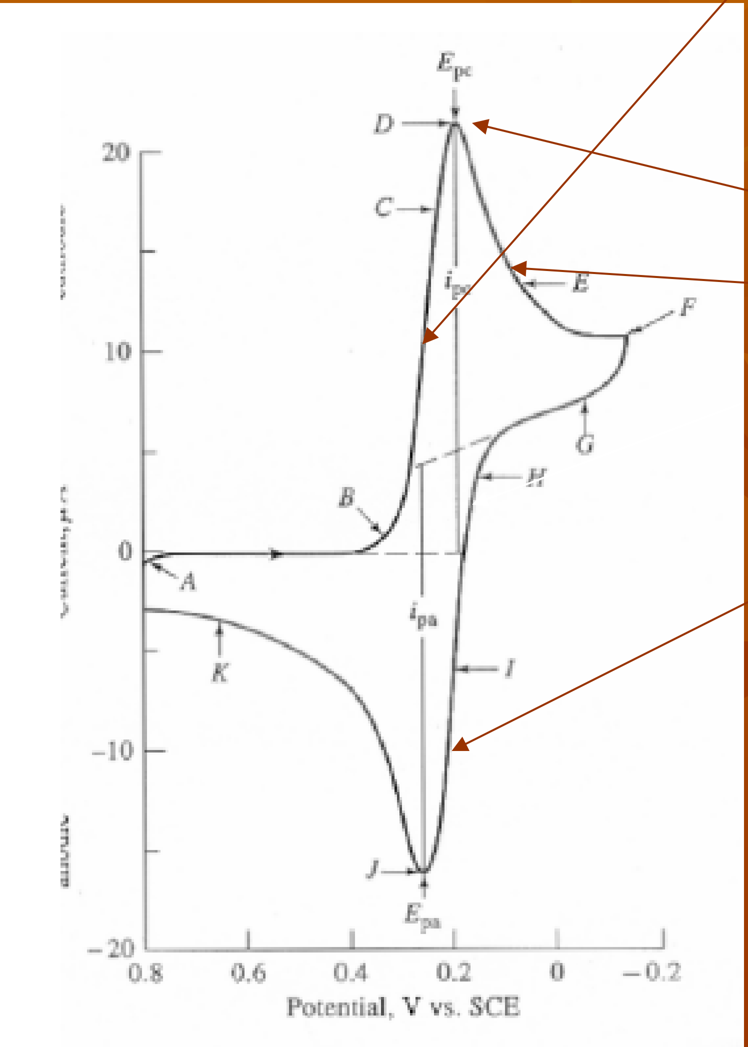
I_p (A) A (cm^2), D (cm^2.s^{-1}), v (V.s^{-1}), c_{ox} (mol.cm^{-3})

Delahay equation

$$I_p = 2.99 .\, 10^5 \; n(\alpha n_a)^{1/2} A \; D^{1/2} \; c_{Ox}^0 \; v^{1/2}$$

Cyclic Voltammetry (CV) - evaluation

Start at E >> E^0 $M_{ox} + ne^- = M_{red}$



- in forward scan, as E approaches E^0 get current due to

$M_{ox} + ne^- = M_{red}$

- driven by Nernst equation
  - ② concentrations made to meet Nernst equation at surface
- eventually reach $I_{max} = I_p$
- solution <u>not</u> stirred, so δ grows with time and see decrease in I_{max}

- in reverse scan see less current as potential increases until reduction no longer occurs

then reverse reaction takes place (if reversible reaction)

- important parameters

E_{pc} – cathodic peak potential
E_{pa} – anodic peak potential
I_{pc} – cathodic peak current
I_{pa} – anodic peak potential

