

POLAROGRAPHY/ VOLTAMMETRY

- *Introduction*
- *Instrumentation, common techniques*
- *Direct Current (DC) polarography*
- *Mercury electrodes (DME, SMDE, HMDE)*
- *Polarographic currents*
- *Fast 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

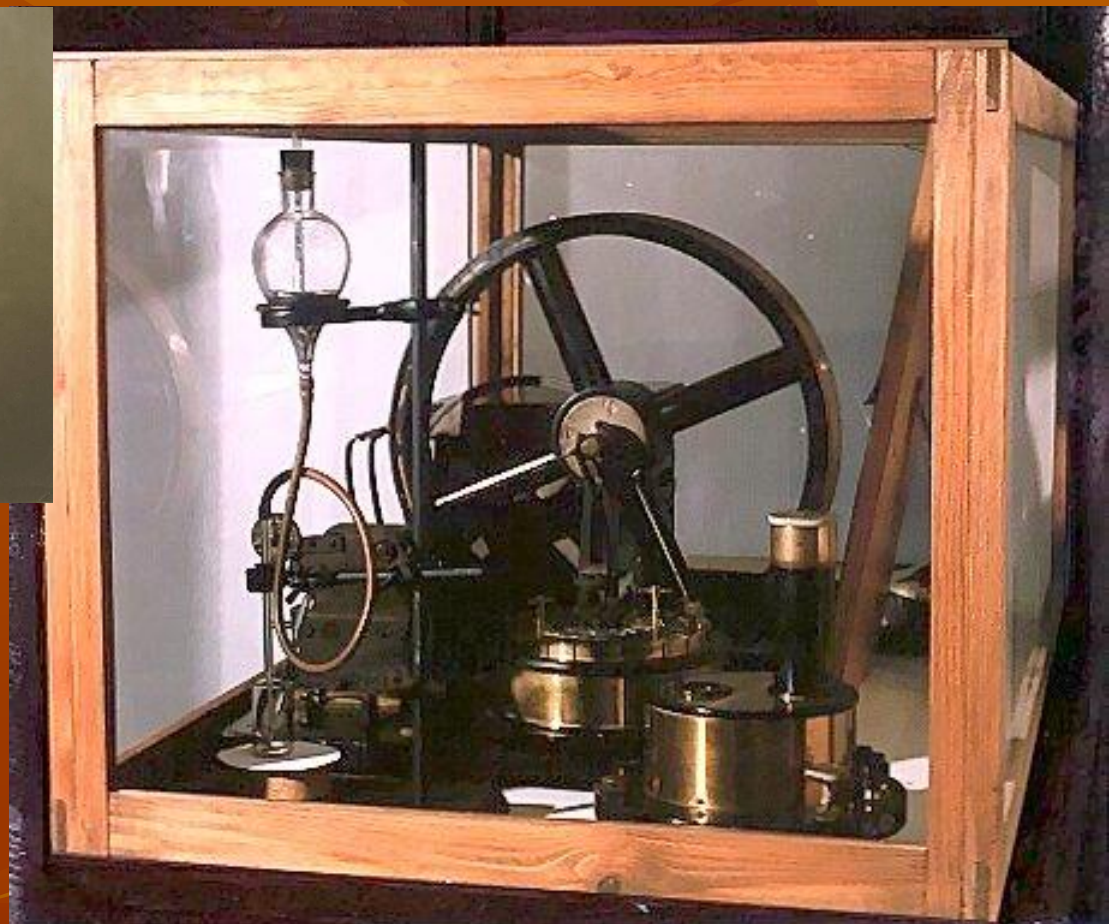


Jaroslav Heyrovský was an inventor of the polarographic method, father of electroanalytical chemistry, recipient of the Nobel Prize (1959). His contribution to electroanalytical chemistry can not be overestimated. All voltammetry methods used now in electroanalytical chemistry originate from polarography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

J. Heyrovský

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

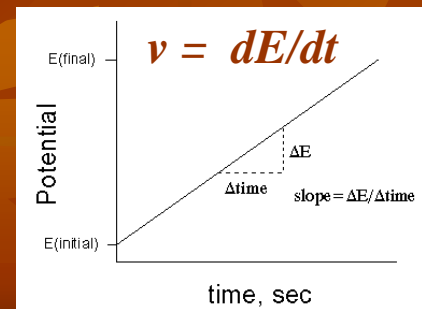
- *Polarography is an voltammetric measurement whose response is determined by combined diffusion/convection mass transport. Polarography is a specific type of measurement that falls into the general category of linear-sweep voltammetry where the electrode potential is altered in a linear fashion from the initial potential E_i to the final potential E_f . 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.*

$$I = f(E)$$

$$E = E_i \pm \nu t$$

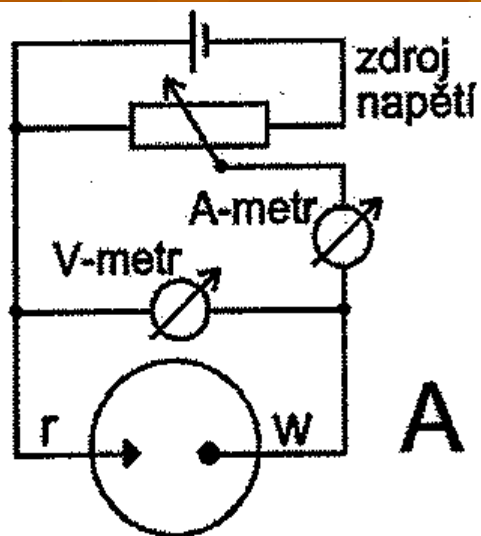
E – electrode potential, ν – scan rate, t - time, I - current

also LSV - Linear Sweep Voltammetry or CV – Cyclic Voltammetry

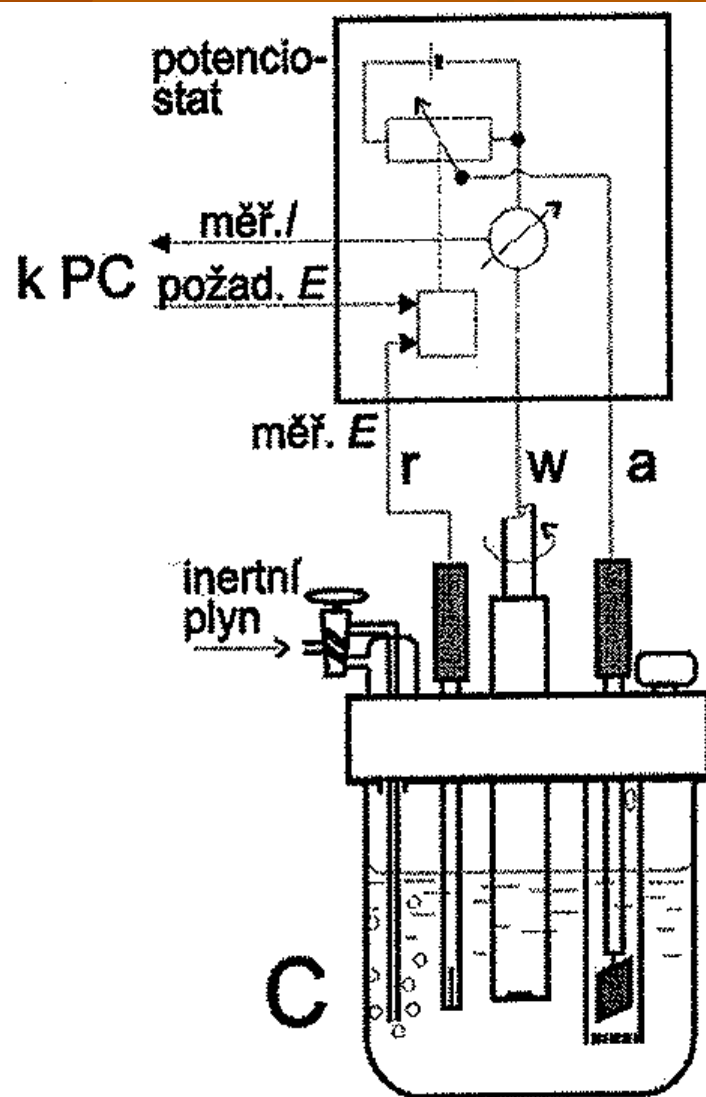
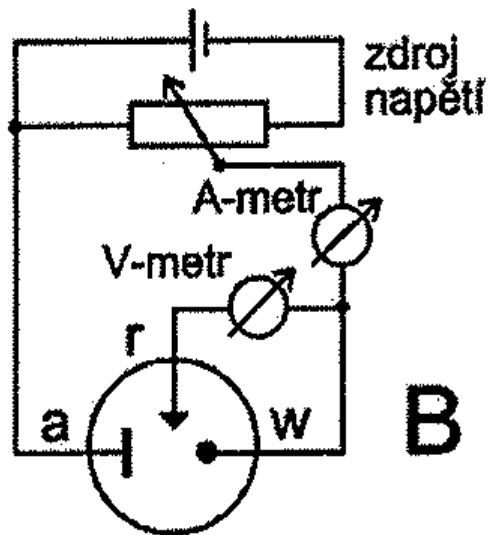


