Electrochemistry

CHEM 5390

Electrical Double Layer

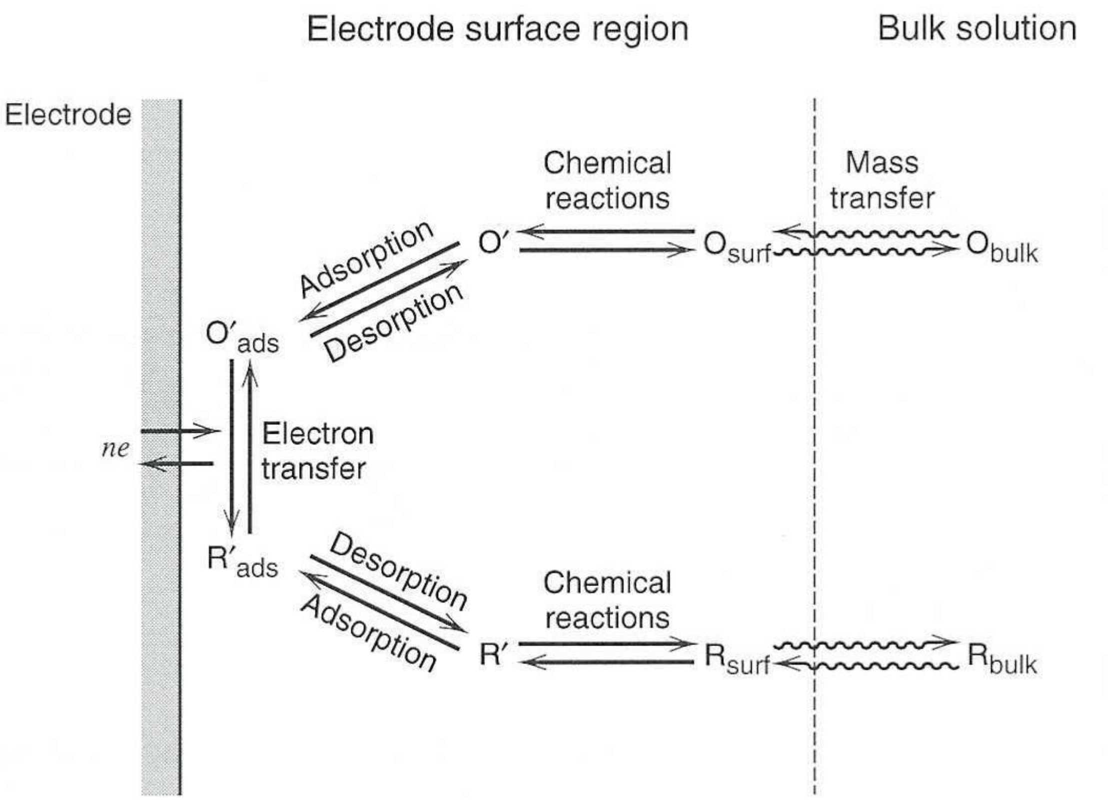


Figure 1.3.6 Pathway of a general electrode reaction.

Mass Transfer

Nernst-Planck Equation

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

$J_i(x)$ – flux of species i (mol/s cm^2) at distance x from surface.

D_i – diffusion coefficient (cm^2/s)

$\partial Ci(x)/\partial x$ – concentration gradient at distance x

$\partial \phi(x)/\partial x$ – potential gradient

z_i and C_i – charge (dimensionless) and concentration (mol/cm^3) of species i

$\upsilon(x)$ – velocity (cm/s)

Mass Transfer

<u>Diffusion</u>

Boundary Conditions

For an electrochemical problem, a diffusion equation is written for each dissolved species. The equation for C_O, C_R,… as a function of x and t requires an initial condition (concentration profile at t = 0) and two boundary conditions (functions at certain values of x).

Mass Transfer

Steady State Mass Transfer

$O + ne \leftarrow\rightarrow R$

When electrolysis starts, [O] at electrode surface, Co(x = 0) becomes smaller than value in the bulk, C_O^*.

Mass Transfer

Steady State Mass Transfer

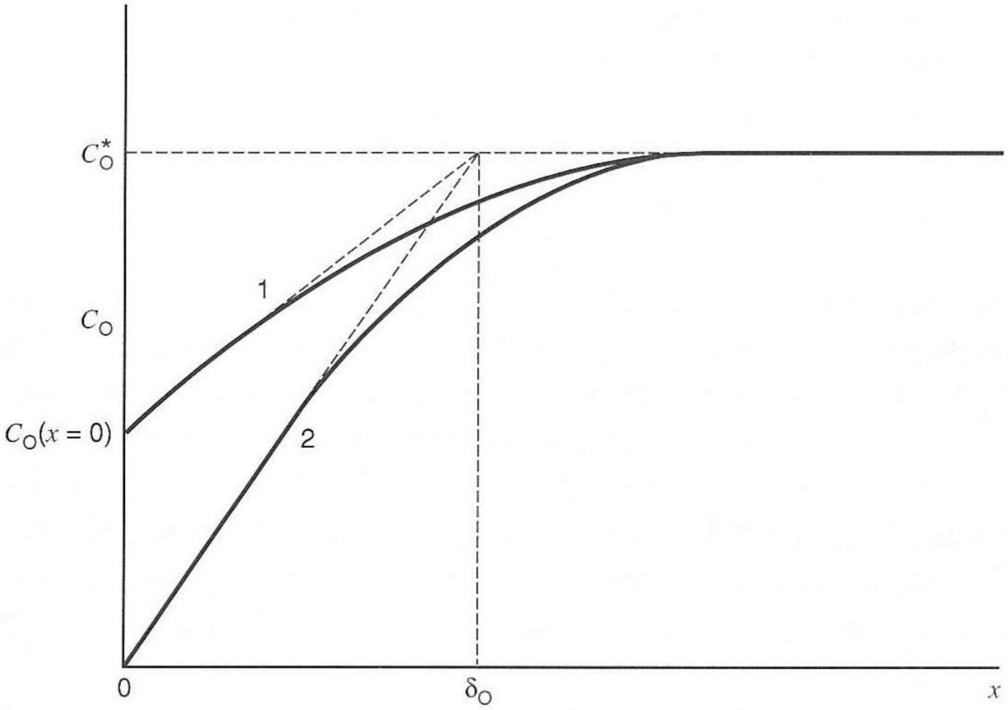


Figure 1.4.1 Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). $x = 0$ corresponds to the electrode surface and δ_O is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (*1*) where $C_O(x = 0)$ is about $C_O^*/2$, (*2*) where $C_O(x = 0) \approx 0$ and $i = i_l$.

Potential Step Methods

Quantitative Information

Alternatives

- Large amplitude step***

  Potential is stepped to mass controlled region (diffusion control), so concentration at electrode is near zero, i controlled by mass transfer.

- Small-amplitude potential changes

  Close to equilibrium, $i = -i_o f \eta$

- Reversible electrode process

  $E = E^{o\prime} + RT/nF \ \ln C_O(0,t)/C_R(0,t)$

- Totally reversible process

  k^o is small – in tafel regions

- Quasireversible system

  Much more complicated (Ch. 12)

Potential Step Methods

Potential Step Methods – have mass transport of electroactive species only by diffusion and have an electrode area, A, small compared to solution volume, so the bulk is not altered.

Potential Step Methods

Considered a large amplitude controlled potential technique.

(small amplitude techniques fall into the linear region and are useful for kinetic studies – electron transfer)

Operate in the non-linear region in which current is exponentially related to overpotential.

Useful for certain analytical problems and studies of coupled chemical reactions.

Mass Transfer

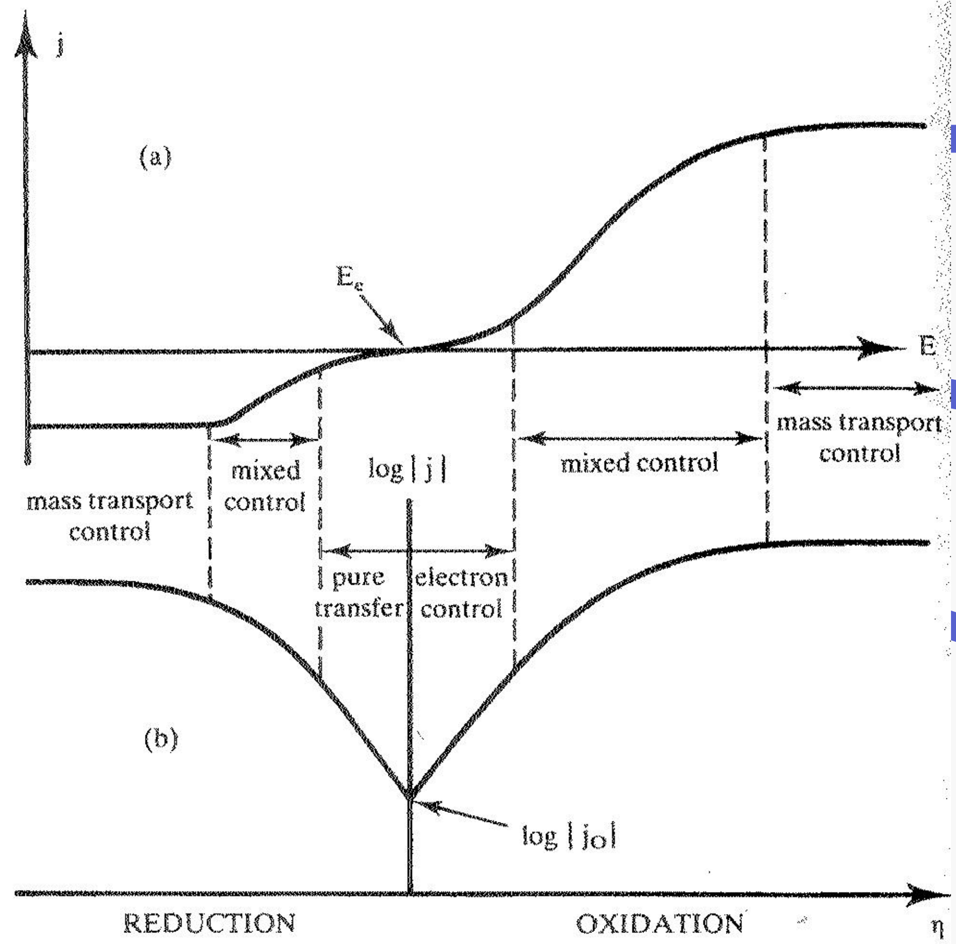


Figure 1.14 *j — E response and the corresponding log j — η curve for an irreversible electrode reaction* $O + e^- \rightleftharpoons R$. $c_R = 10c_O$.