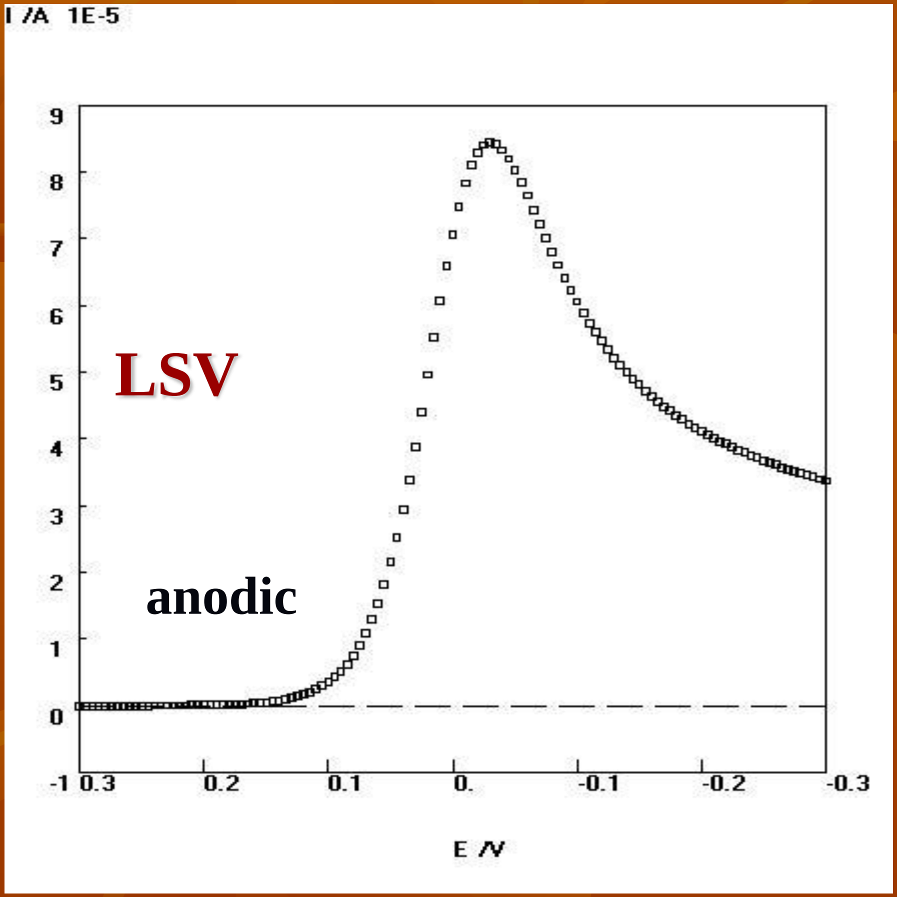
- I_{pc} / I_{pa}
- $\delta(E_{pa} - E_{pc}) = 0.0592/n$,
  where n = number of electrons in reaction
- E^0 = midpoint of $E_{pa} \rightarrow E_{pc}$

$$(E_p)_a - (E_p)_c = 0.0565/n$$

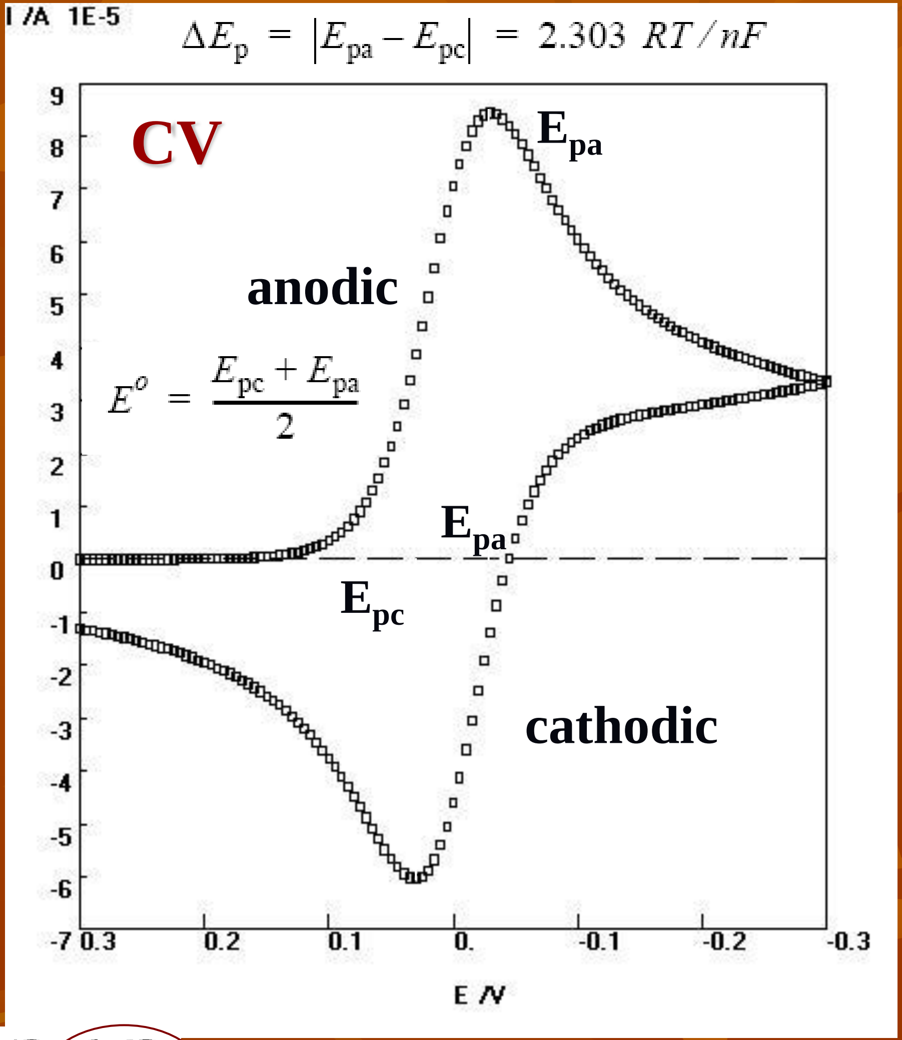
$$\left|E_p - E_{p/2}\right| = 0.0565/n$$