Instrumentation, common techniques

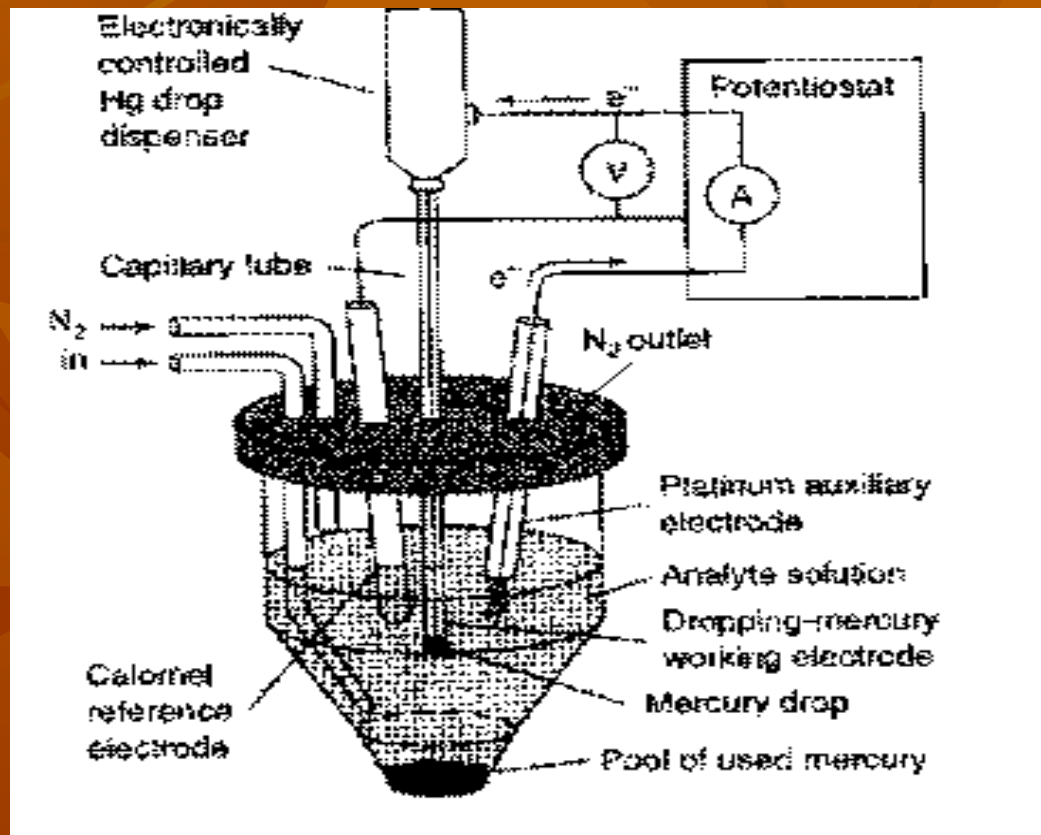
Two-electrode set



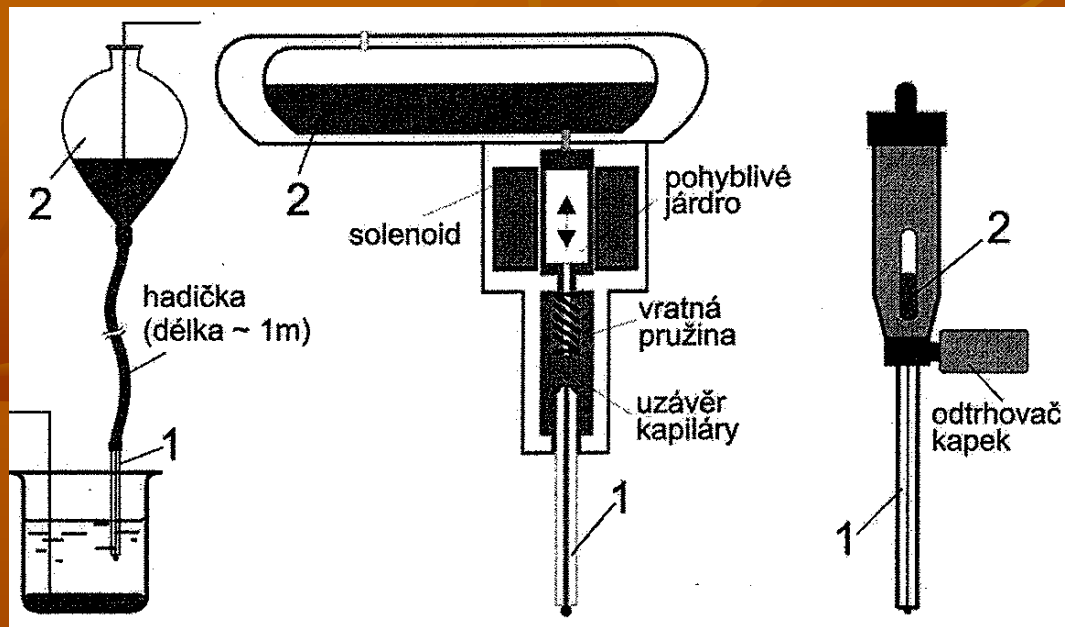
Three-electrode set



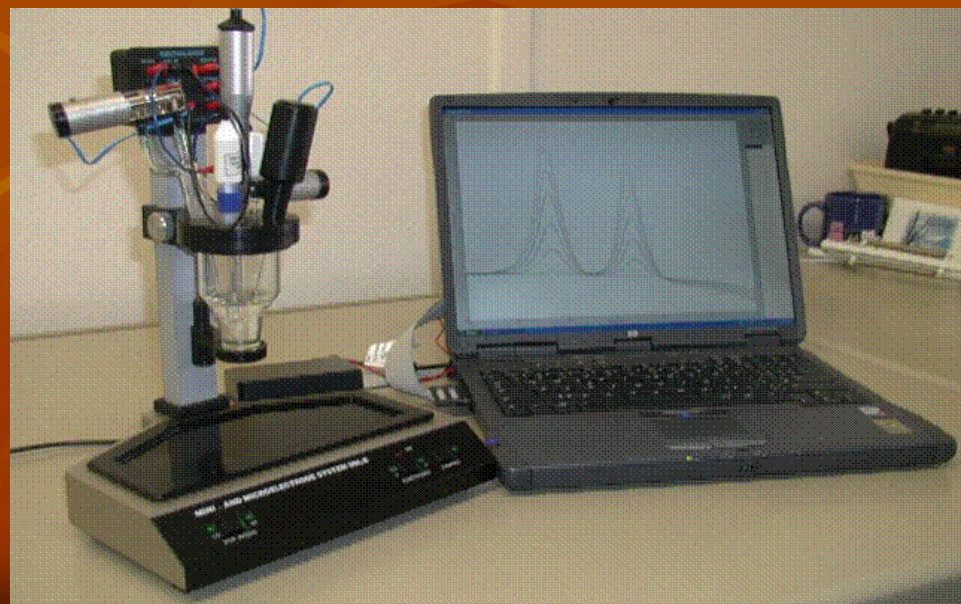
Instrumentation, common techniques



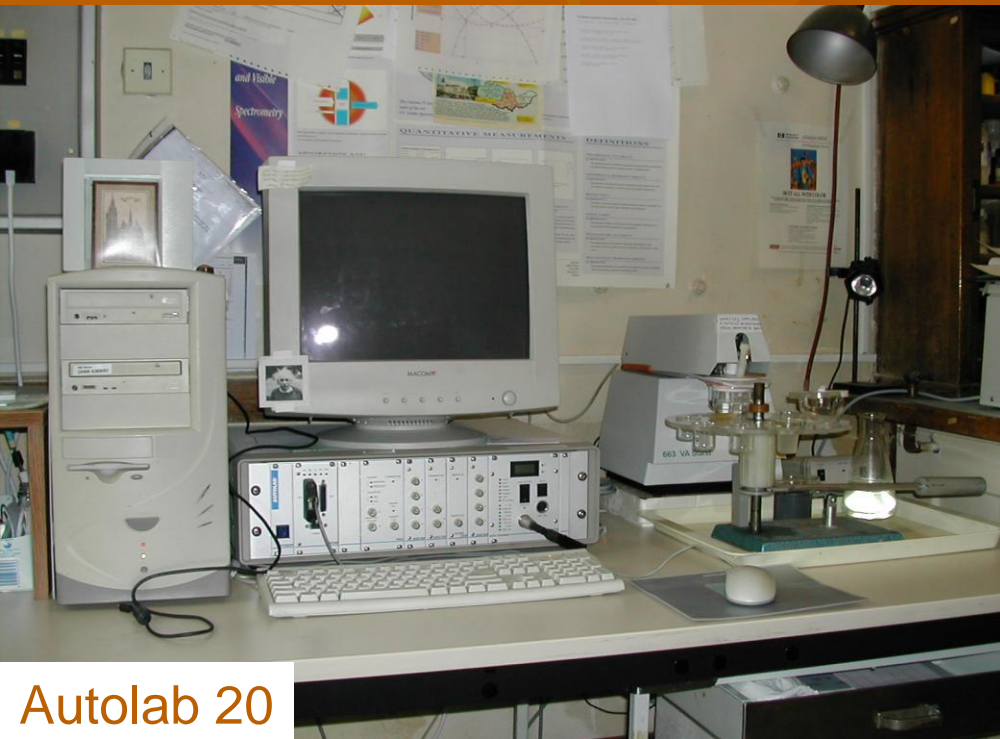
Instrumentation, common techniques



EcoTribo Polarograph
Polaro Sensors - Eco Trend
Prague, Czech Republic



Instrumentation, common techniques



Autolab 20

Autolab
Ecochemie
Utrecht
The Netherlands

VA-Stand 663
Metrohm
Zurich
Switzerland

Electrochemical
analyzer
AUTOLAB



Autolab 30

Mercury electrodes (DME, SMDE, HMDE)

Dropping Mercury Electrode - DME

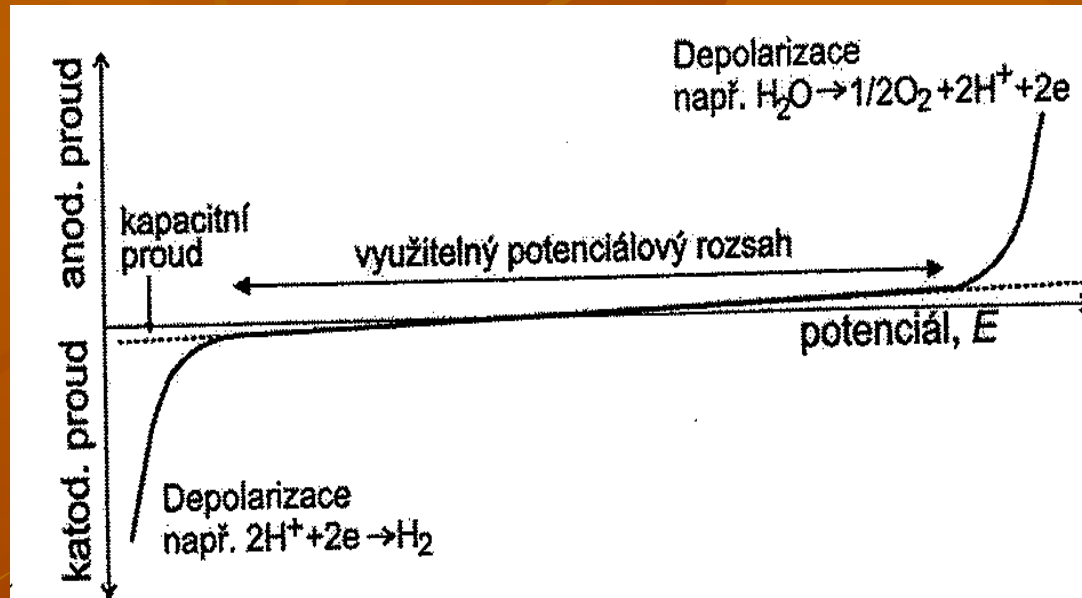
Static Mercury Drop Electrode - SMDE

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

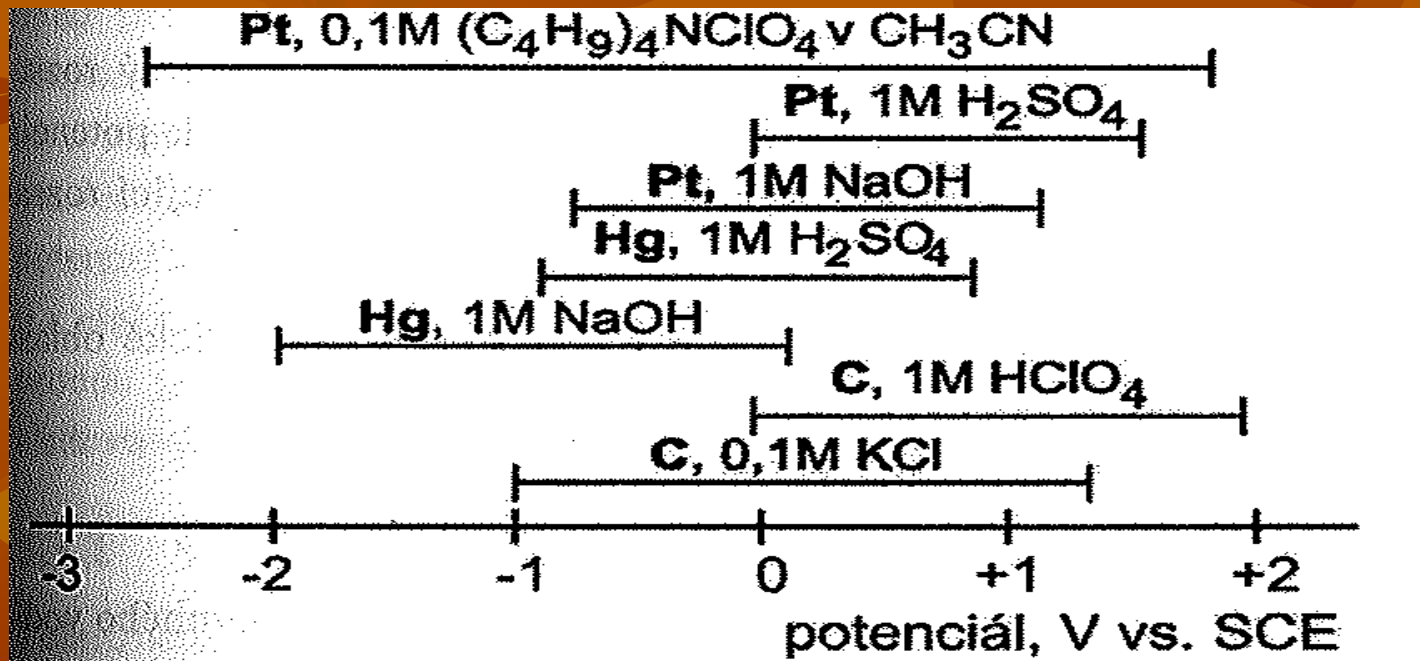


Roztok	Katodická oblast	Anodická oblast
Vodný	redukce iontu H^+ $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	oxidace vody $2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ oxidace materiálu elektrody $\text{Hg} \rightleftharpoons \text{Hg}^{2+} + 2\text{e}^-$
Nevodný	redukce kationtu elektrolytu (např. - R_4N^+ , Li^+)	oxidace materiálu elektrody oxidace stop vody oxidace základního elektrolytu*

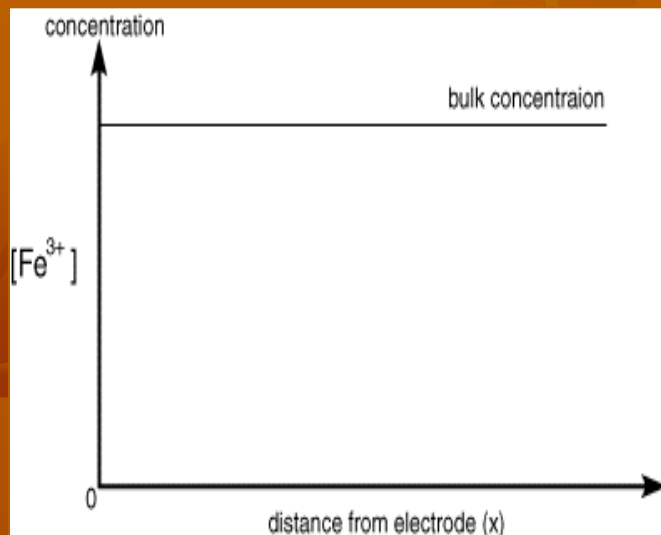
*reakce omezující anodickou oblast v nevodných roztocích nejsou často zcela jasné

Instrumentation, common techniques

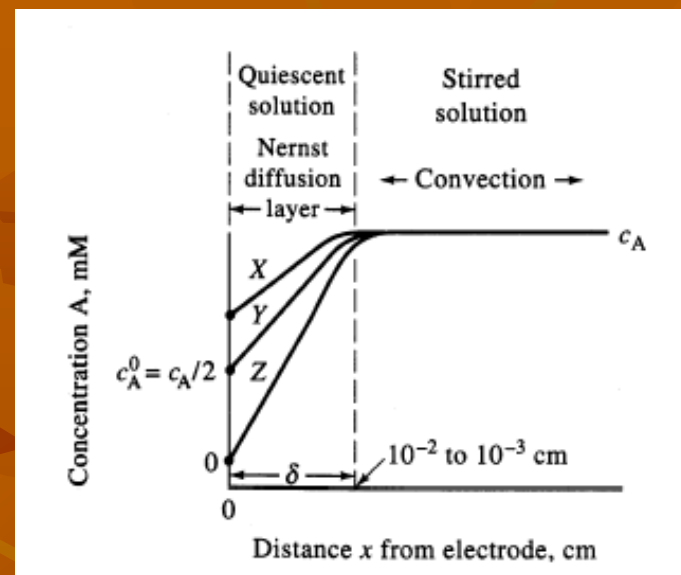
Potential windows for different electrodes