Potential Step Methods

Overview of Step Experiments

For controlled step experiments can record:

- current as a function of time (chronoamperometry)
- potential as a function of time (chronopotentiometry)
- charge as a function of time (chronocoulometry)
- absorbance as a function of time (chronoabsorptometry)

All based on the same excitation function of one or more potential steps.

Potential Step Methods

Chronocoulometry

Integrate the current, to obtain the charge as a function of time, Q(t).

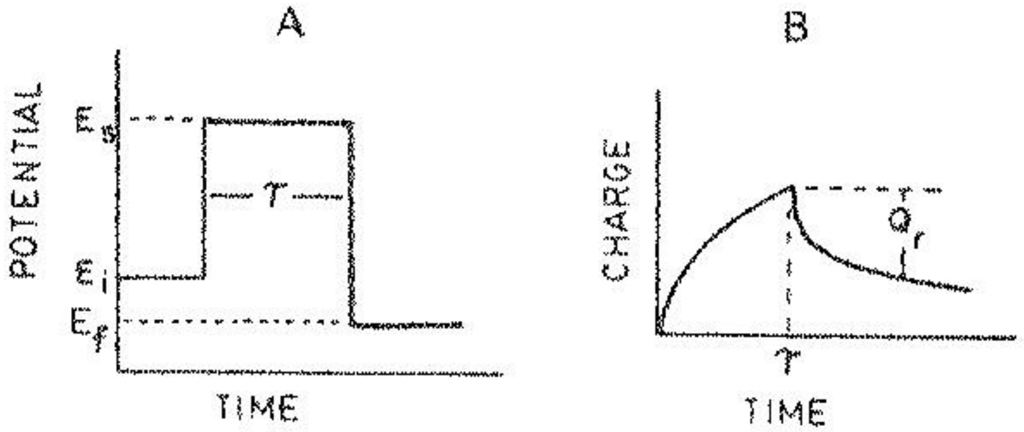


Figure 3.5 (A) Potential excitation for double potential step. (B) Charge-time monitored response (chronocoulogram).

Potential Step Methods

The number of electrons that cross an interface is related stoichiometrically to the chemical reaction (amount of reactant and product).

The number of electrons is measured in terms of total charge, Q.

Charge is in units of coulombs (C),

$1\ C = 6.24 \times 10^{18}$ electrons

Potential Step Methods

Faraday’s Law

Passage of 96,485.4 C equals consumption of 1 mole of reactant or production of 1 mole of product in a one electron reaction.

Current, i, = rate of flow of coulombs (or e-’s), where 1 ampere (A) = 1 C/sec.

Potential Step Methods

Chronocoulometry

Large Amplitude Potential Step

Simplest experiment is Cottrell case for planar electrode.

$$Q_d = (2nFA\, D_O^{1/2}\, C_O^*\, t^{1/2})/\pi^{1/2}$$

Plot of Q_d vs $t^{1/2}$ is linear, slope can help determine n, A, D_O, or C_O^*

Potential Step Methods

Chronocoulometry

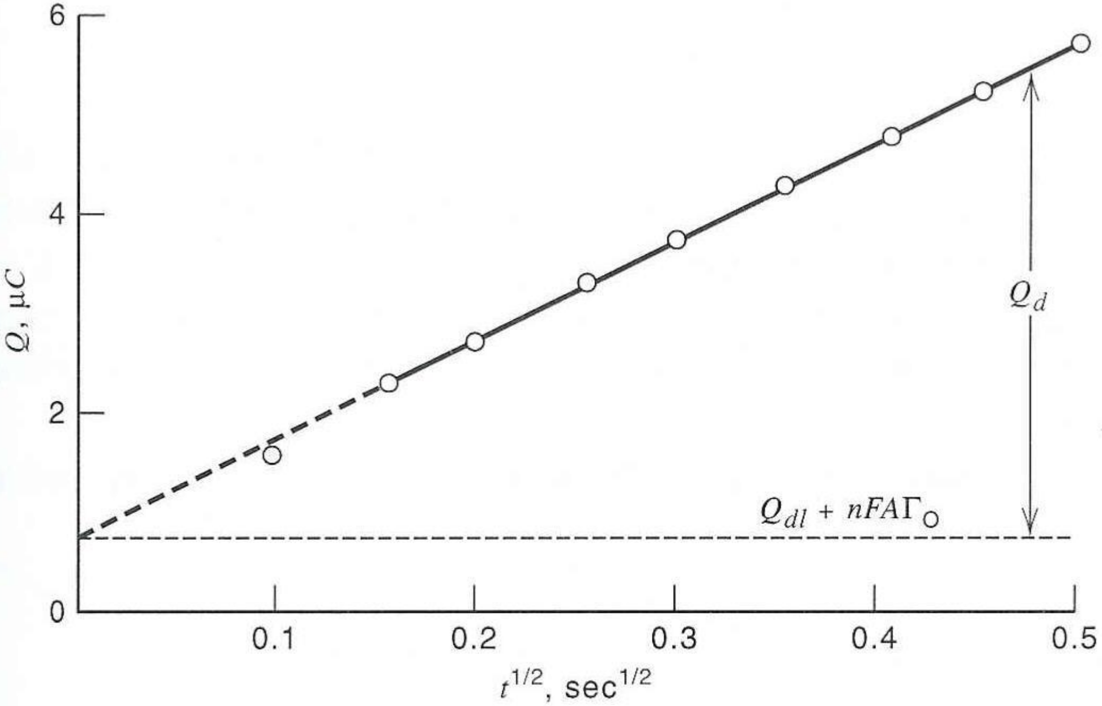


Figure 5.8.1 Linear plot of chronocoulometric response at a planar platinum disk. System is 0.95 m*M* 1,4-dicyanobenzene (DCB) in benzonitrile containing 0.1 *M* tetra-*n*-butylammonium fluoborate. Initial potential: 0.0 V *vs.* Pt QRE. Step potential: −1.892 V *vs.* Pt QRE. $T = 25°\text{C}$, $A = 0.018\ \text{cm}^2$. $E^{0'}$ for $\text{DCB} + e \rightleftarrows \text{DCB}^{\bar{\cdot}}$ is −1.63 V *vs.* QRE. The actual chronocoulometric trace is the part of Figure 5.8.2 corresponding to $t < 250$ ms. [Data courtesy of R. S. Glass.]

Potential Step Methods

Chronocoulometry

The measured charge represents contributions from three possible sources:

- Electrolysis of electroactive species in solution at a rate that is controlled by diffusion to the electrode
- Electrolysis of electroactive species that is absorbed on the electrode surface
- Charging of the electrode-electrolyte double layer capacitance to the new potential

$$Q_{total} = Q_{diff} + Q_{ads} + Q_{dl}$$

Potential Step Methods

Chronocoulometry

$$Q_{\text{total}} = Q_{\text{diff}} + Q_{\text{ads}} + Q_{\text{dl}}$$

$$Q_{total} = \int_0^i dt = \frac{2nFAC_o D_o^{\frac{1}{2}} t^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} + nFA\Gamma_o + Q_{dl}$$

Potential Step Methods

Chronocoulometry

Taking into account additional components of Q:

$$Q = (2nFA\,D_O^{1/2}\,C_O^*\,t^{1/2})/(\pi^{1/2}) + Q_{dl} + nFA\Gamma_o$$

Q_{dl} = capacitive charge

$nFA\Gamma_o$ – for reduction of surface species, Γ_o (mol/cm^2) of adsorbed O

Approximate value for $nFA\Gamma_o$ can be obtain from the y-intercept and subtract out Q_{dl} by a supporting electrolyte only experiment.

Potential Step Methods

Chronocoulometry

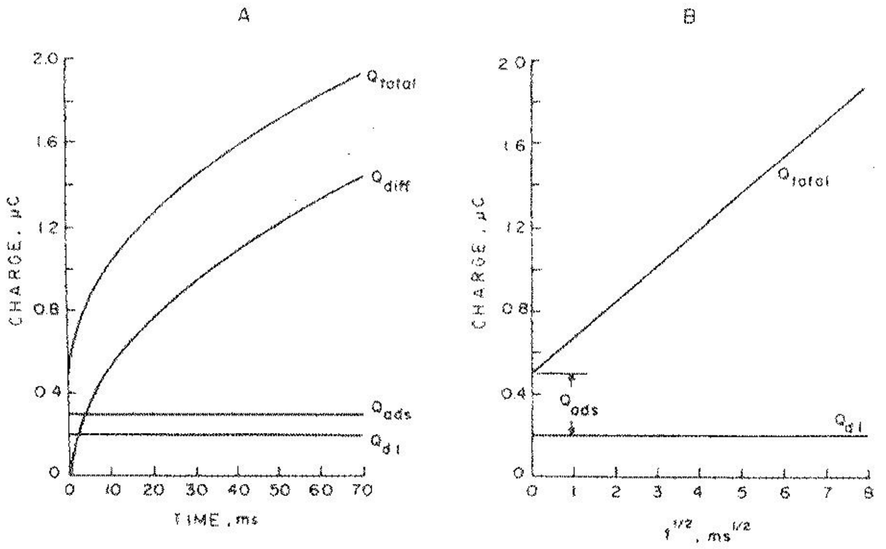


Figure 3.6 Effect of adsorption of electroactive species on chronocoulometry. (A) Charge-time curves for individual components contributing to total charge (Q_{total}) as in Equation 3.8b. (B) Plots of charge versus $t^{1/2}$ for Q_{total} and Q_{dl}.