Voltammetry

Linear sweep voltammetry (LSV)



Cyclic voltammetry (CV)



$$\Delta E_p = |E_{pa} - E_{pc}| = 2.303\ RT/nF$$

$$E^o = \frac{E_{pc} + E_{pa}}{2}$$

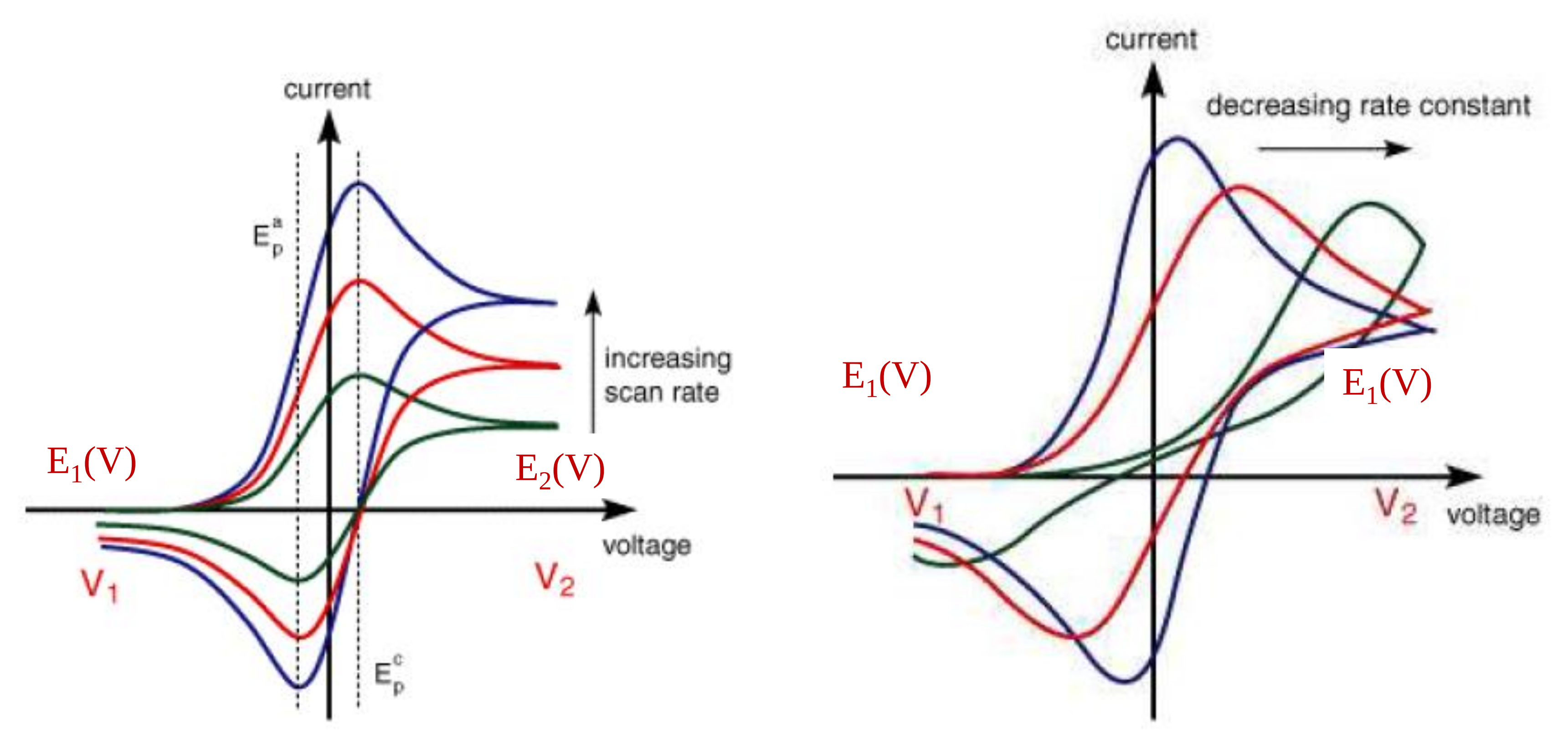
- Randles-Sevcik equation

$$i_p = 2.686 \times 10^5 n^{3/2} A c^0 D^{1/2} v^{1/2}$$

diffusion control

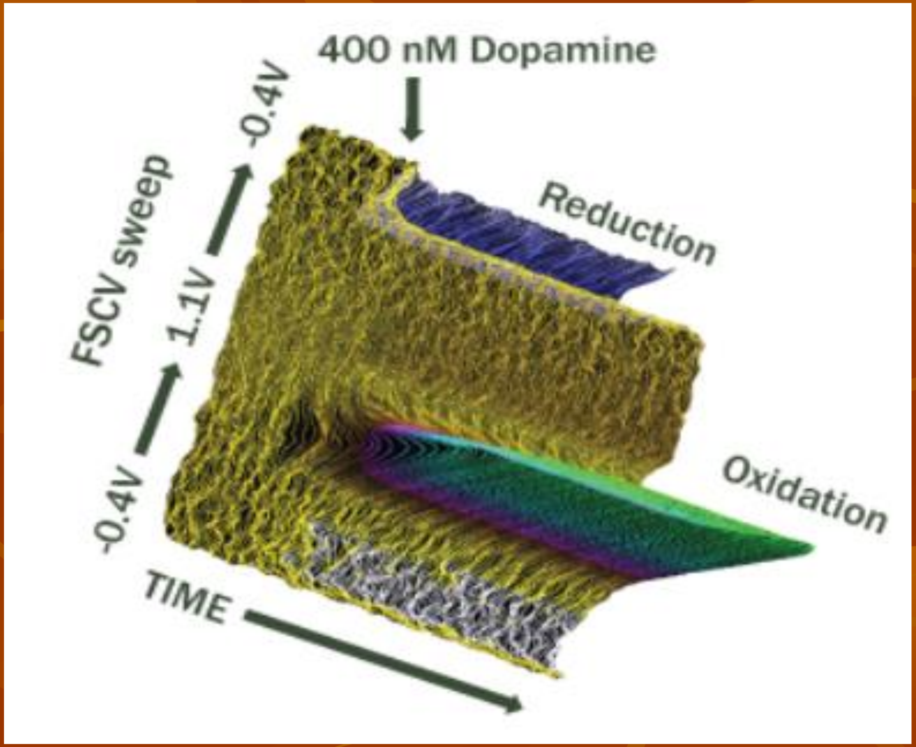