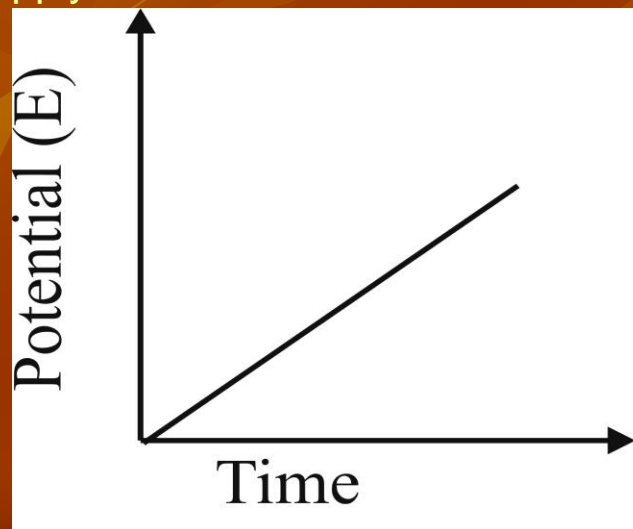
Direct Current (DC) polarography



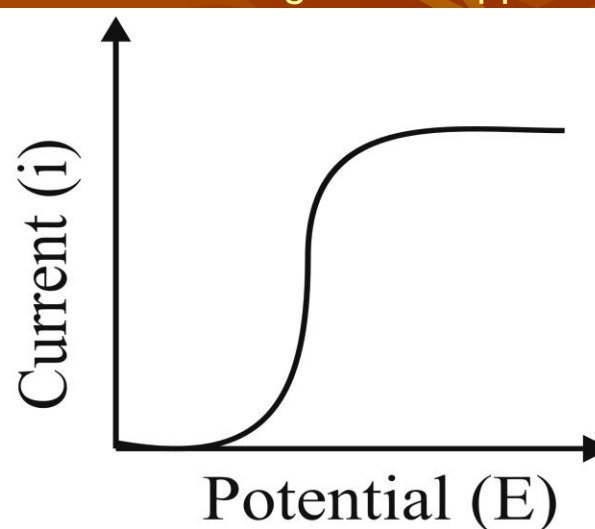
Apply
Potential
 $E \ll E^\circ$



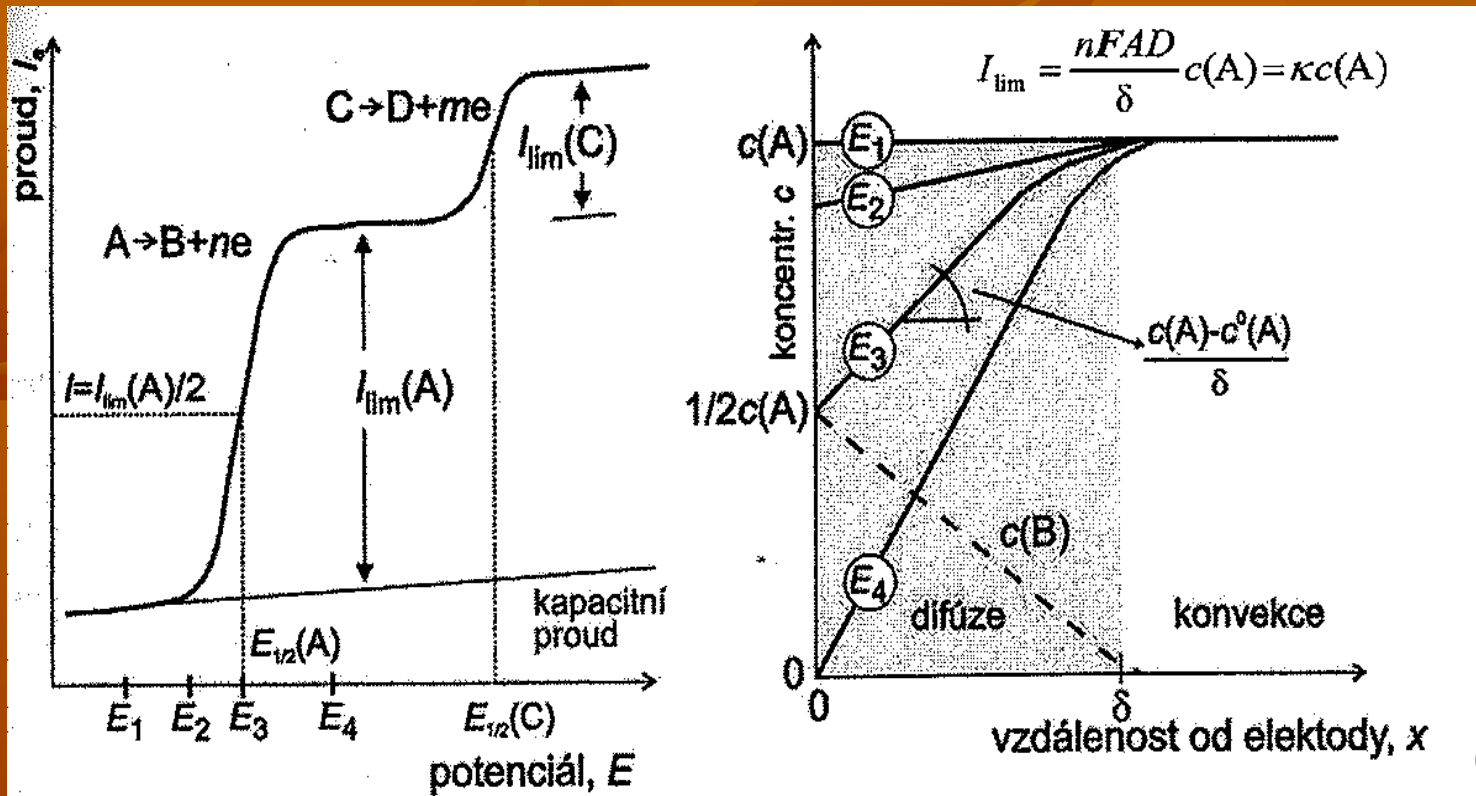
Apply Linear Potential with Time



Observed Current Changes with Applied Potential

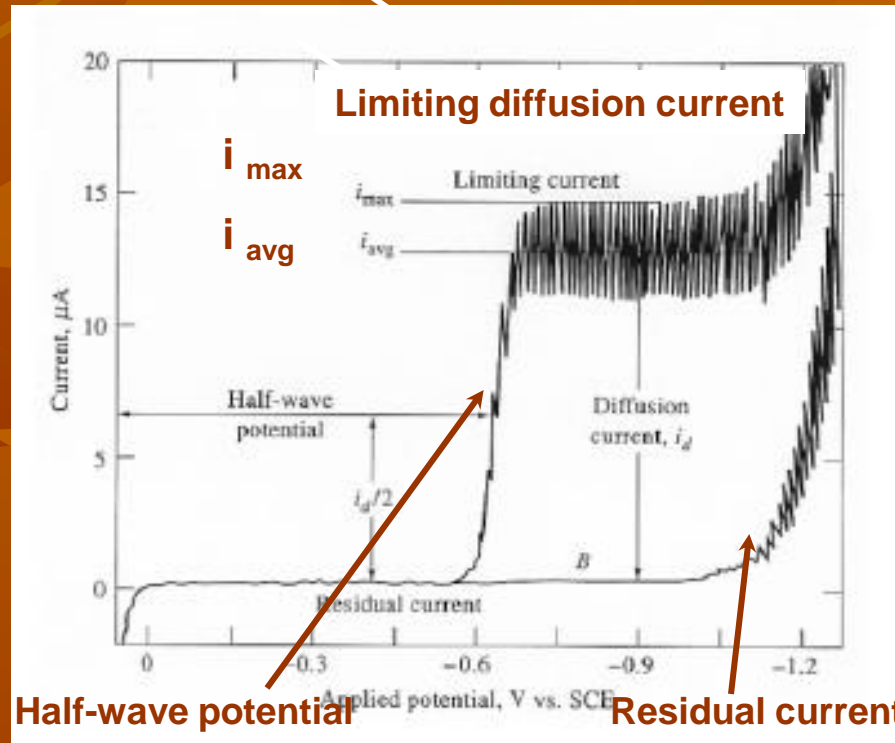
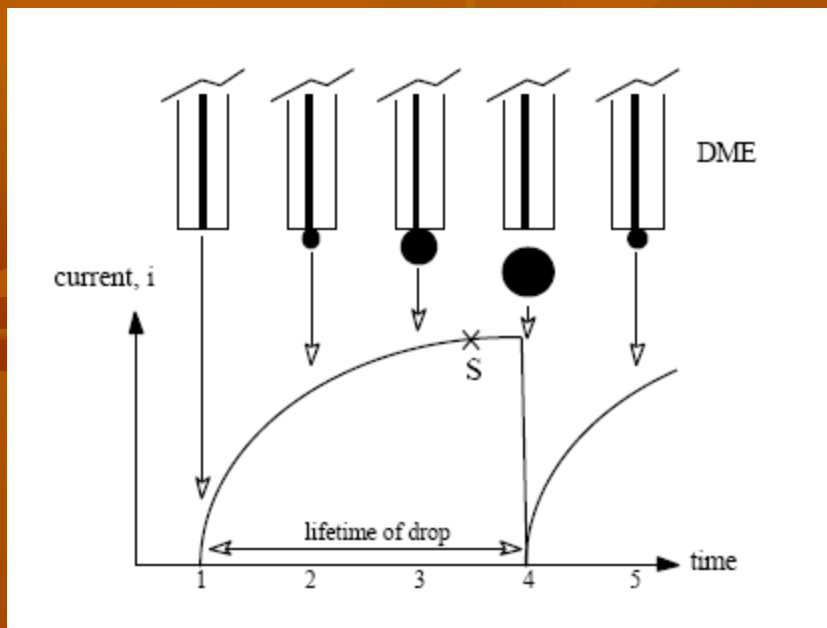


Direct Current (DC) polarography



concentration before step

Half-wave potential, limited diffusion current



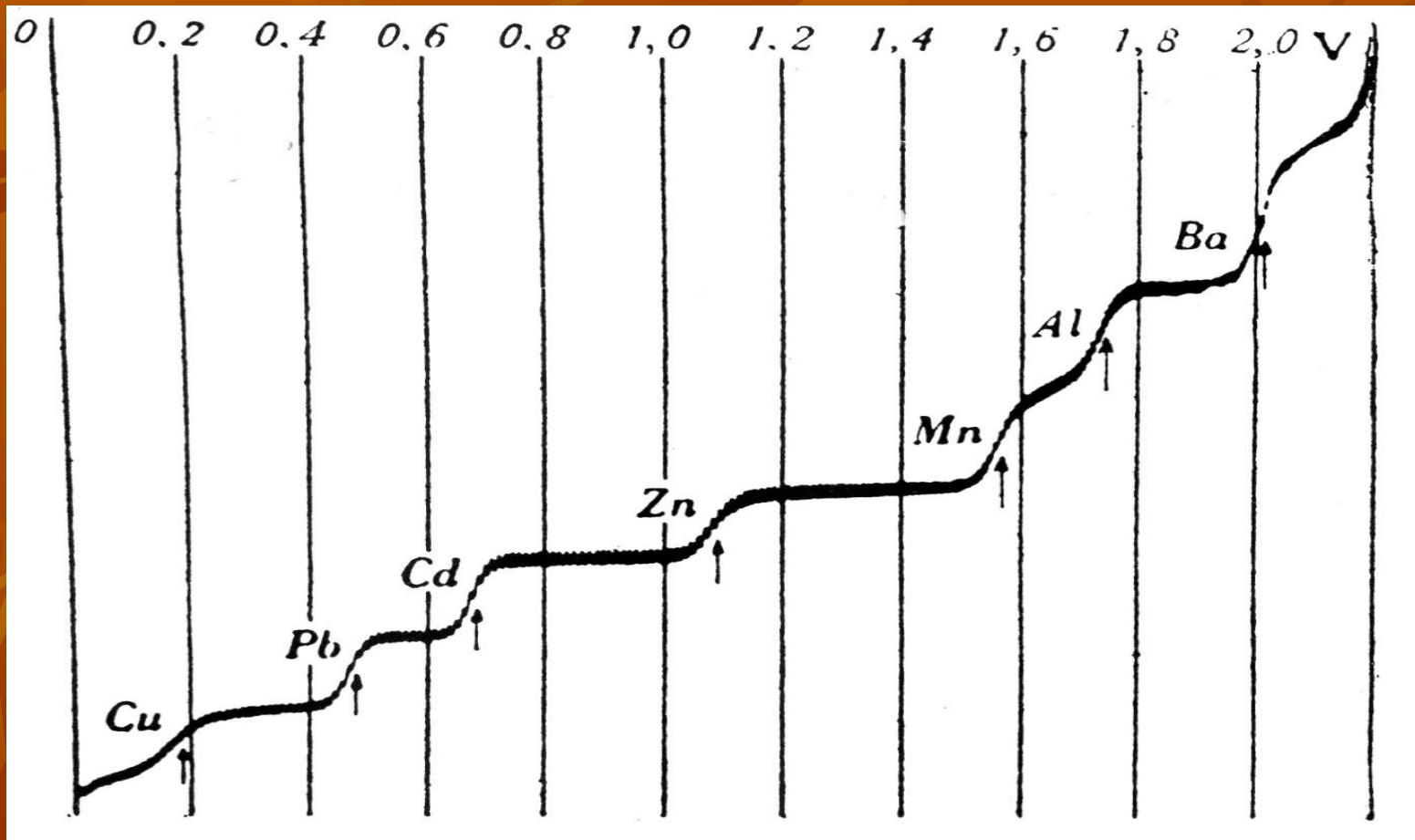
- a) $\frac{1}{2}$ wave potential ($E_{1/2}$) characteristic of M^{n+} (E)
- b) height of either average current maxima (i_{avg}) or top current max (i_{max}) is \sim analyte concentration
- c) size of i_{max} is governed by
 - rate of growth of DME $>$ drop time (t , sec)
 - rate of mercury flow (m , mg/s)
 - diffusion coefficient of analyte (D , cm^2/s)
 - number of electrons in process (n)
 - analyte concentration (c , mol/ml)