Plot Q versus $t^{1/2}$:

The double layer charging and reducing of absorbed O is instant whereas the charging for reduction of O in solution is diffusion controlled (time dependence)

Potential Step Methods

Chronocoulometry

Integrate the current, to obtain the charge as a function of time, Q(t).

Advantages:

- measured signal often grows with time, so later part of transient (least distorted) offers better signal-to-noise ratio.
- integration smooths random noise on the current transients.
- can distinguish contributions to Q(t) from double-layer charging and from electrode reactions of absorbed species to diffusing electroreactants (study surface processes).

Potential Step Methods

Double Step Chronocoulometry

Reversal Experiments under Diffusion Control

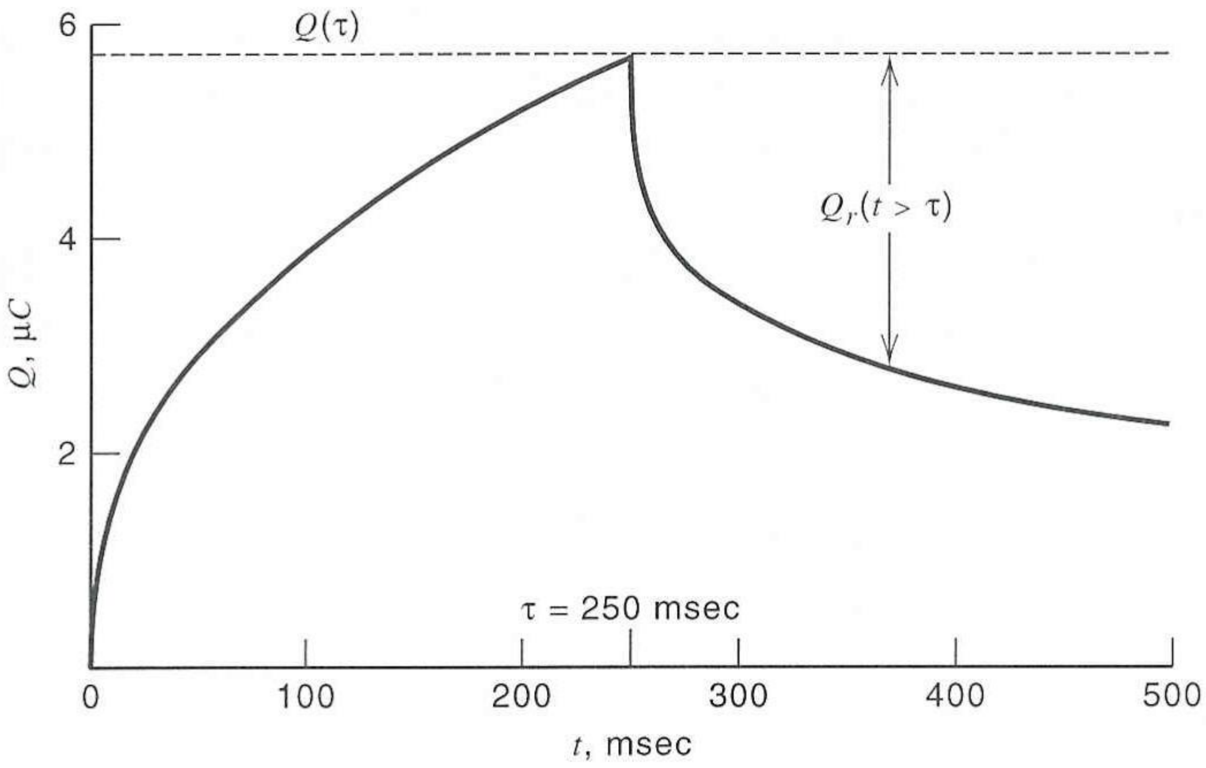


Figure 5.8.2 Chronocoulometric response for a double-step experiment performed on the system of Figure 5.8.1. The reversal step was made to 0.0 V *vs.* QRE. [Data courtesy of R. S. Glass.]

Potential Step Methods

Chronocoulometry

Reversal Experiments under Diffusion Control

Plot of Q_r versus θ is linear (Anson plot)

where $\theta = [\tau^{1/2} + (t - \tau)^{1/2} - t^{1/2}]$

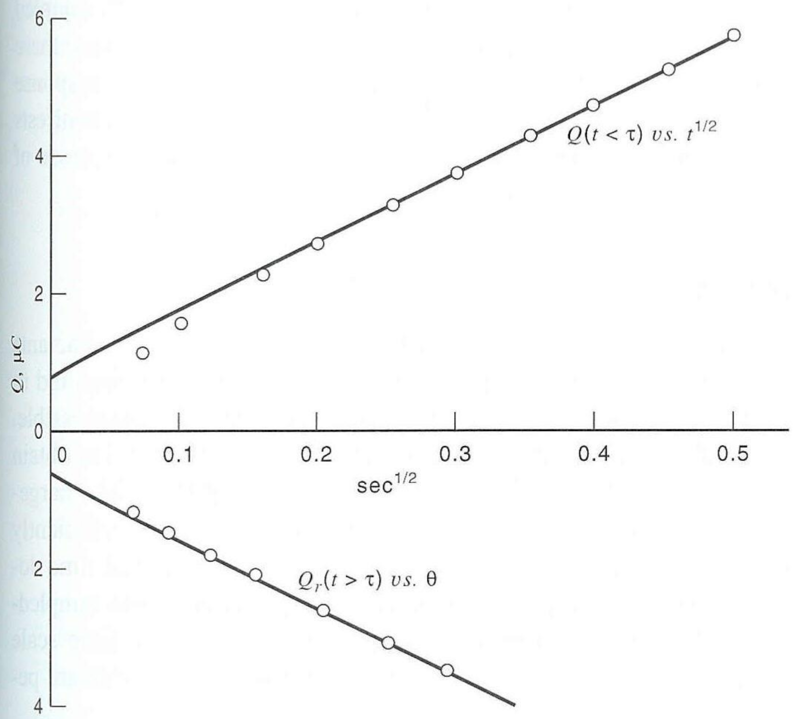


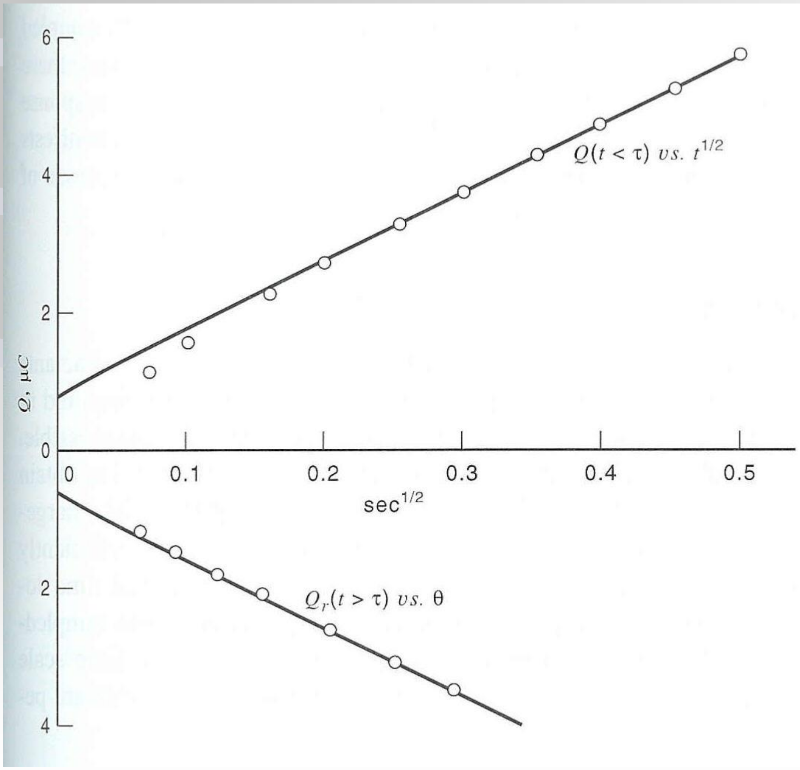
Figure 5.8.3 Linear chronocoulometric plots for data from the trace shown in Figure 5.8.2. For $Q(t < \tau)$ *vs.* $t^{1/2}$, the slope is 9.89 $\mu C/s^{1/2}$ and the intercept is 0.79 μC. For $Q_r(t > \tau)$ *vs.* θ, the slope is 9.45 $\mu C/s^{1/2}$ and the intercept is 0.66 μC. [Data courtesy of R. S. Glass.]

Potential Step Methods

Chronocoulometry

Reversal Experiments under Diffusion Control

Good to evaluate adsorbed species, from plot, O is adsorbed and R is not, the difference between the intercepts is $nFA\Gamma_o$.



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Potential Step Methods

Double Step Chronocoulometry

Can also give information on the kinetics of coupled homogeneous reactions.

Potential Step Methods

Chronoabsorptometry

Plot of absorbance as a function of time.

With development of electrodes that exhibit optical transparency can combine electrochemistry with spectroscopy.

The electrodes are usually very thin films of conducting material, i.e. Pt, Au, or ITO on a glass or quartz substrate.