Cyclic voltammetry

Scan rate and rate constant dependence of the I-V curves

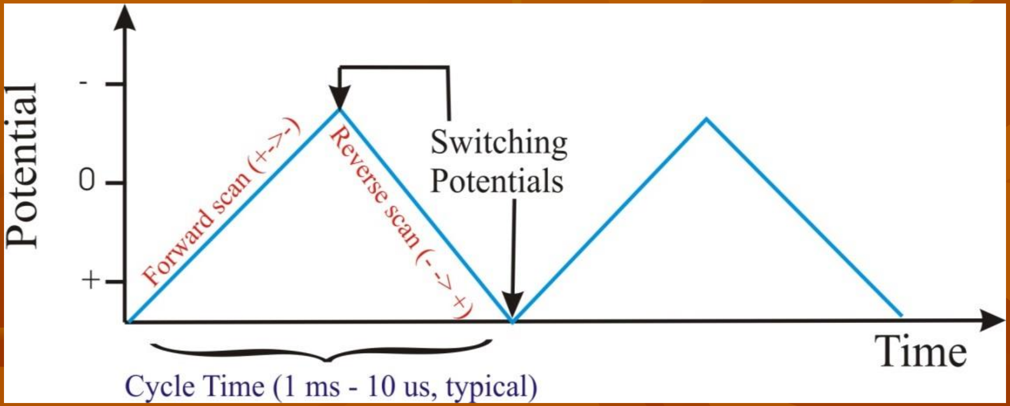


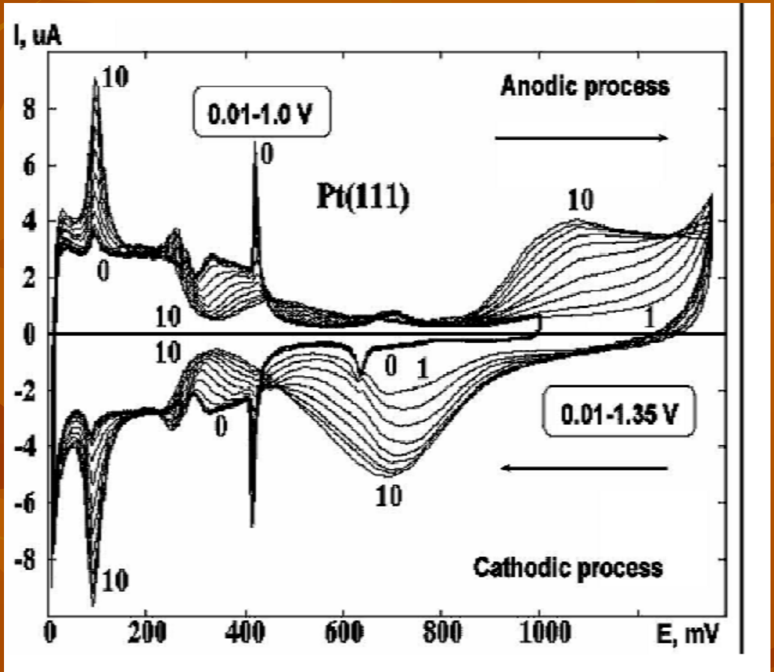
Fast Scan Cyclic Voltammetry (FSCV)

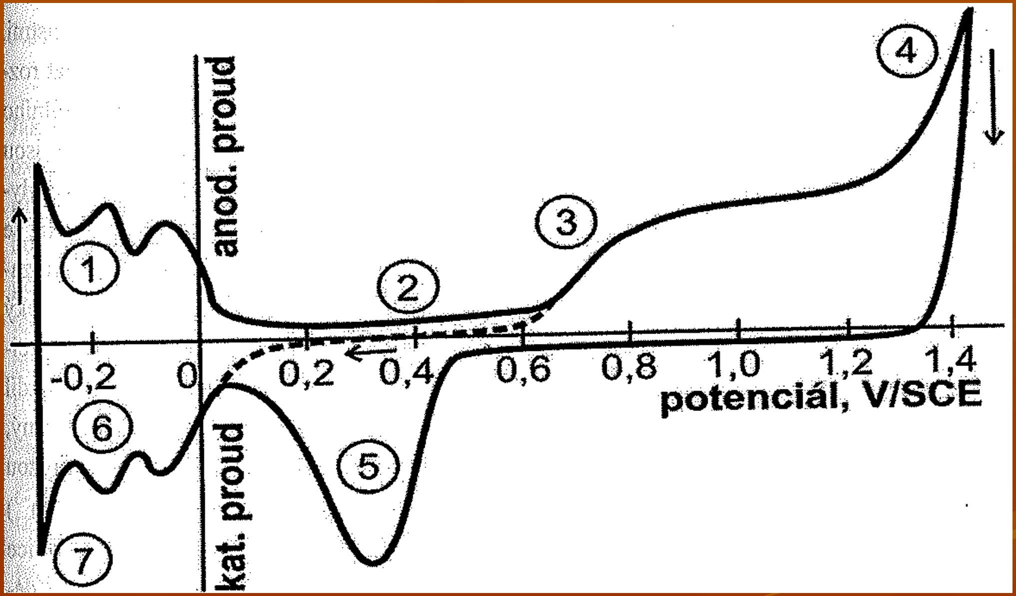
Biogenic amine levels are detected by rapidly cycling a voltage across an implanted carbon fiber sensor and measuring the resultant current. Our systems can measure spontaneous sub-second neurotransmitter release events while conducting detailed behavioral studies. Both the wireless and tethered systems sweep from 250 to 400 V/s in a user-selectable range spanning -1.1 to +1.3 V. All systems have built-in support for controlling an external stimulus.