Ilkovič equation

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

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

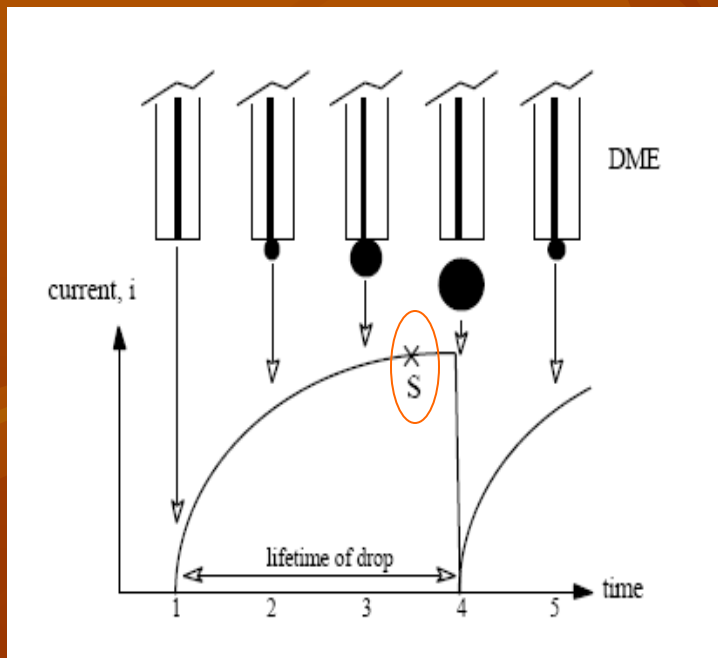
Typical polarographic curves - polarographic spectrum



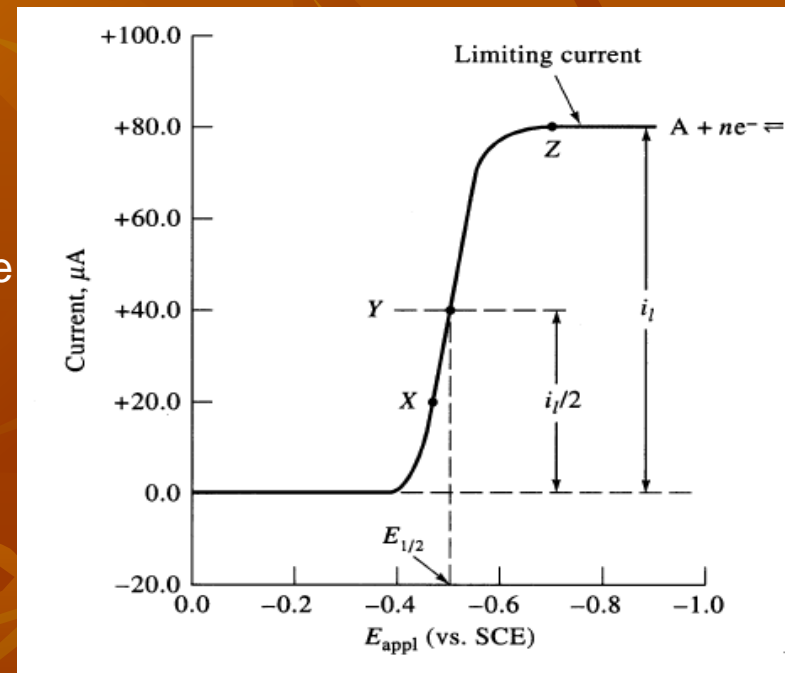
Tast polarography

- 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



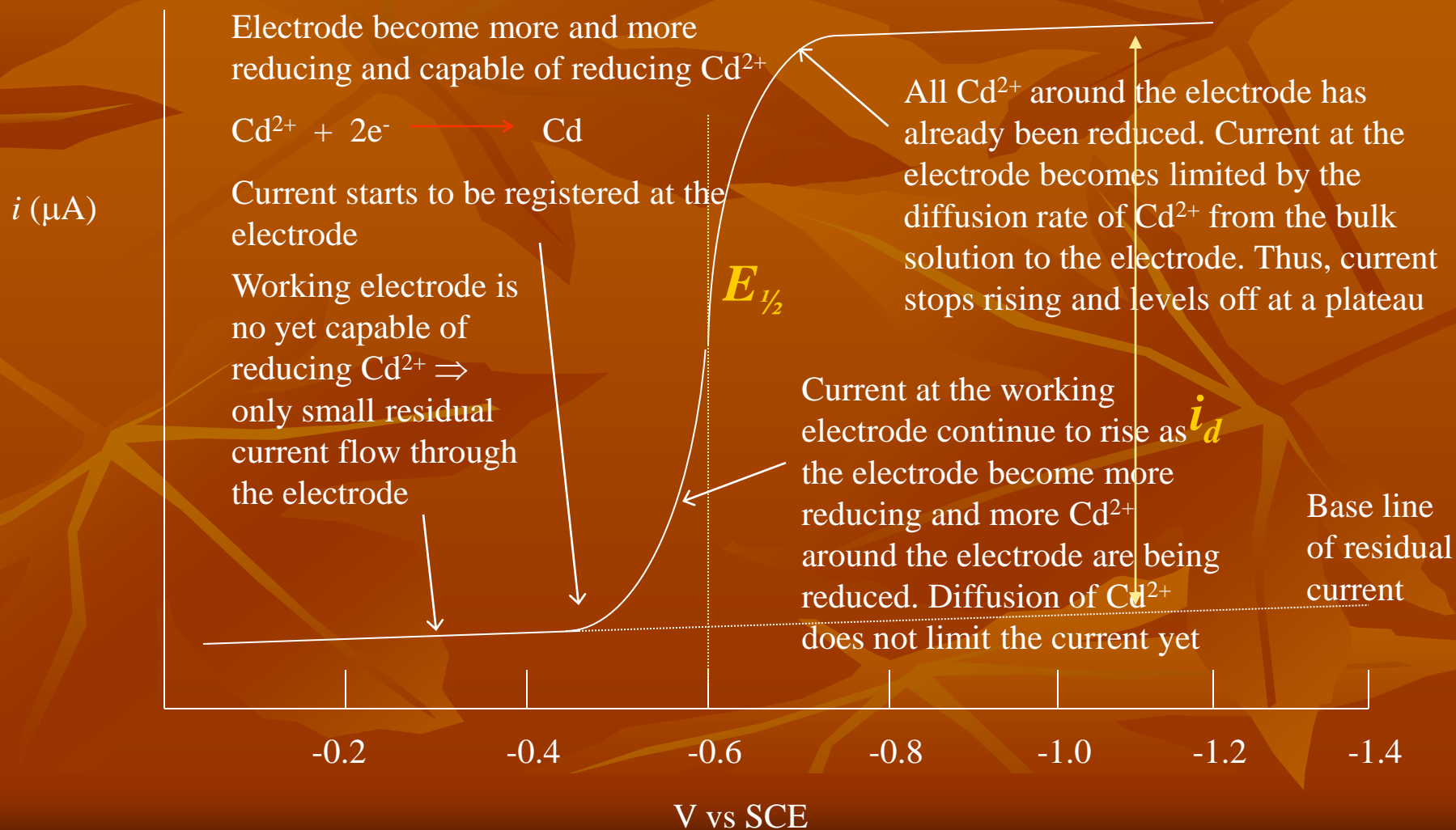
Sample i at same
time interval



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



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

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

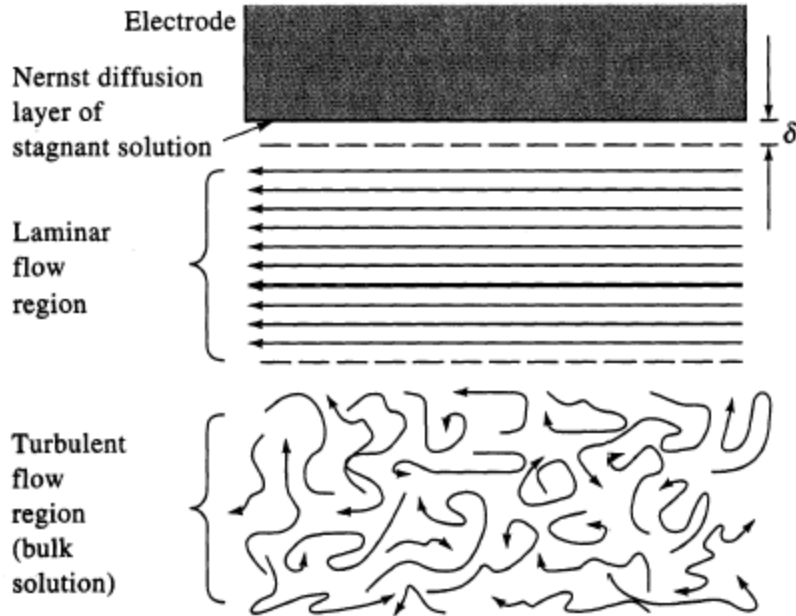
Select about four or five readings on each side of the half-wave potential from the graph of current versus voltage in order to calculate the values of the logarithmic term in the above equation. Indicate on the graph:

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

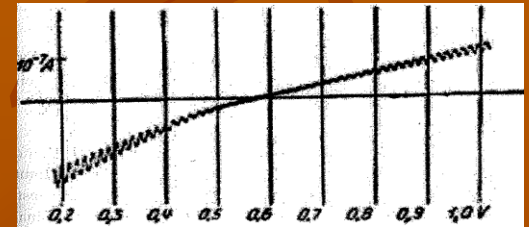
Three transport mechanisms:

- (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)

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

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

■ Where D is the diffusion coefficient of the analyte in the medium (cm^2/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/cm^3 .

Direct Current (DC) polarography

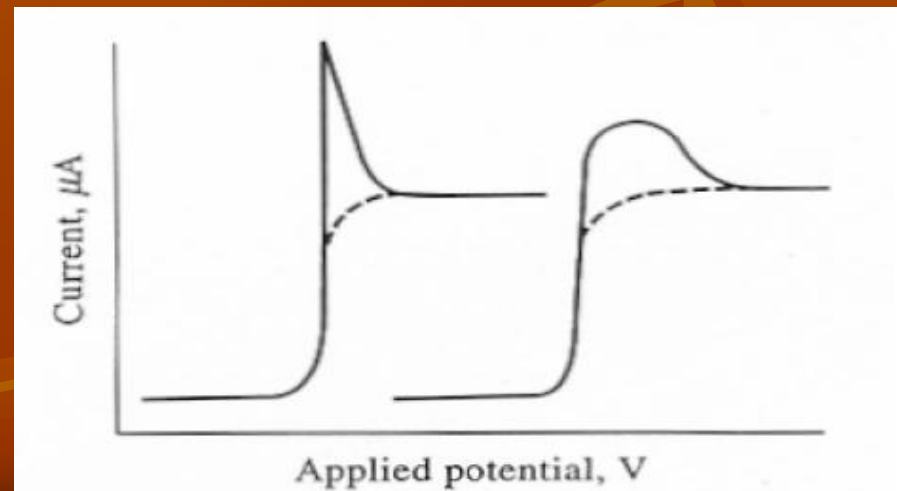
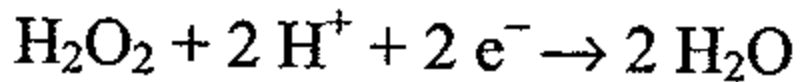
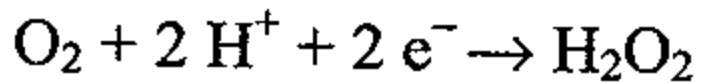
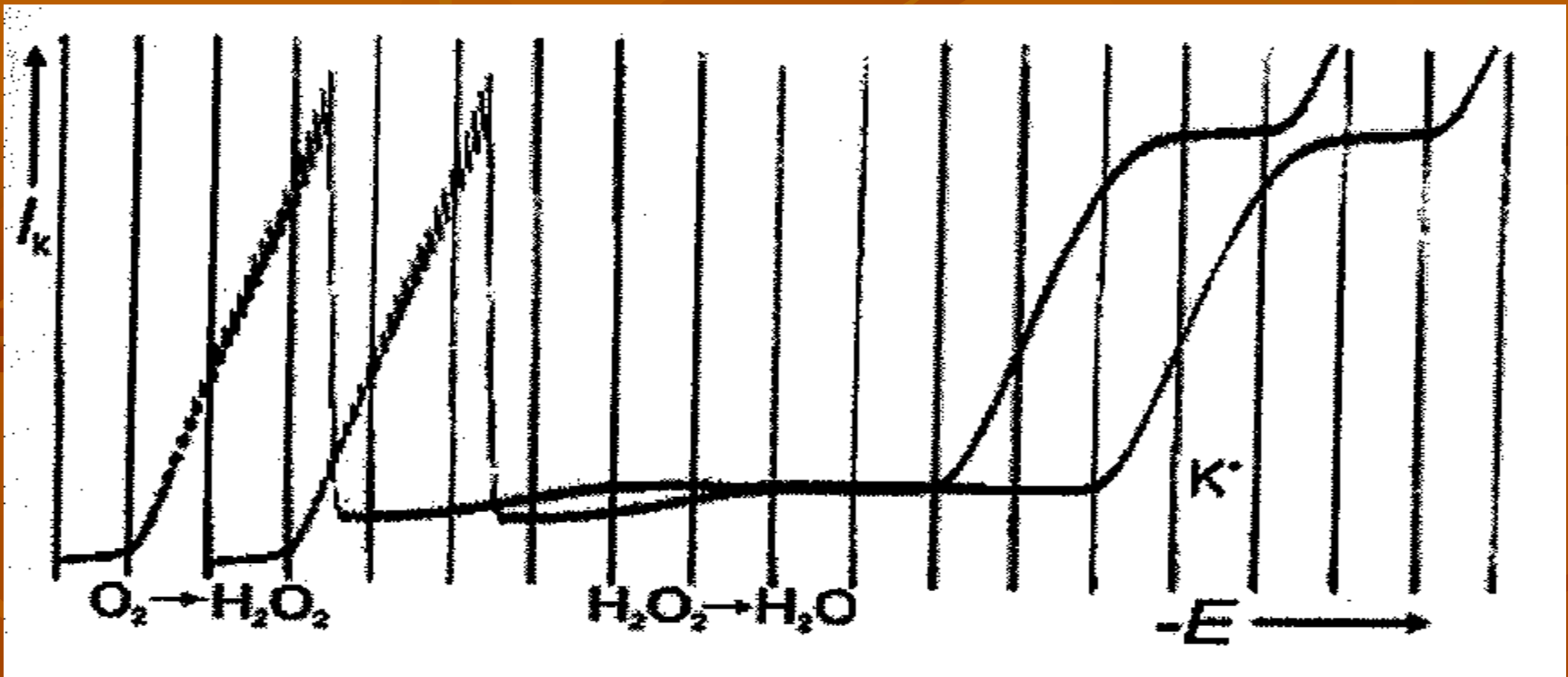
Ilkovič equation