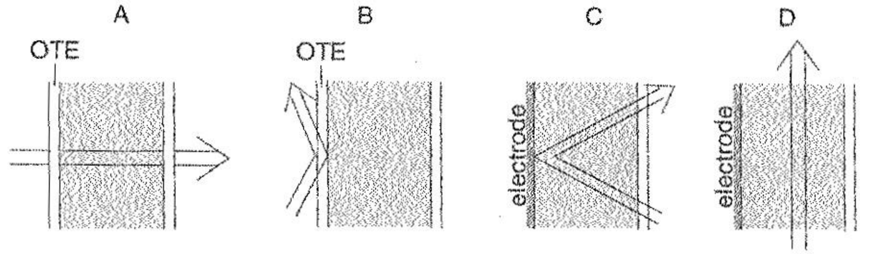


Figure 3.7 Spectroelectrochemical techniques: (A) transmission, (B) internal reflectance, (C) specular reflectance, (D) parallel.

Potential Step Methods

<u>Chronoabsorptometry</u>

If O is reduced to R and R absorbs light, the resulting increase in absorbance can be measured.

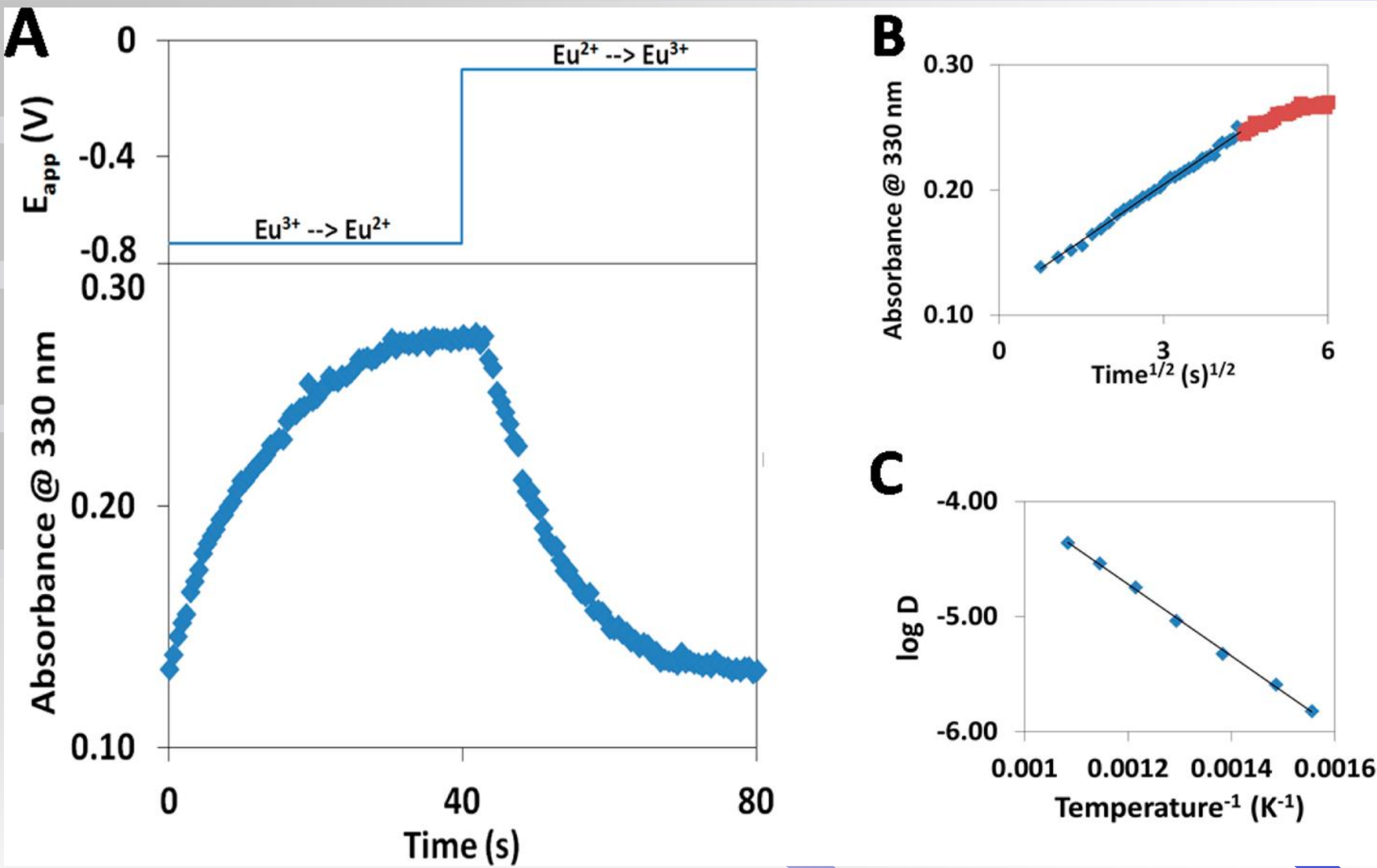
Integration of Beer's law combined with diffusion:

$$A_t = \frac{2}{\pi^{\frac{1}{2}}} \varepsilon_R C_O^* D_O^{\frac{1}{2}} t^{\frac{1}{2}}$$

Where ε is molar absorptivity ($M^{-1}cm^{-1}$) of R at wavelength used, and C and D are the molar concentration and diffusion coefficient of O (formation of R is controlled by diffusion of O), and t is time

Potential Step Methods

Chronoabsorptometry



Plot of A versus $t^{1/2}$ gives a straight line with ε obtained from the slope.

Potential Step Methods

Chronoabsorptometry

Useful technique in obtaining ε’s of electrogenerated species.

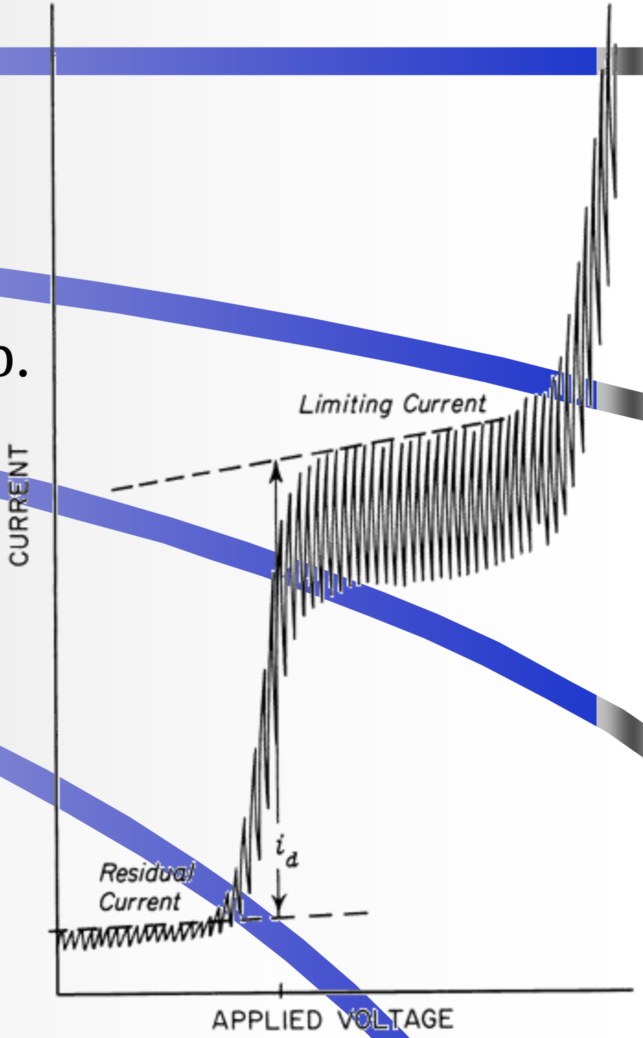
Also useful in studying homogeneous chemical reactions involving electrogenerated species.

Potential Sweep Methods

Polarography

Subclass of voltammetry,
where the WE is a Hanging Mercury Drop.

Excitation signal is a linearly increasing potential ramp. Potential is scanned cathodically while measuring the current.



Potential Step Methods

Normal Pulse Voltammetry

A series of pulses of increasing amplitude is applied to the WE. After the potential is stepped, the faradaic current decays more slowly than the charging current.

The way in which the current is measured at each pulse aids in minimizing the measurement of background (charging) current.