CV Pt electrodes







1 - desorption of hydrogen

2 - Pt surface without hydrogen

3 - oxidation Pt (oxides)

4 – oxidation of solvent (H_2O)

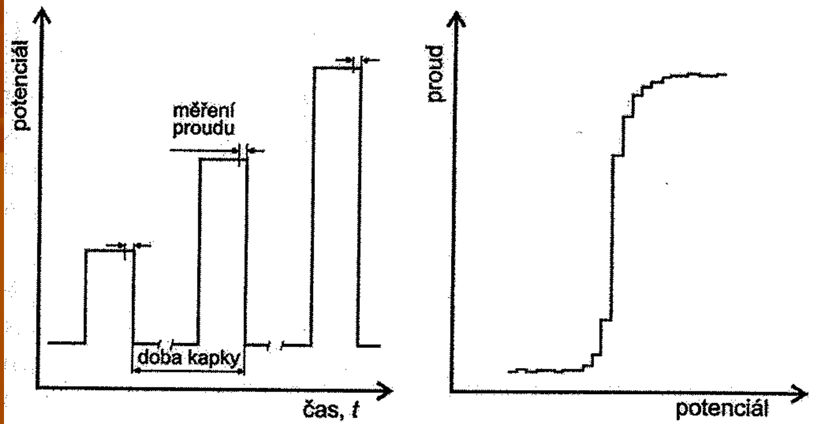
5 – reduction of oxides at Pt surface

6 – reduction and adsorption of hydrogen

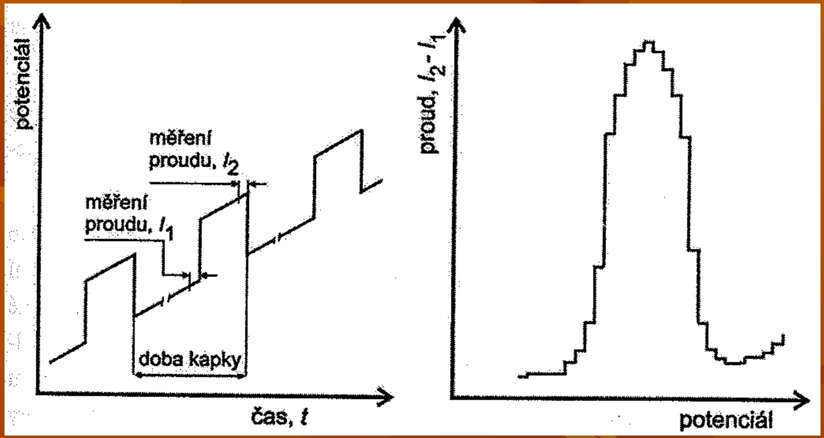
7 – adsorption of hydrogen

Pulse Polarography (Voltammetry)

Normal pulse (NPP, NPV)



Differential pulse (DPP,DPV)



Cottrell equation

$$I_{NPP} = \frac{nFAD^{1/2}c}{\sqrt{\pi t_m}}$$

t_m time after application of the pulse where the current is sampled

$$I_{DPP} = \frac{nFAD^{1/2}c}{\sqrt{\pi t_m}} \left(\frac{1-\sigma}{1+\sigma} \right)$$

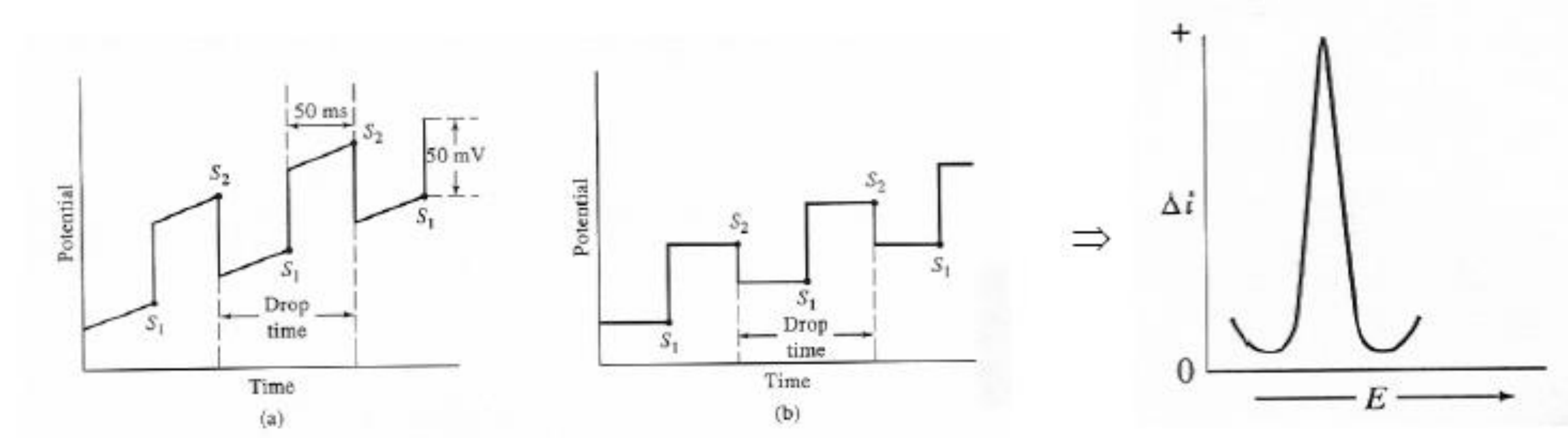
$$\sigma = \exp\left[(nf / RT)(\Delta E / 2) \right]$$