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

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

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

Current maxima

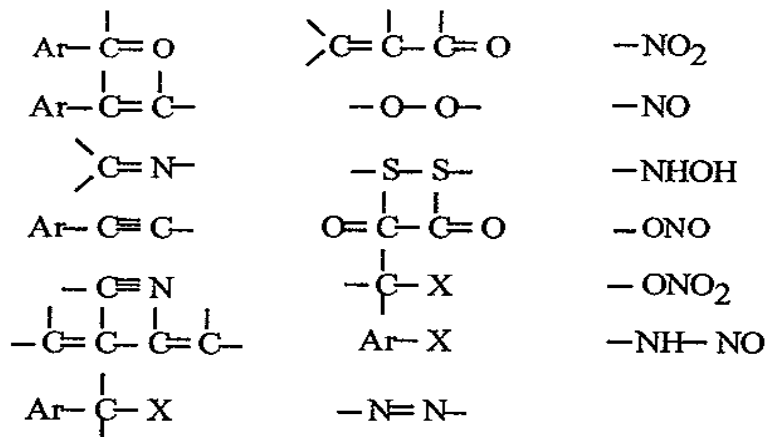


Analytical applications

Skupiny projevující se katodickou vlnou

cathodic

aldehydy, ketony:

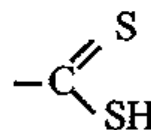
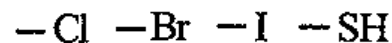


heterocyklické sloučeniny (O,S,N), alkaloidy, vitaminy, hormony, steroidy, sacharidy

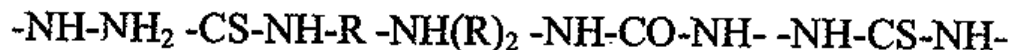
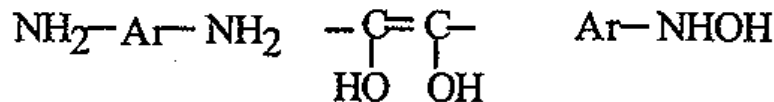
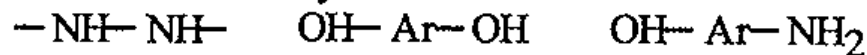
Skupiny projevující se anodickou vlnou

anodic

skupiny reagující se rtuťí:

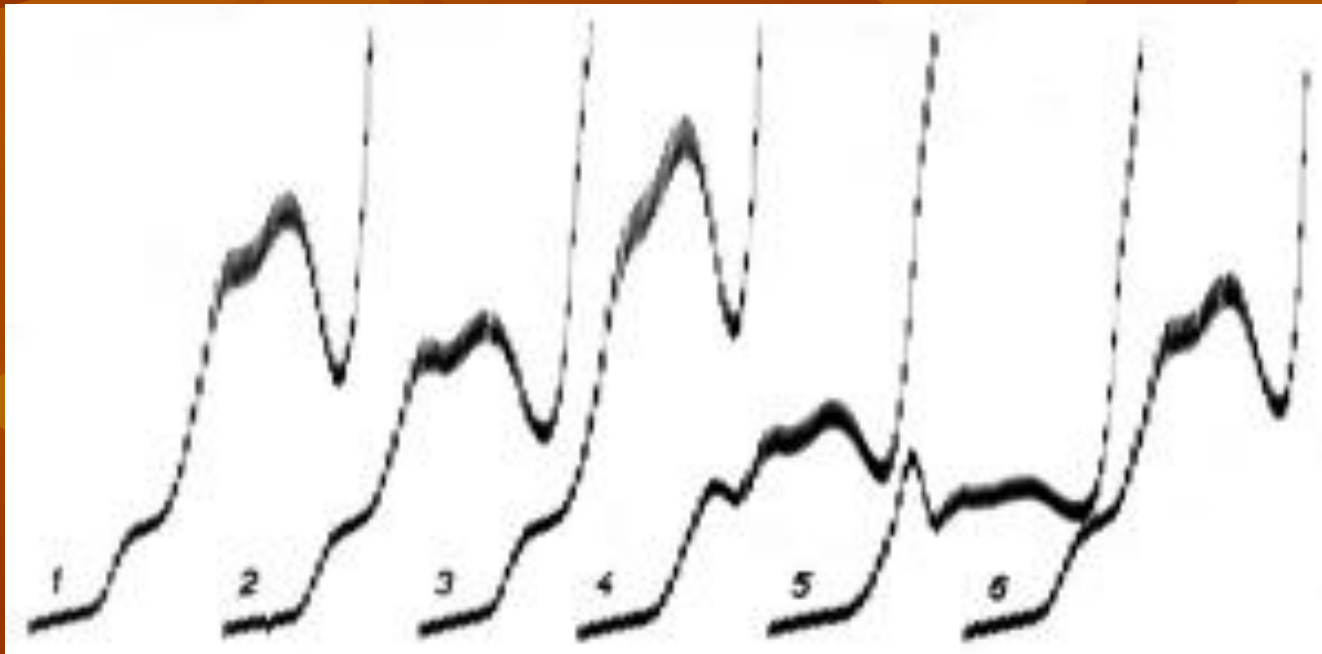


oxidovatelné látky:



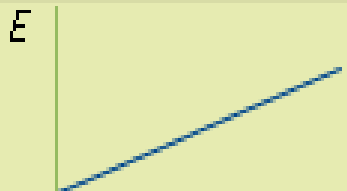
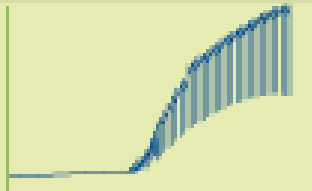
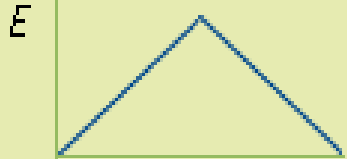
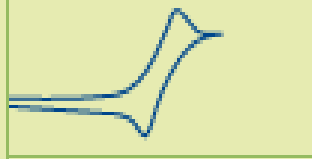
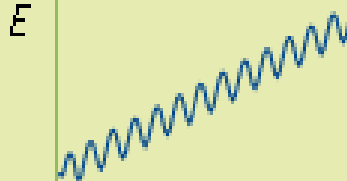
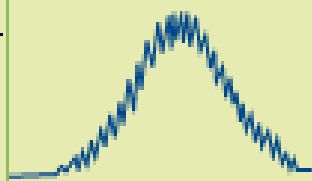
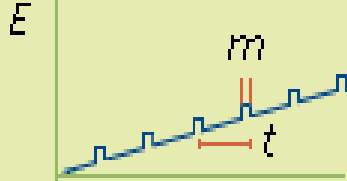
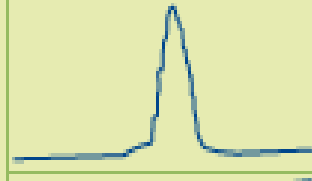
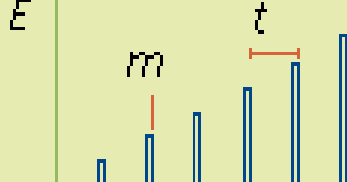
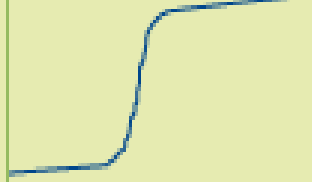
Brdička reaction

Heyrovsk'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.

VOLTAMMETRY

method	potential ramp	polarogram
classical LSV (linear sweep)		
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

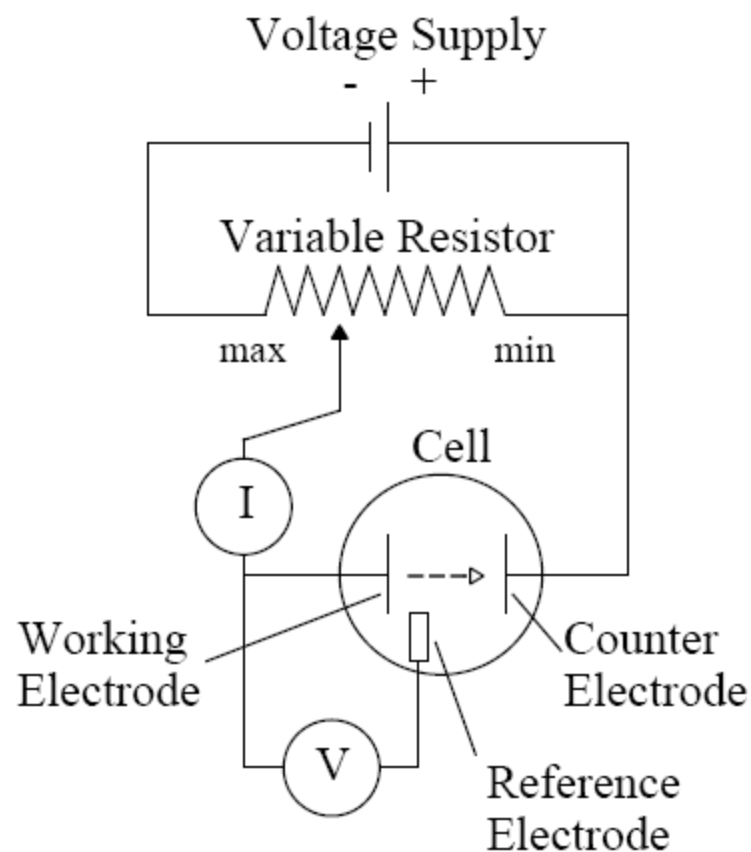
Instrumentation – Three electrodes in solution containing analyte

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:

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

- reaction at the surface of the electrode

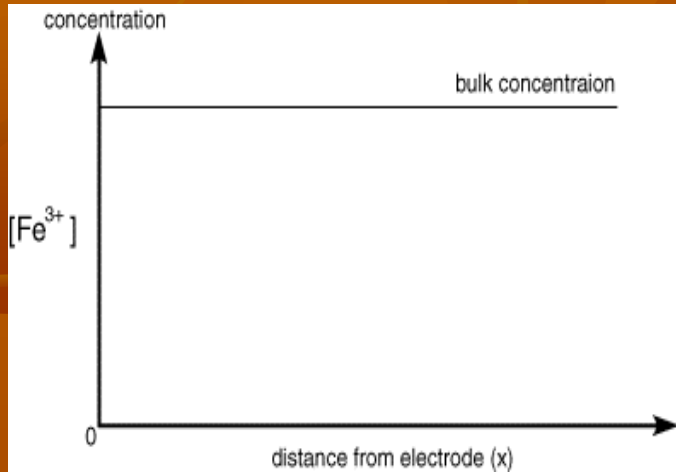
-current generated at electrode by this process is proportional to concentration at surface, which in turn is equal to the bulk concentration

For a planar electrode:

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

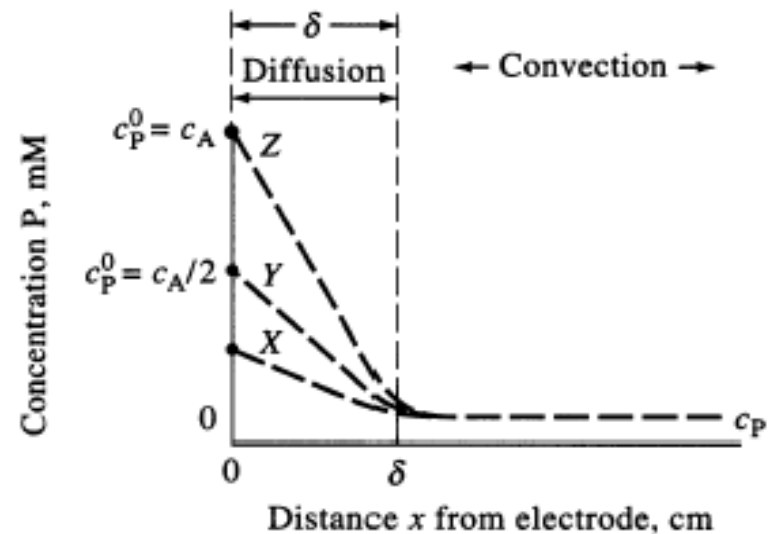
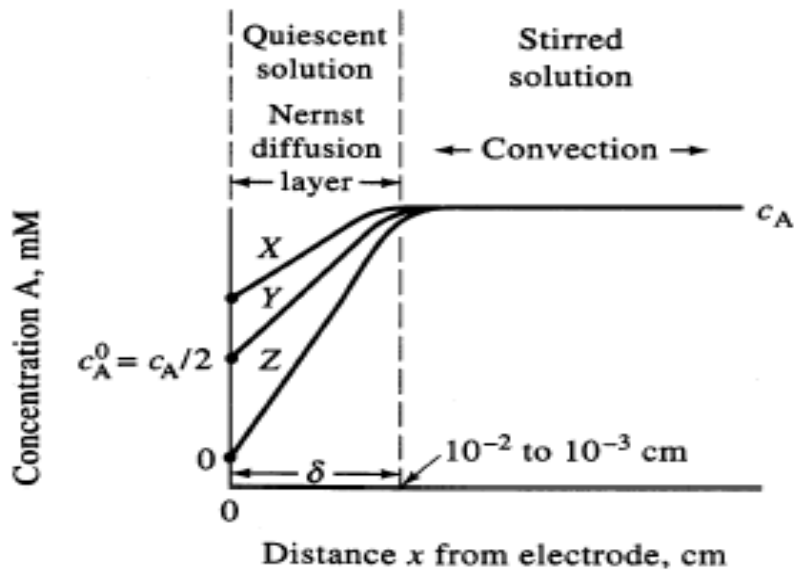
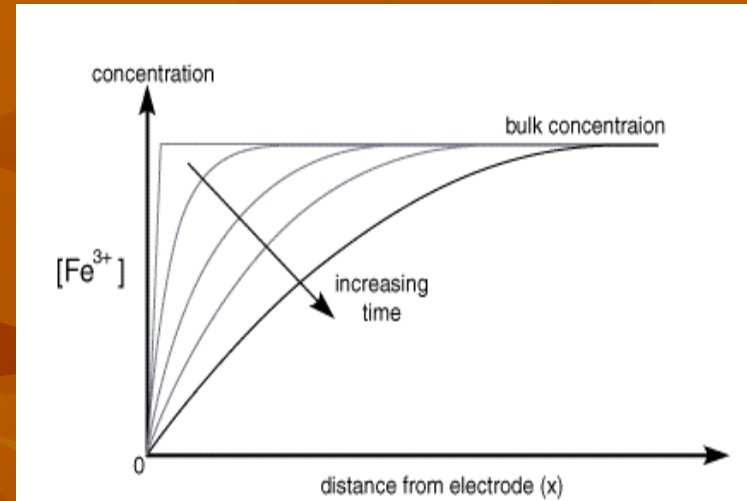
n = number of electrons in ½ cell reaction, F = Faraday's constant, A = electrode area (cm²), D = diffusion coefficient (cm²/s) of A (oxidant)