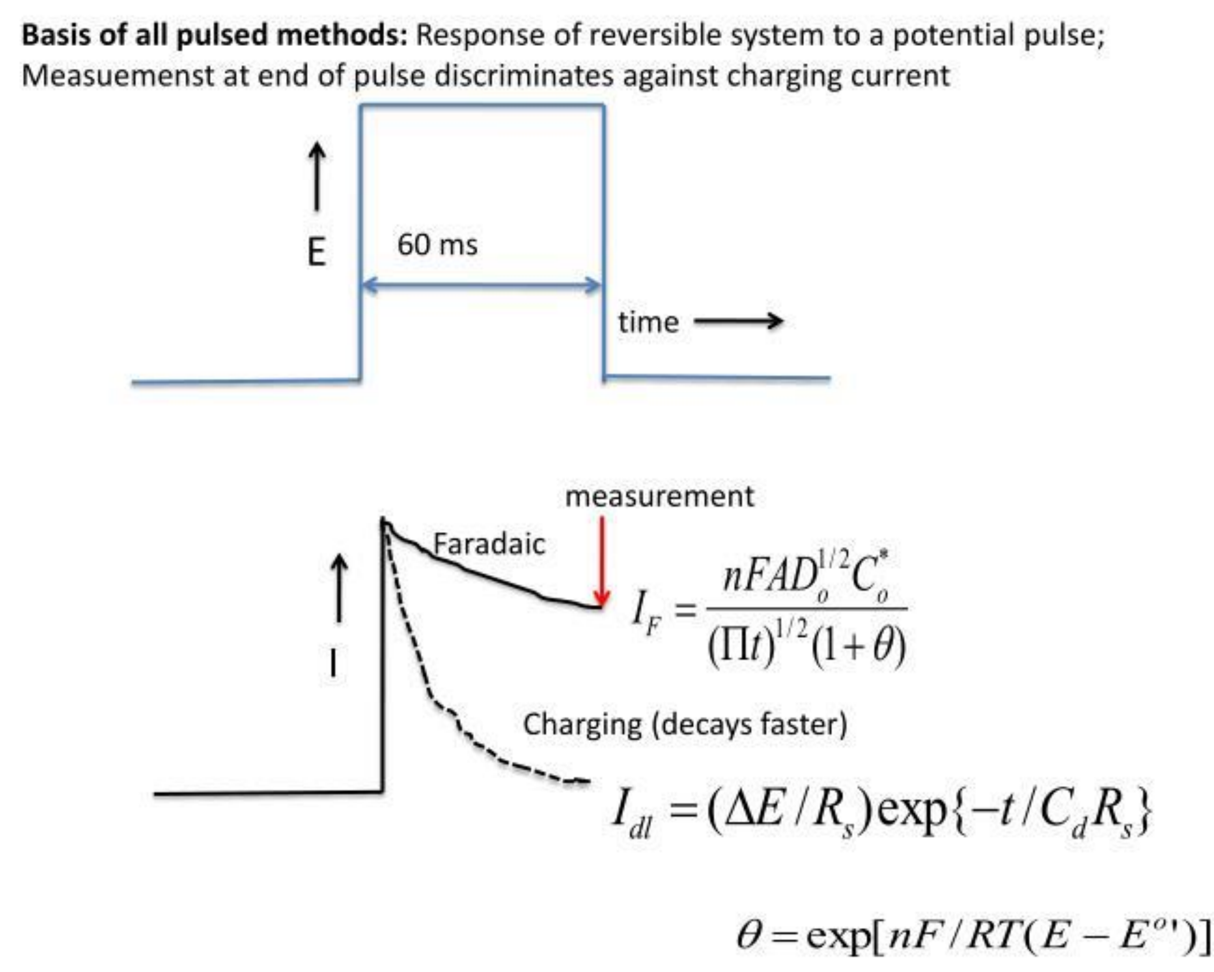
The current is sampled later in the pulse.

Quantification down to 10^{-8} M

The WE can be a DME or solid electrode.

Potential Step Methods

Normal Pulse Voltammetry



Basis of all pulsed methods: Response of reversible system to a potential pulse; Measuemenst at end of pulse discriminates against charging current

$$I_F = \frac{nFAD_o^{1/2}C_o^*}{(\Pi t)^{1/2}(1+\theta)}$$

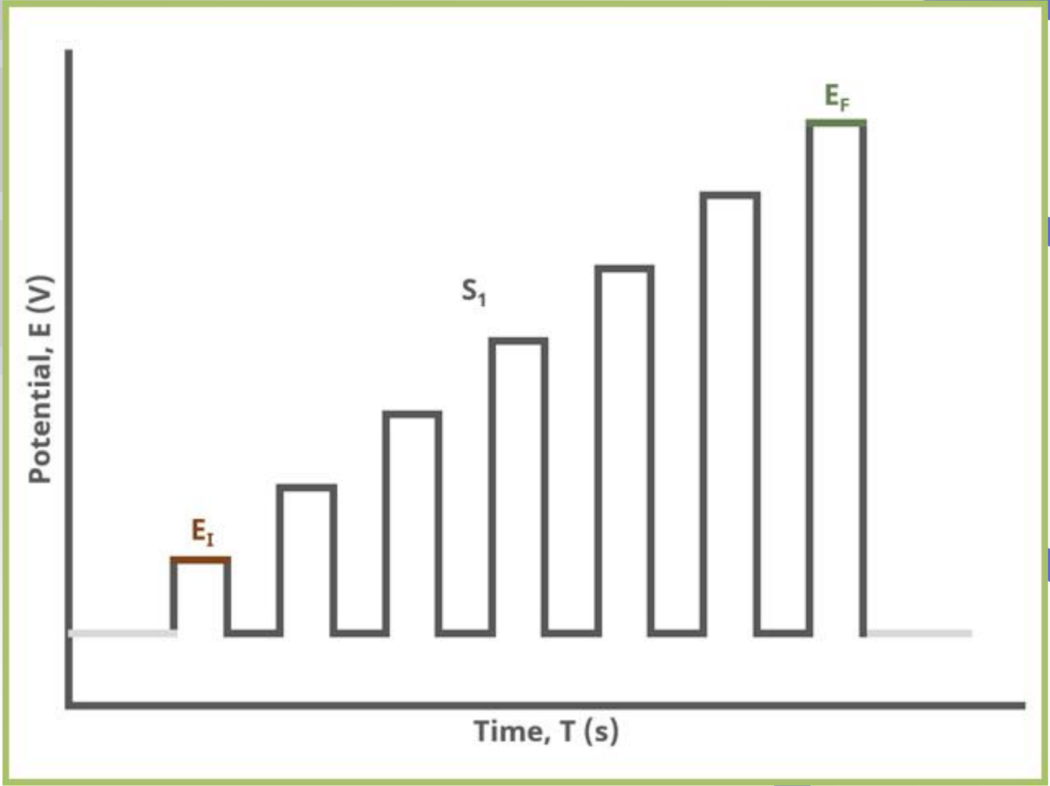
$$I_{dl} = (\Delta E/R_s)\exp\{-t/C_dR_s\}$$

$$\theta = \exp[nF/RT(E-E^{o}{}')]$$

Potential Step Methods

Normal Pulse Voltammetry

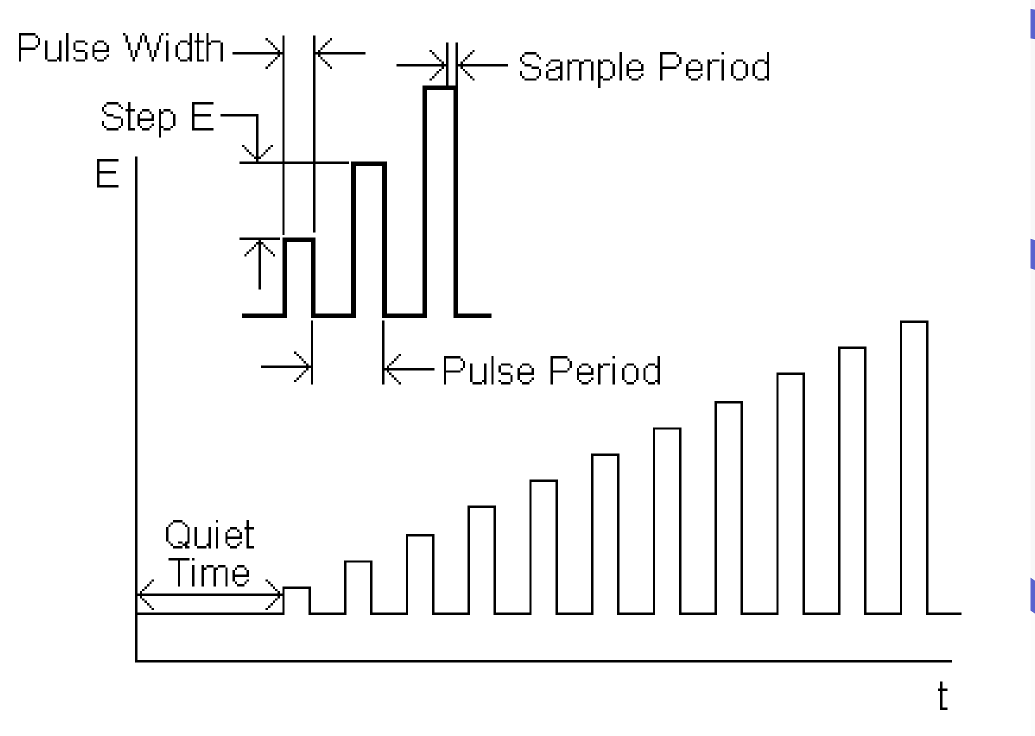
Current sampling occurs at the same time in each pulse of the NPV waveform. For each pulse, the current is sampled as a function of the pulse sequence.



Potential Step Methods

Normal Pulse Voltammetry

For a 50 ms pulse, the current is sampled about 40 ms into the pulse. The contribution of the charging current is nearly zero at this point.



Potential Step Methods

Normal Pulse Voltammetry

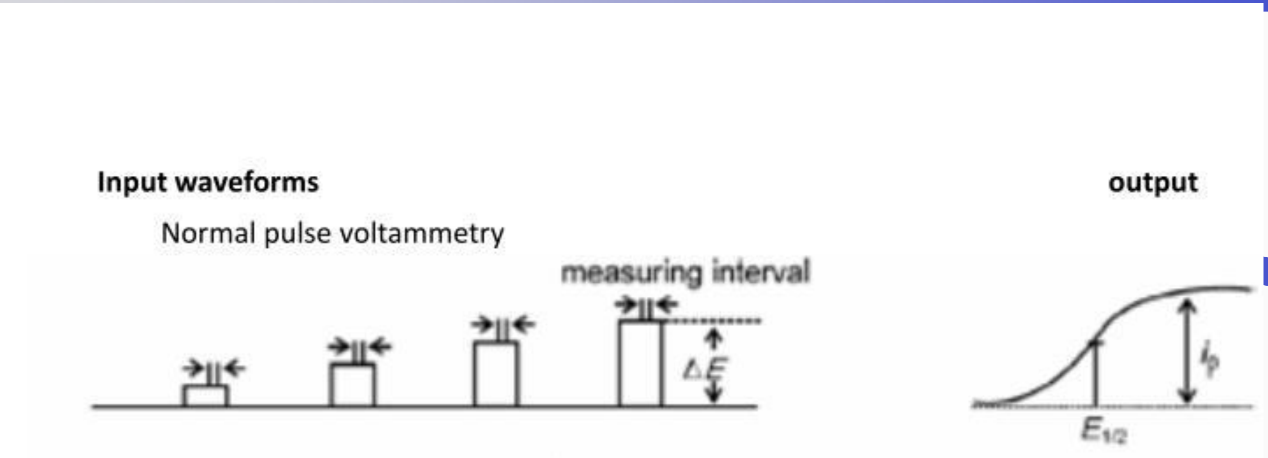
The magnitude of this current plateau is given by

$$i_{d,NPV} = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}(\tau - \tau')^{1/2}}$$

where n is the number of electrons, F is Faraday’s constant, A is the electrode area, D is the diffusion coefficient, and C is the concentration

Potential Step Methods

Normal Pulse Voltammetry



For each step, sample current at fixed τ and plot i(τ) versus E.