ΔE...*pulse amplitude*

f...*frenquency*

Pulse Polarography (Voltammetry)

Instead of linear change in E_{appl} with time use step changes (pulses in E_{appl}) with time



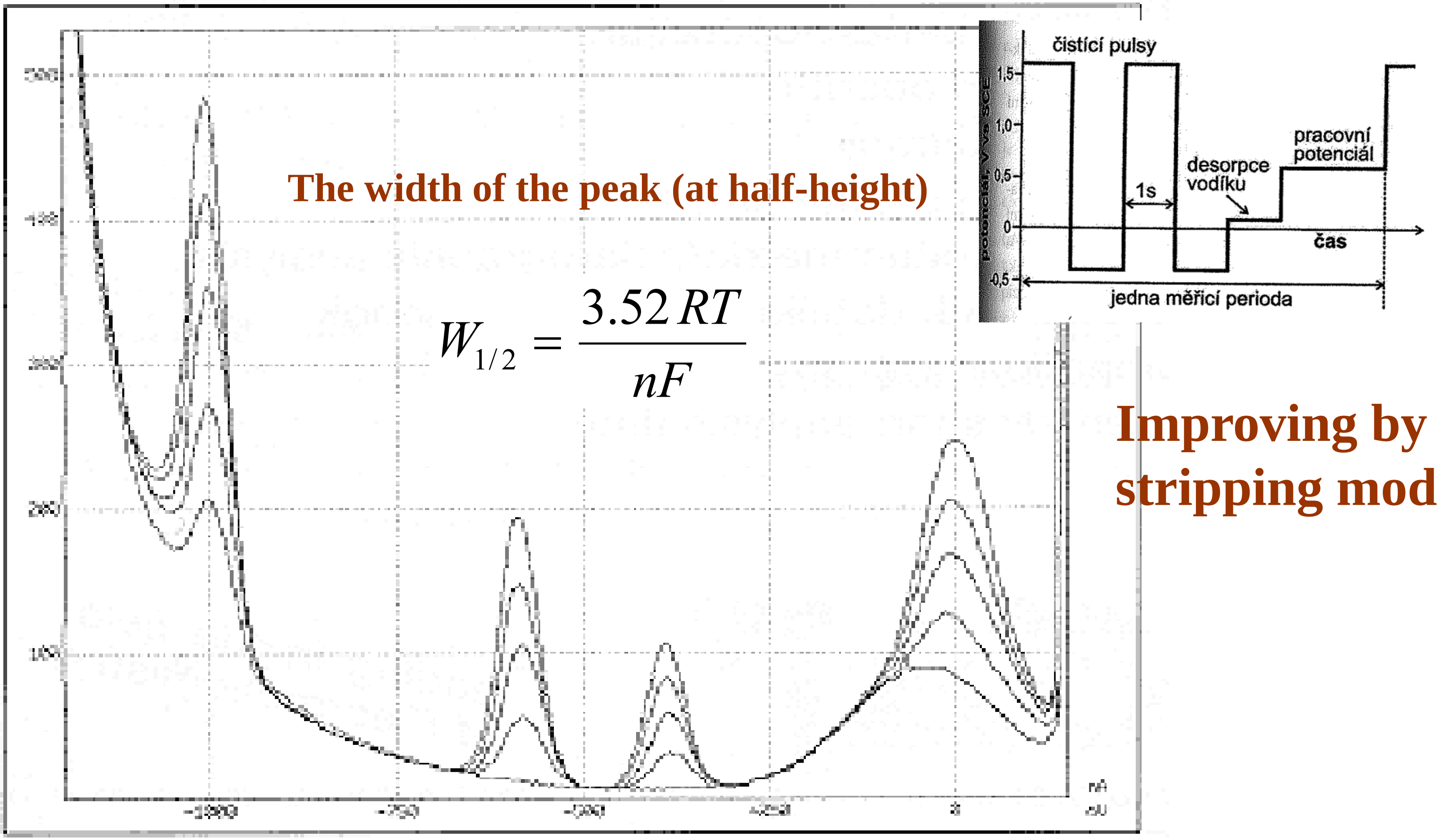
Measure two potentials at each cycle

- S_1 before pulse S_2 at end of pulse
- plot Δi vs. E (Δi = $E_{S2} – E_{S1}$)
- peak height ~ concentration
- for reversible reaction, peak potential -> standard potential
- derivative-type polarogram

Advantages of DPP (DPV)

- can detect peak maxima differing by as much as 0.044 – 0.05 V
- 0.2V peak separatioin for normal polarography
- can do more elements per run
- decrease limits of detection by 100-1000x compared to normal polarography

Differential Pulse Polarography (Voltammetry)



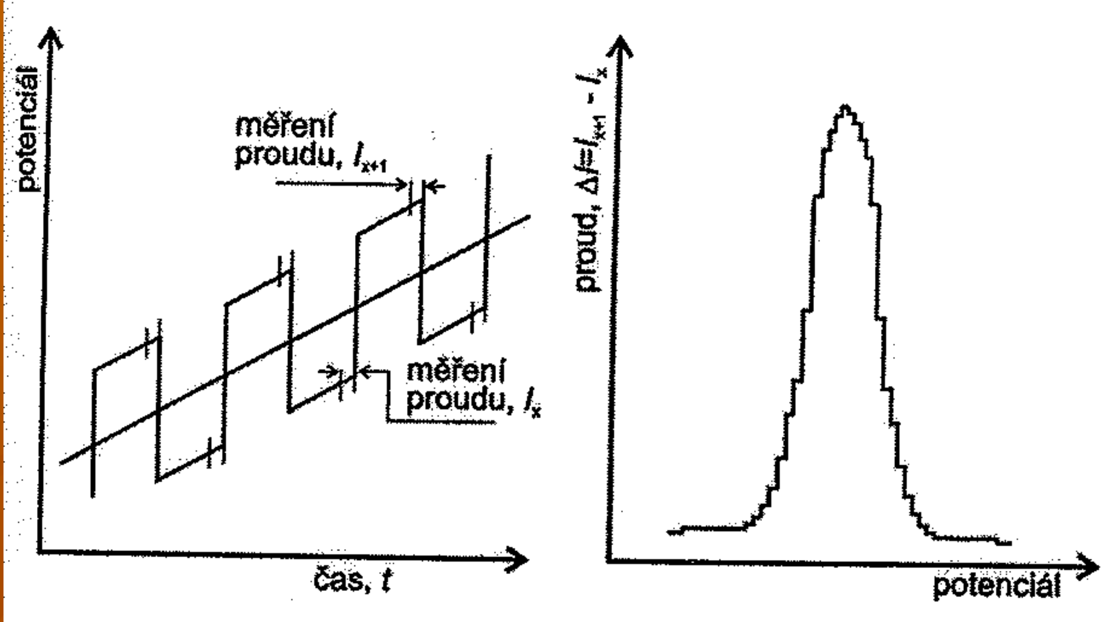
The width of the peak (at half-height)

$$W_{1/2} = \frac{3.52\,RT}{nF}$$

Improving by stripping mode

The example above shows the simultaneous determination of Zn , Cd, Pb and Cu using standard addition

Square Wave (SW) Polarography or Voltammetry



Large amplitude differential technique in which a waveform composed of a symmetric square wave, superimposed on a base staircase potential, is applied to the working electrode. The current is sampled twice during each SW cycle. Once at the end of the forward pulse (t_1) and once at the end of the reverse pulse (t_2).

difference between the two measurements = f (staircase potential)

A man must either resolve to bring out nothing new or to become a slave to defend it.
(Isaac Newton)

A problem solved is dead.
(Frederick Soddy)

Progress is made by trial and failure.
(William Ramsay)

Work, finish, publish !
(Michael Faraday)