$\frac{\delta C_A}{\delta x}$ = slope of curve between $C_{Mox,bulk}$ and $C_{Mox,s}$

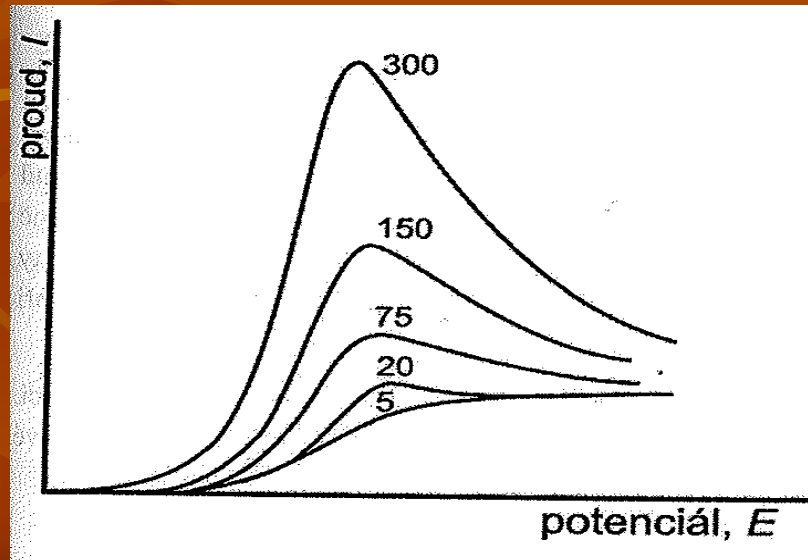
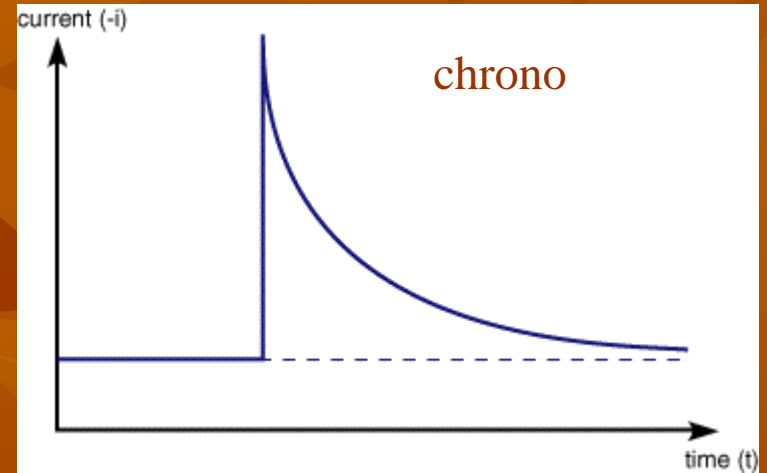
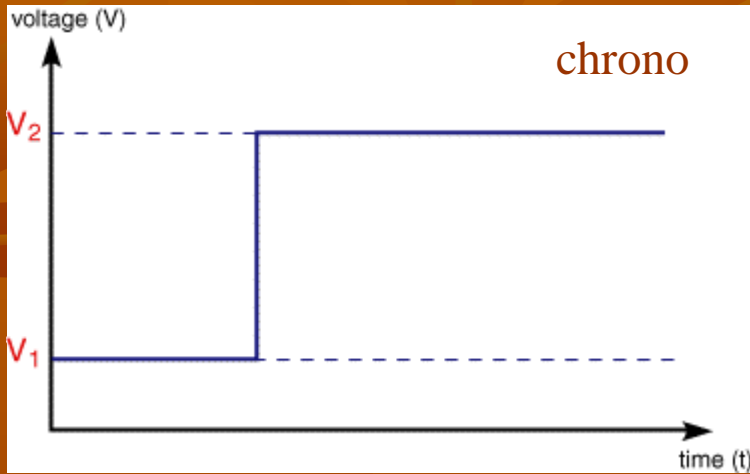


Apply

Potential



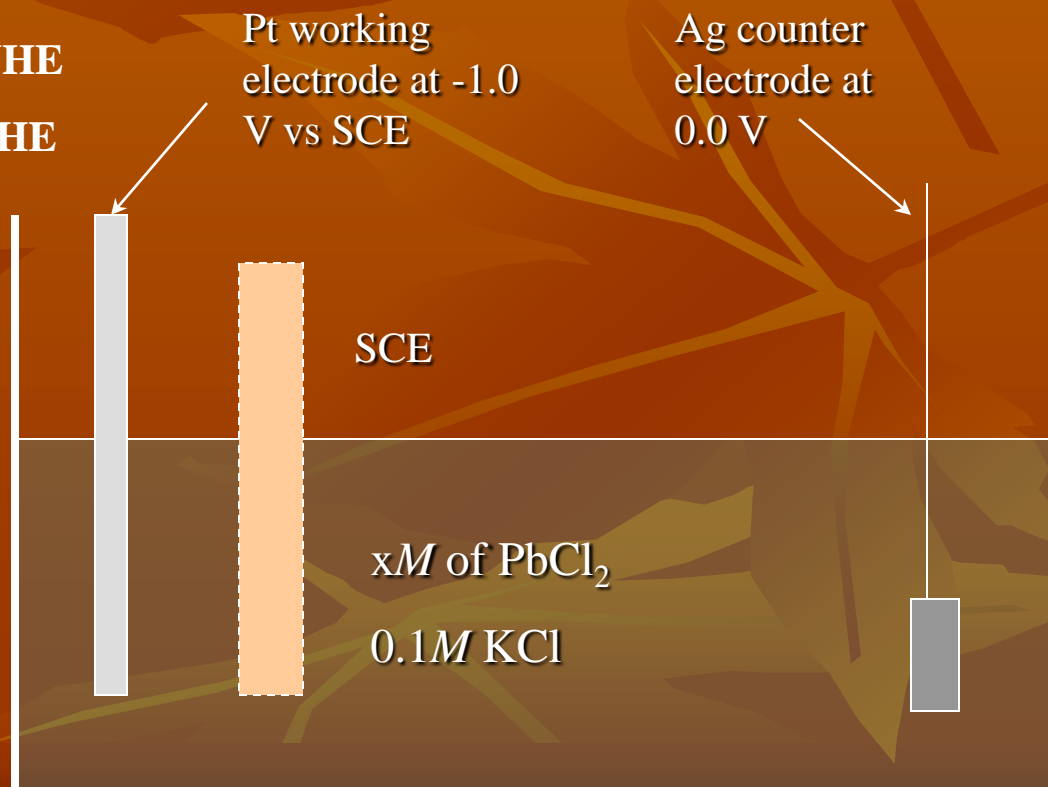
As time increases, push banding further and further out.
Results in a decrease in current with time until reach point where convection of analyte takes over and diffusion no longer a rate-limiting process.

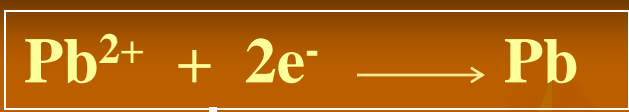


Voltammetric analysis

Analyte selectivity is provided by the applied potential on the working electrode.

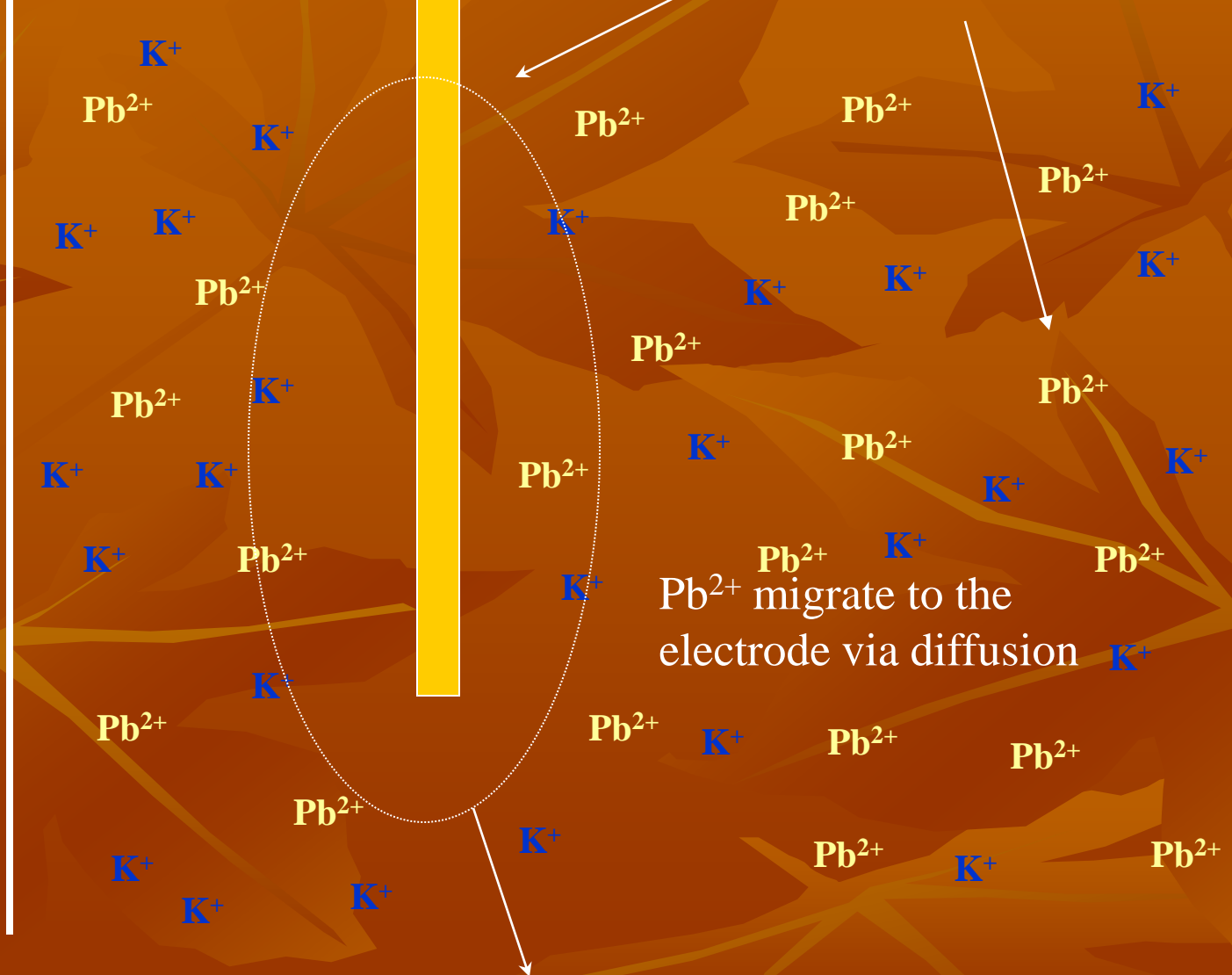
- ♦ Electroactive species in the sample solution are drawn towards the working electrode where a half-cell redox reaction takes place.
- ♦ Another corresponding half-cell redox reaction will also take place at the counter electrode to complete the electron flow.
- ♦ The resultant current flowing through the electrochemical cell reflects the activity (i.e. \approx concentration) of the electroactive species involved





-1.0 V vs SCE

Concentration gradient created between the surrounding of the electrode and the bulk solution