Potential Step Methods

Normal Pulse Voltammetry

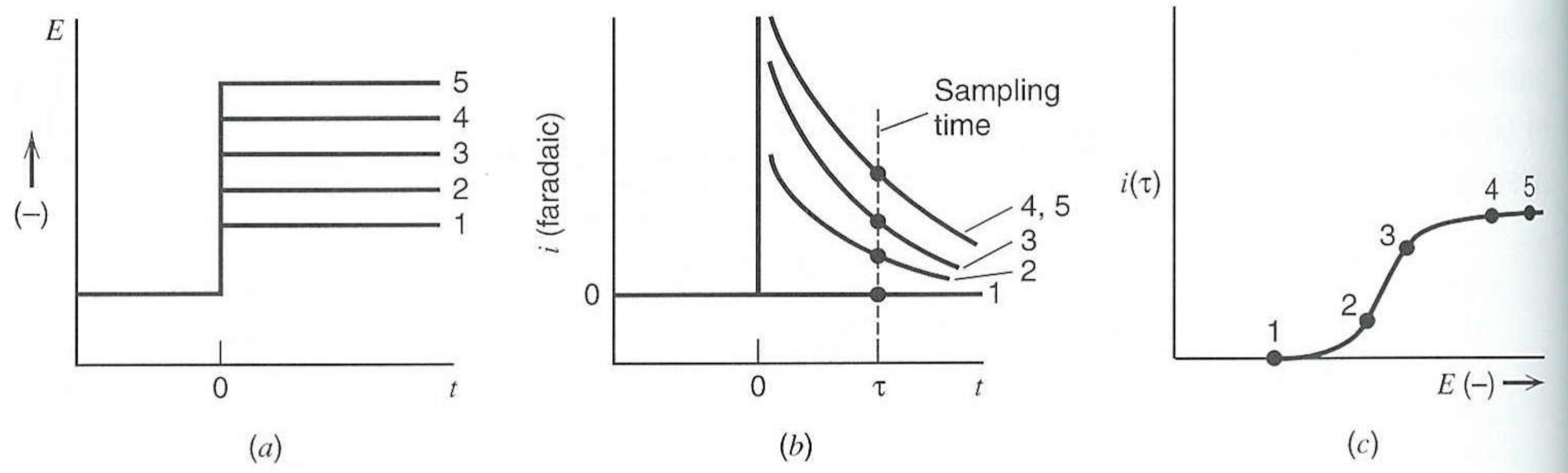


Figure 5.1.3 Sampled-current voltammetry. (*a*) Step waveforms applied in a series of experiments. (*b*) Current-time curves observed in response to the steps. (*c*) Sampled-current voltammogram.

For each step, sample current at fixed τ and plot i(τ) versus E.

Potential Step Methods

Normal Pulse Voltammetry

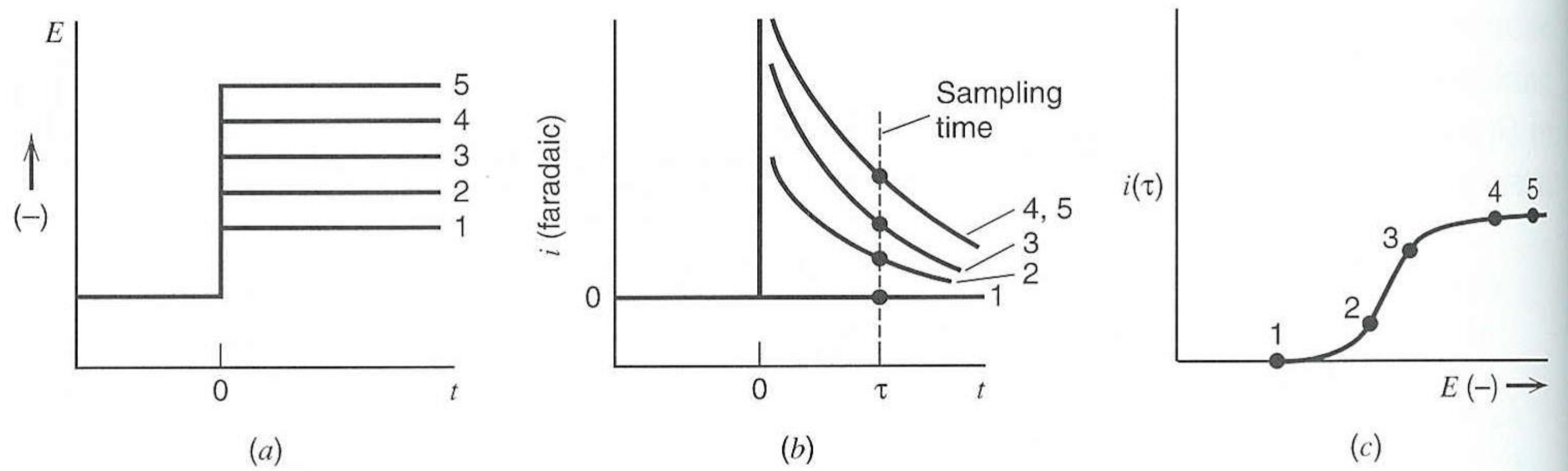


Figure 5.1.3 Sampled-current voltammetry. (*a*) Step waveforms applied in a series of experiments. (*b*) Current-time curves observed in response to the steps. (*c*) Sampled-current voltammogram.

1 – no electron-transfer

2, 3 – reduction or oxidation occurs but $C_O(0,t)$ and $C_R(0,t) \neq 0$

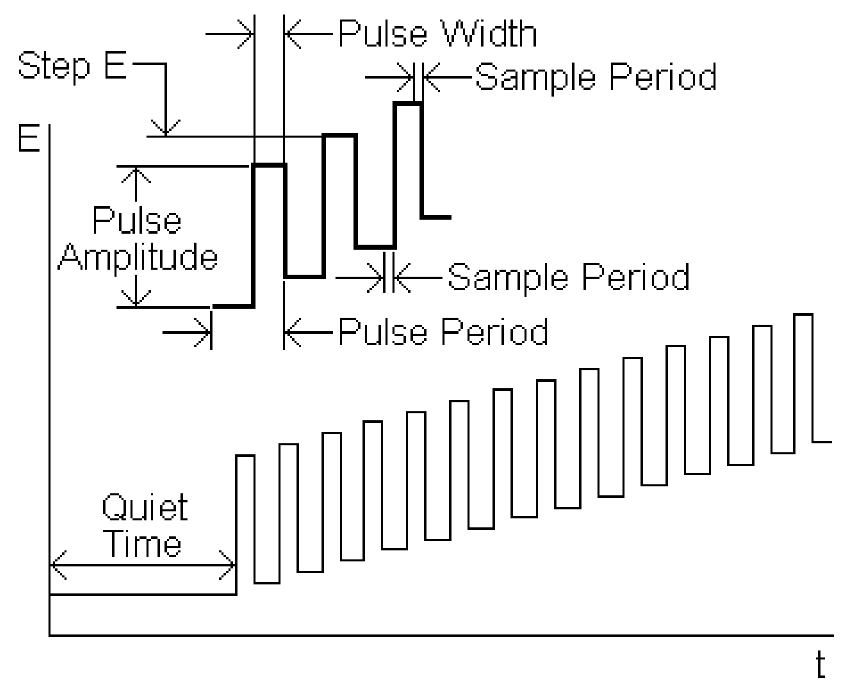
4, 5 – reduction or oxidation occurs in the mass-transfer-limited region $C_O(0,t)$ or $C_R(0,t) = 0$ under diffusion control

Potential Step Methods

Differential Pulse Voltammetry

Fixed magnitude pulses are superimposed on the linear potential ramp.

Current sampled twice: before the pulse (1) and just before the end of the pulse (2). i.e. for a 50 ms pulse, sample at 40 ms after the pulse begins.



Potential Step Methods

Differential Pulse Voltammetry

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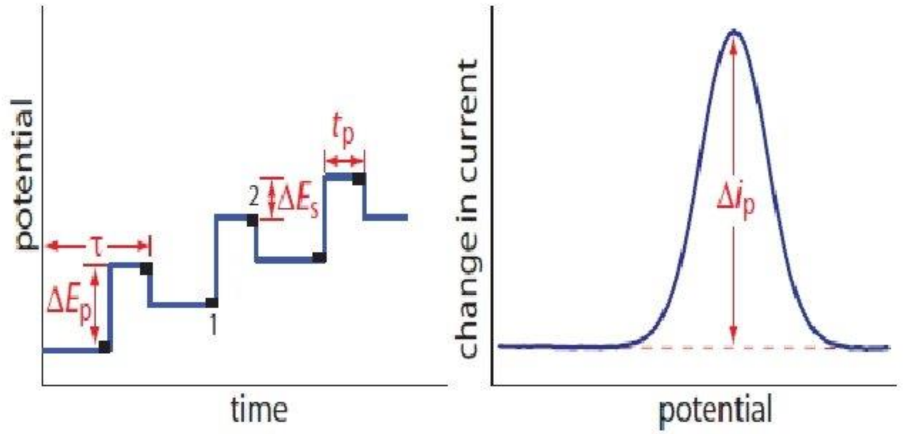


Potential Step Methods

Differential Pulse Voltammetry

First current is subtracted from the second current and Δi versus applied potential is plotted.

The peak potential (Ep) can be used to identify the species as it occurs near the polarographic half-wave potential:

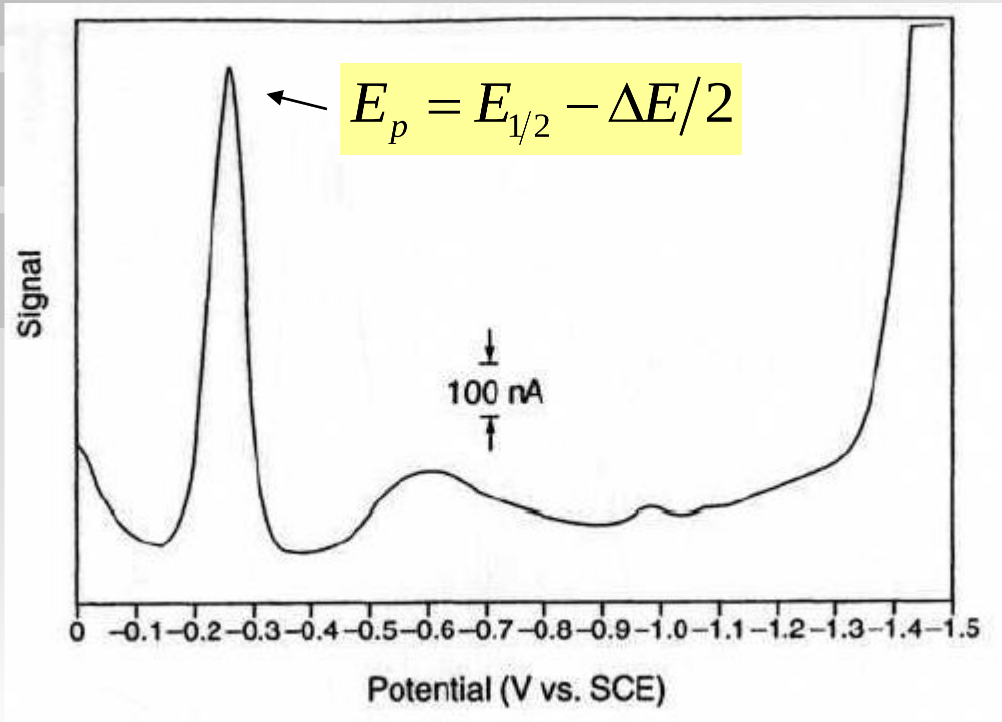
$$E_p = E_{1/2} - \Delta E/2$$

ΔE is the pulse amplitude

Potential Step Methods

Differential Pulse Voltammetry

Pulse amplitudes of 25-50 mV coupled with a 5mV/s scan rate are commonly used. The current peak heights are proportional to the concentration of the analyte.



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

The width of the peak (at half-height) is related to the electron stoichiometry, corresponding to 30.1 mV for n=1 (at 25^{o}C).

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

Potential Step Methods

Differential Pulse Voltammetry

First current is subtracted from the second current and Δi versus applied potential is plotted.

$$\Delta i = t(t_2) - t(t_1) \;\; vs.\; V$$

$$i_p(t) = \frac{nFAD_O C_O(b)}{\sqrt{\pi D_O t_m}} \left(\frac{1-\sigma}{1+\sigma} \right)$$

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

Potential Step Methods

Differential Pulse Voltammetry

The resulting peaks are proportional to the concentration of the analytes.

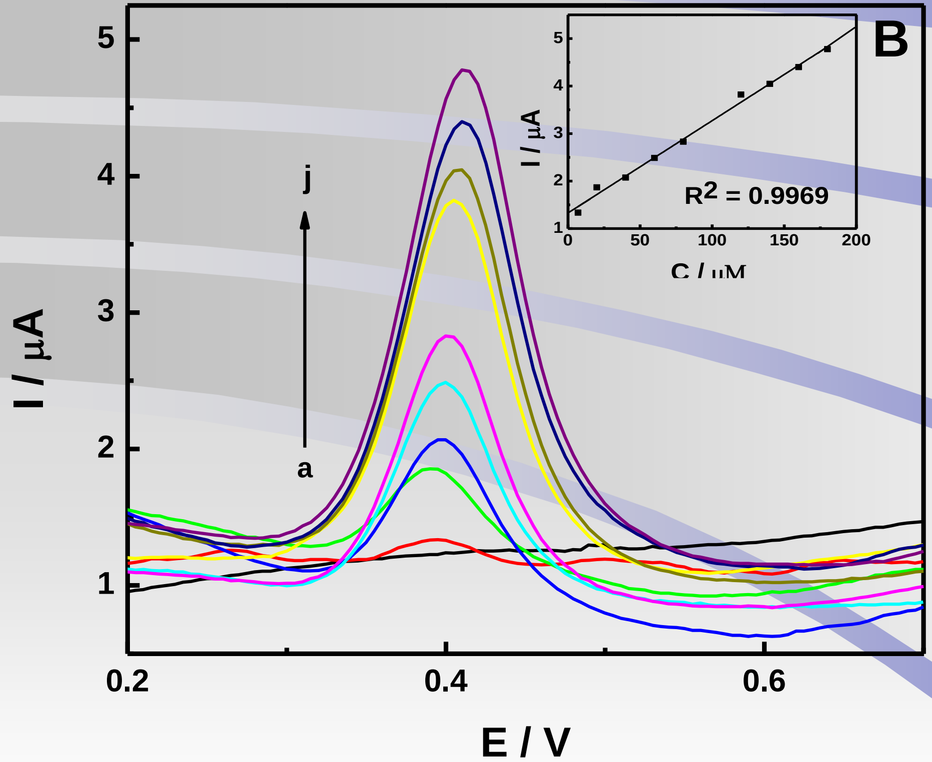
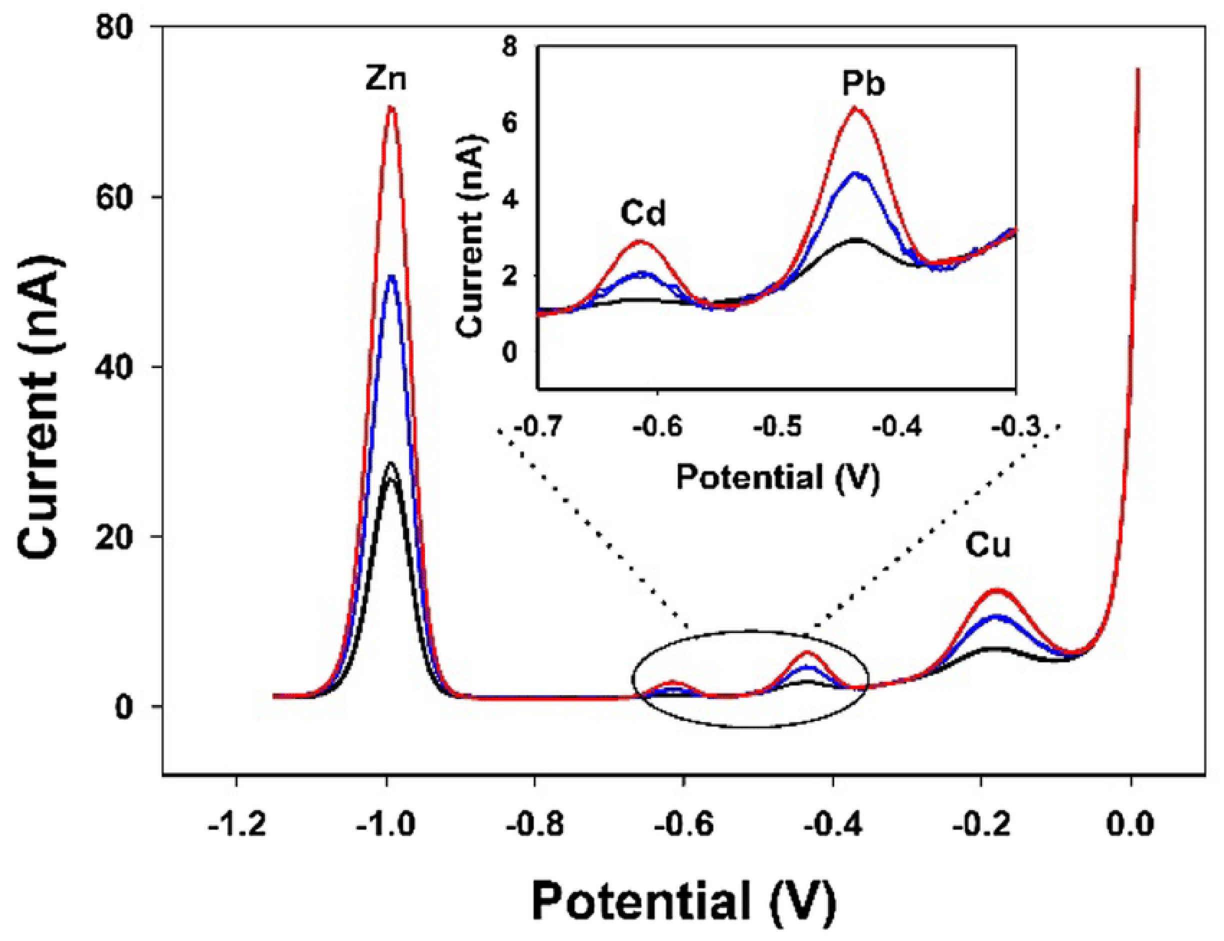


Fig. 7. The differential pulse voltammograms of (A) GA at CA at a) 0, b) 7, c) 20, d) 40, e) 60, f) 80, g) 120, h) 140, i) 160, j) 180. The inset shows the plot of the DPV peak current vs. the concentration. Amplitude: 0.05 V; pulse width: 0.06s; pulse period: 0.2s.