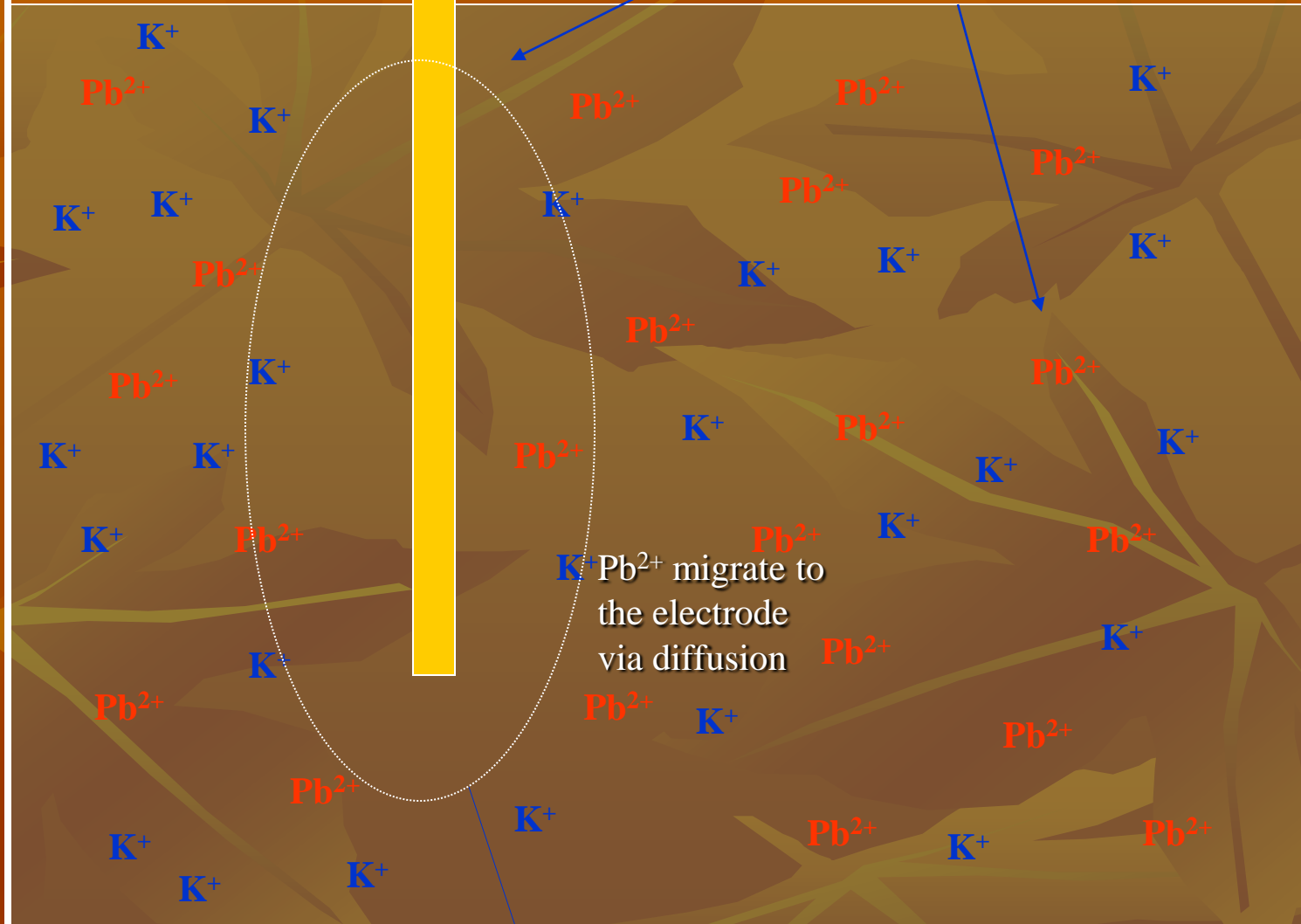


Layers of K^+ build up around the electrode stop the migration of Pb^{2+} via coulombic attraction



-1.0 V vs SCE

Concentration gradient created between the surrounding of the electrode and the bulk solution

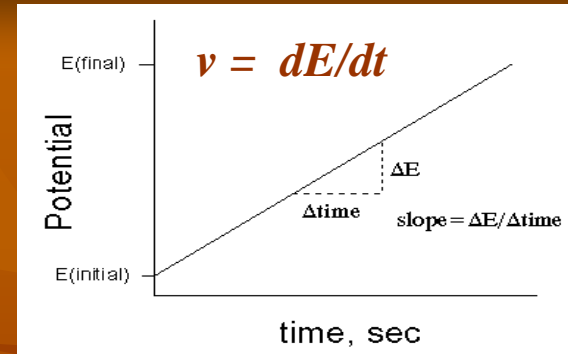
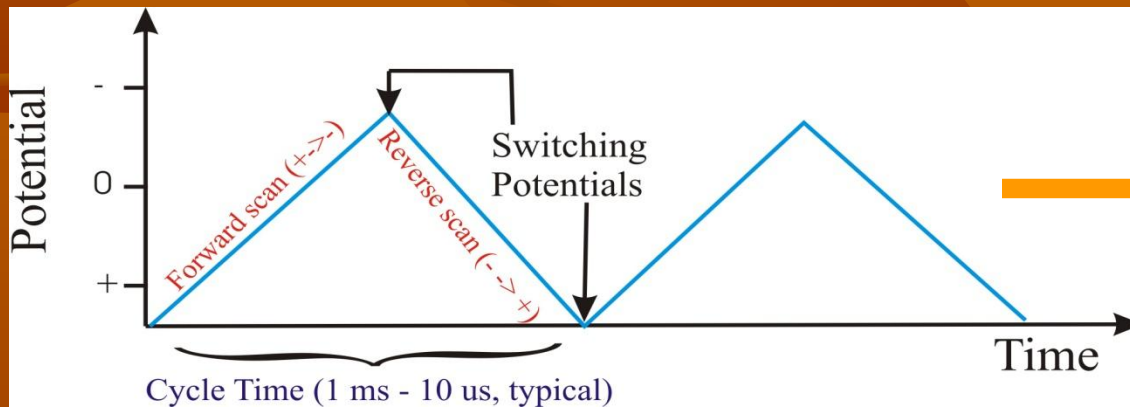


Pb^{2+} migrate to the electrode via diffusion

Layers of K^+ build up around the electrode stop the migration of Pb^{2+} via coulombic attraction

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



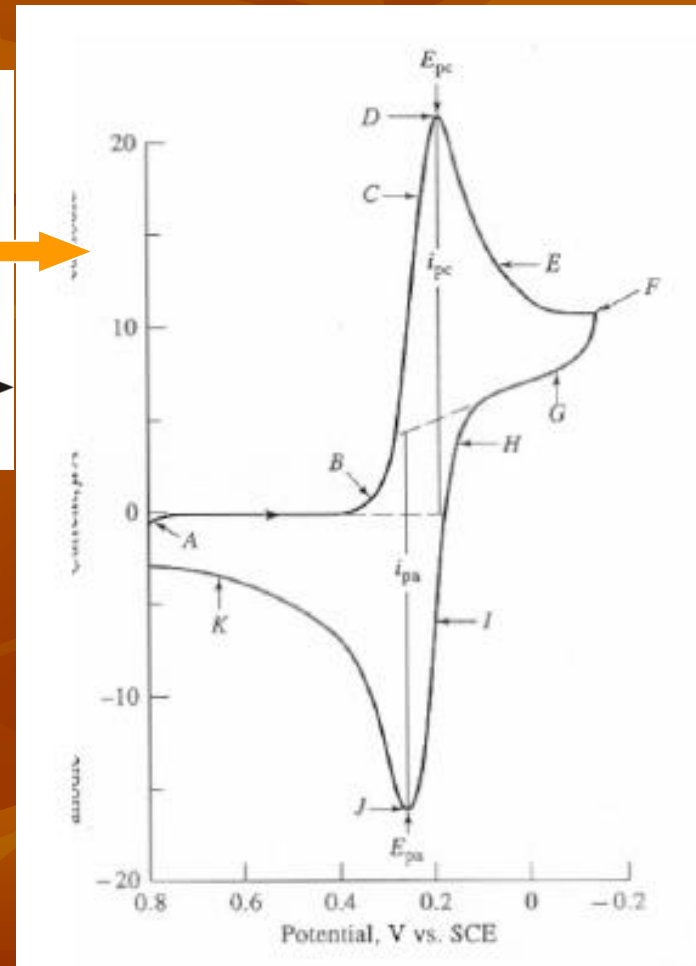
Randles – Sevcik equation

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

I_p (A) A (cm²), D (cm².s⁻¹), v (V.s⁻¹), c_{Ox} (mol.cm⁻³)

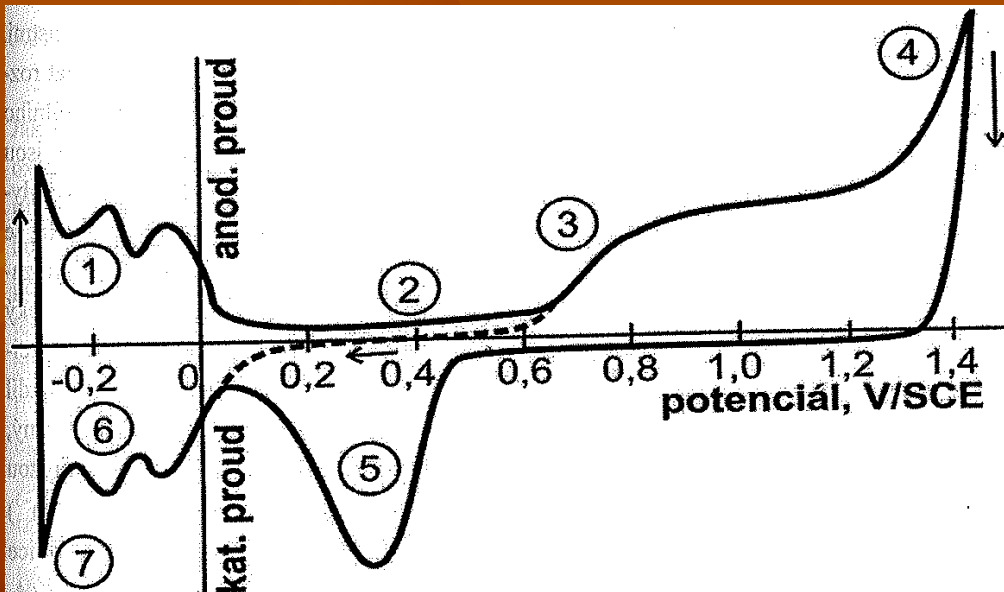
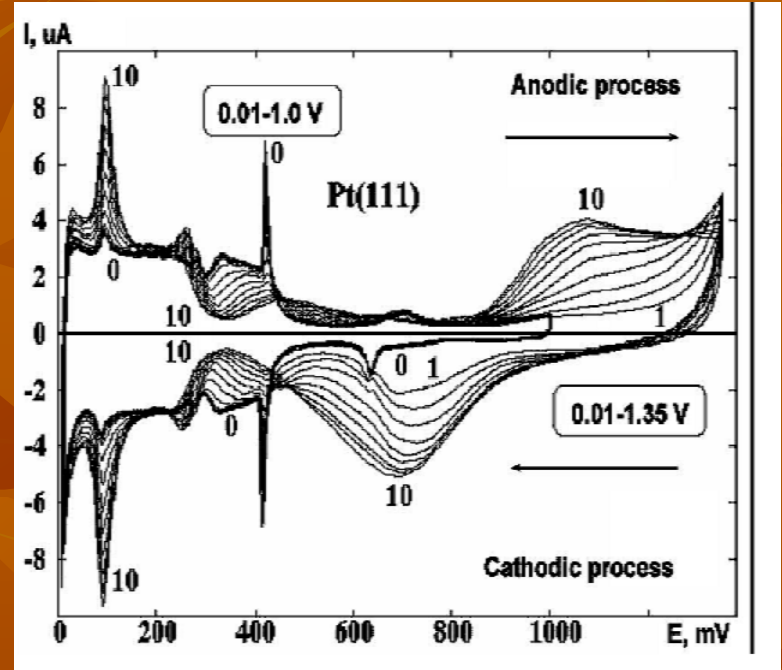
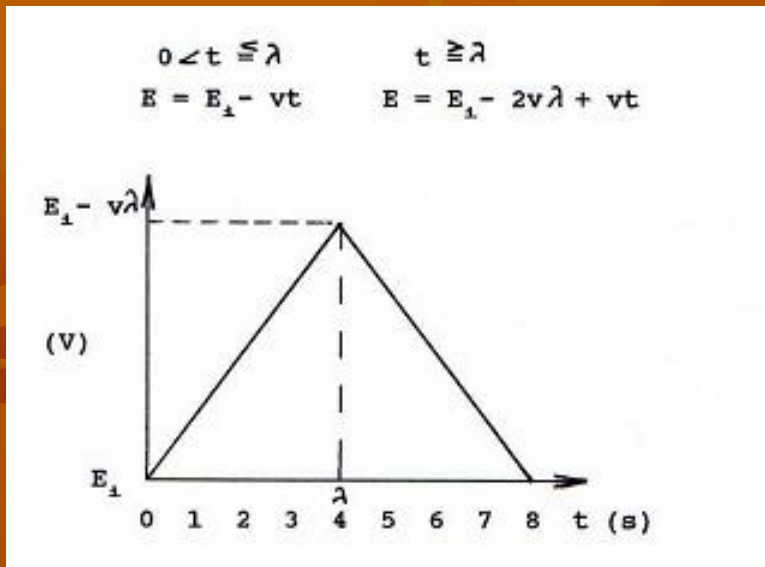
Delahay equation

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



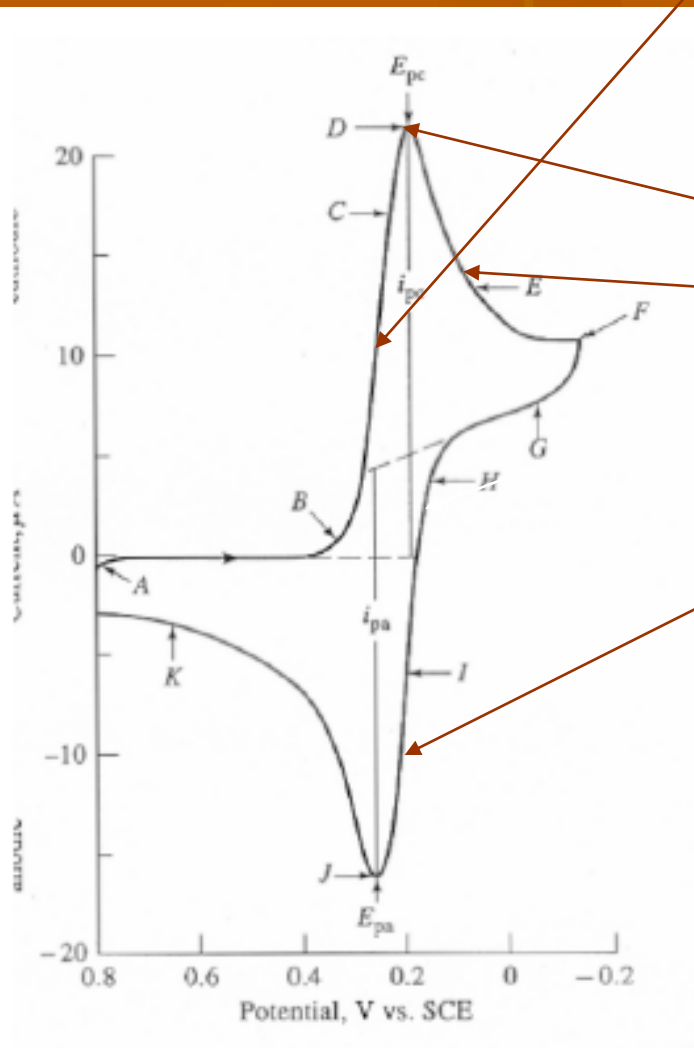
Cyclic voltammogram

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

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



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



☑ driven by Nernst equation

- ② concentrations made to meet Nernst equation at surface

☑ eventually reach i_{max}

☑ solution not 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

- ② E_{pc} – cathodic peak potential
- ② E_{pa} – anodic peak potential
- ② i_{pc} – cathodic peak current
- ② i_{pa} – anodic peak potential

☑ i_{pc} / i_{pa}

☑ $\delta(E_{pa} - E_{pc}) = 0.0592/n$,

where n = number of electrons in reaction

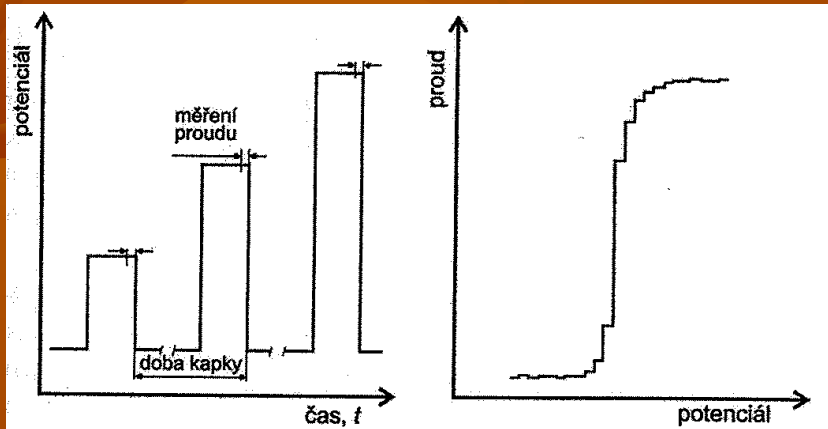
☑ $E^0 = \text{midpoint of } E_{pa} \rightarrow E_{pc}$

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

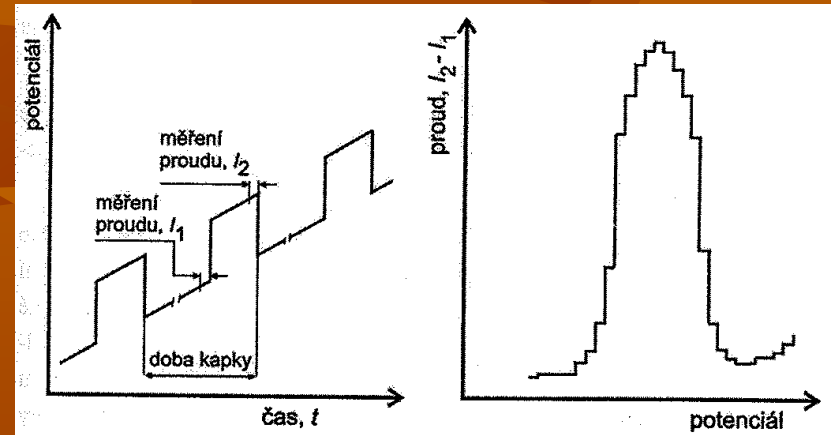
$$|E_p - E_{p/2}| = 0.0565/n$$

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

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

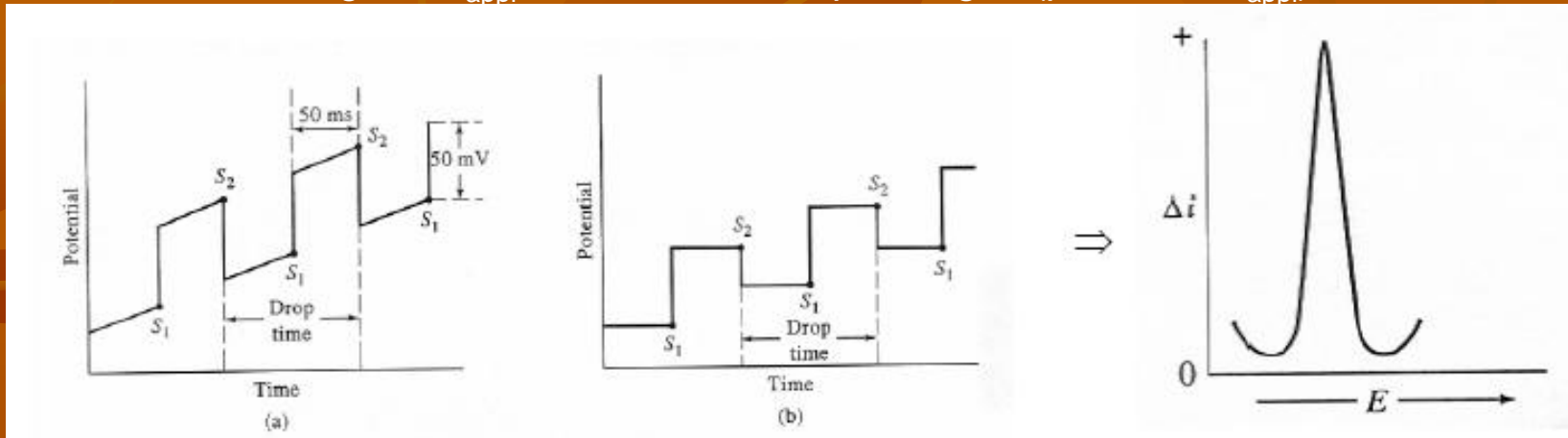
$$\sigma = \exp \left[(nf / RT)(\Delta E / 2) \right]$$

ΔE ... pulse amplitude

f ... frequency

Pulse Polarography (Voltammetry)

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



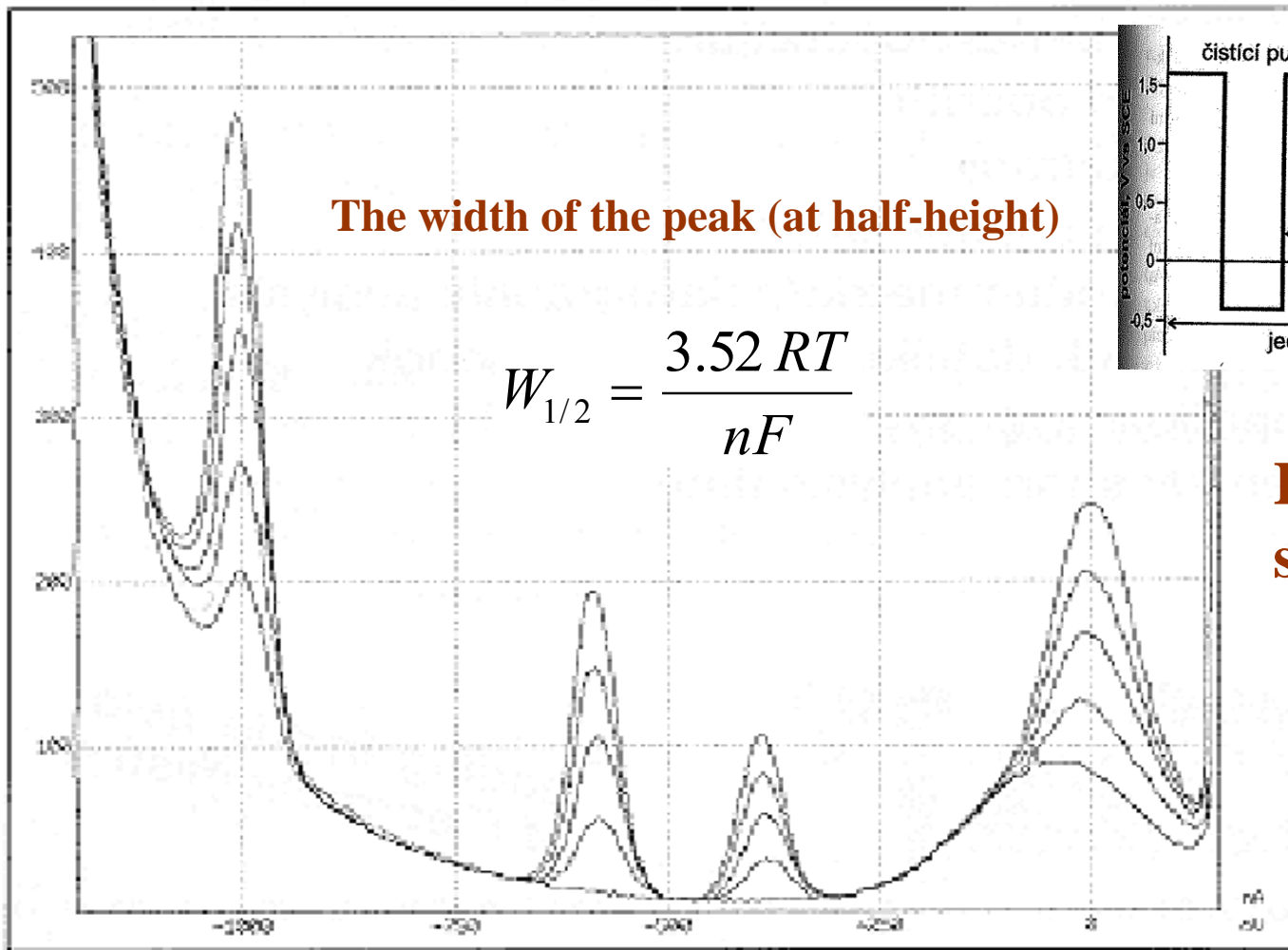
Measure two potentials at each cycle

- S_1 before pulse S_2 at end of pulse
- plot Δi vs. E ($\Delta i = E_{S_2} - E_{S_1}$)
- peak height \sim concentration
- for reversible reaction, peak potential \rightarrow standard potential
- derivative-type polarogram

Advantages of DPP (DPV)

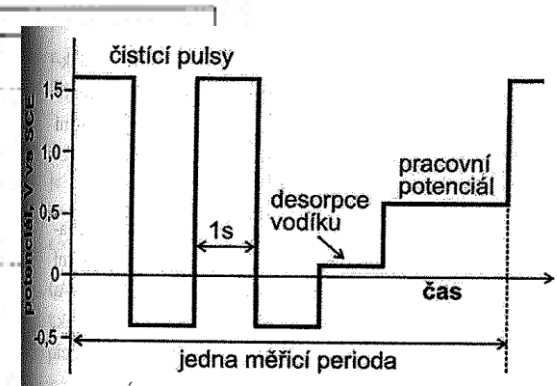
- can detect peak maxima differing by as much as 0.044 – 0.05 V
- 0.2V peak separation for normal polarography
- can do more elements per run
- decrease limits of detection by 100-1000x compared to normal polarography

Differential Pulse Polarography (Voltammetry)



The width of the peak (at half-height)

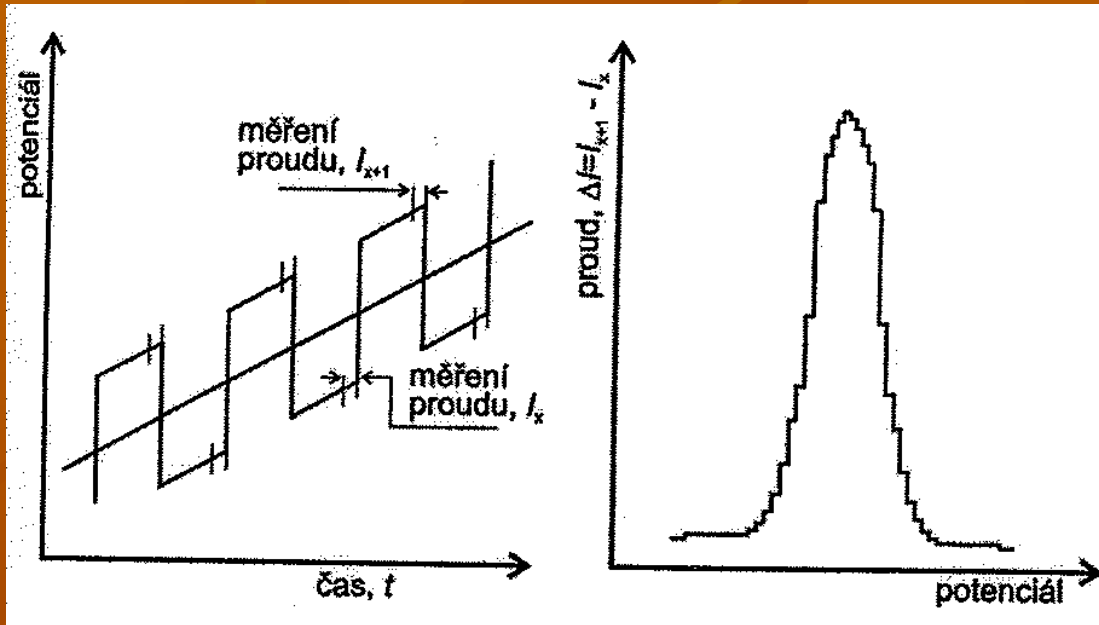
$$W_{1/2} = \frac{3.52 RT}{nF}$$



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)