Potential Step Methods

Differential Pulse Voltammetry

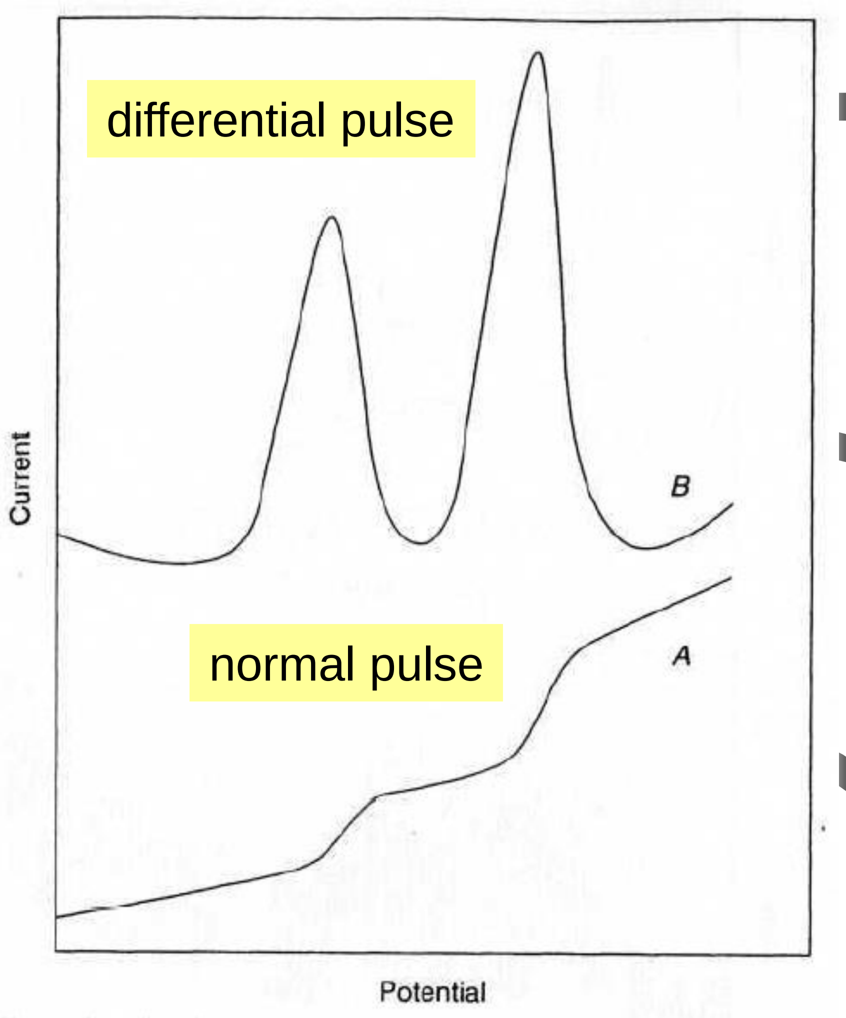


Simultaneous analysis of Cu, Pb, Cd and Zn by differential pulse voltammetry (DPV) in seawater samples

Potential Step Methods

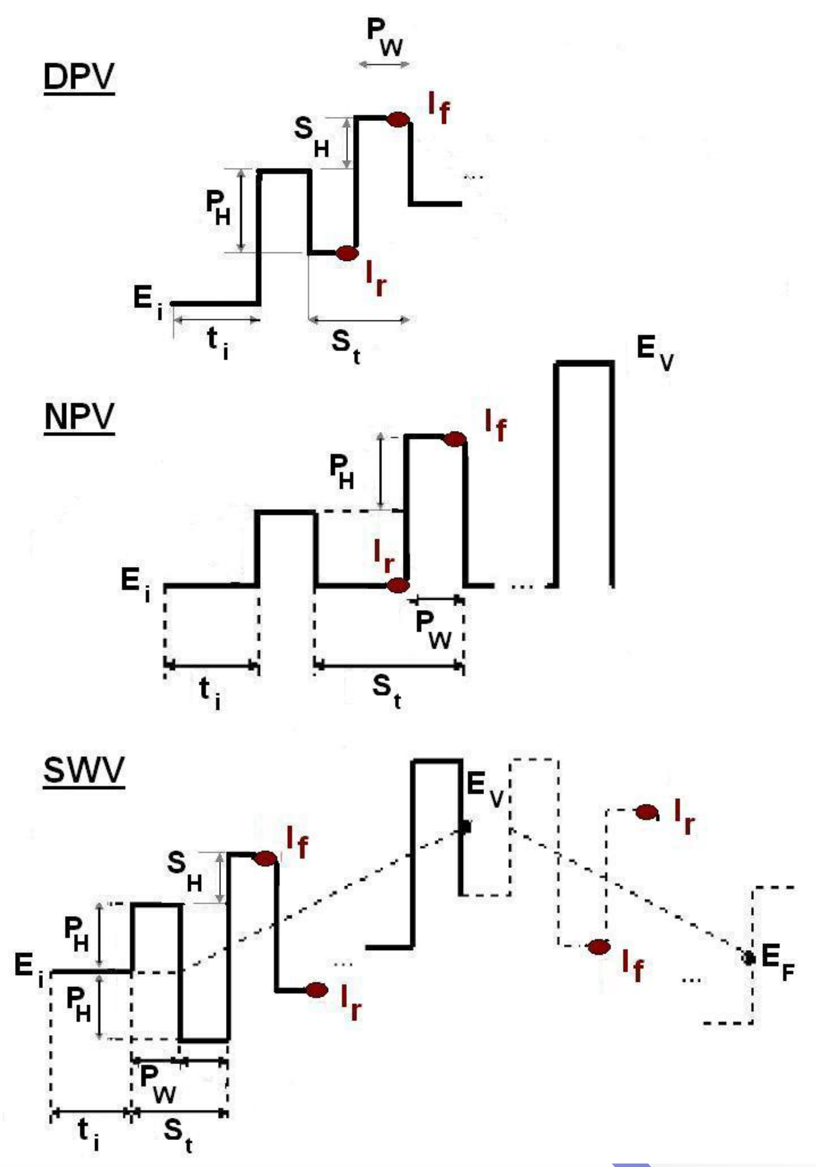
Differential Pulse Voltammetry

- allows measurement down to 10^{-8} M concentration
- improved resolution between the species with similar potential (down to 50 mV)
- typical parameters:
  - pulse 25-50 mV
  - scan rate 5mV/s



mixture of Cd^{2+} and Pb^{2+} in 0.1M HNO_3.

Potential Step Methods



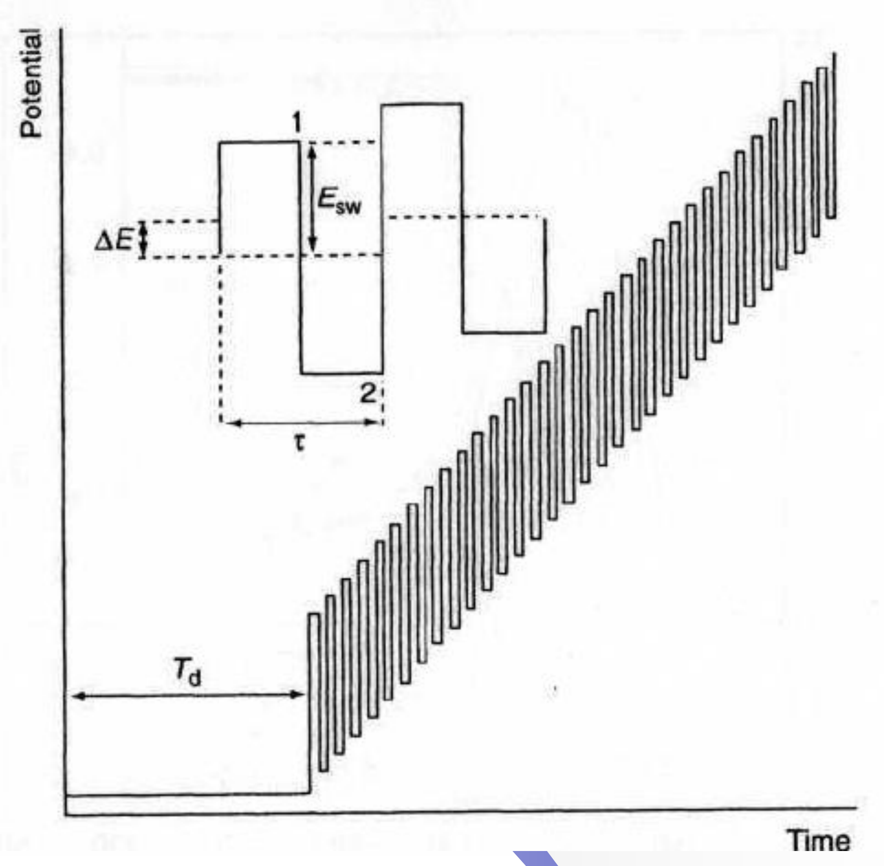
Potential Step Methods

Square Wave Voltammetry

Large-amplitude differential technique, the reverse pulse causes the reverse reaction of the product.

The current is sampled twice: at the end of the forward pulse and at the end of the reversed pulse.

The diffusion layer is not renewed between potential cycles, suppresses background current. Very sensitive down to nanomolar range.



Potential Step Methods

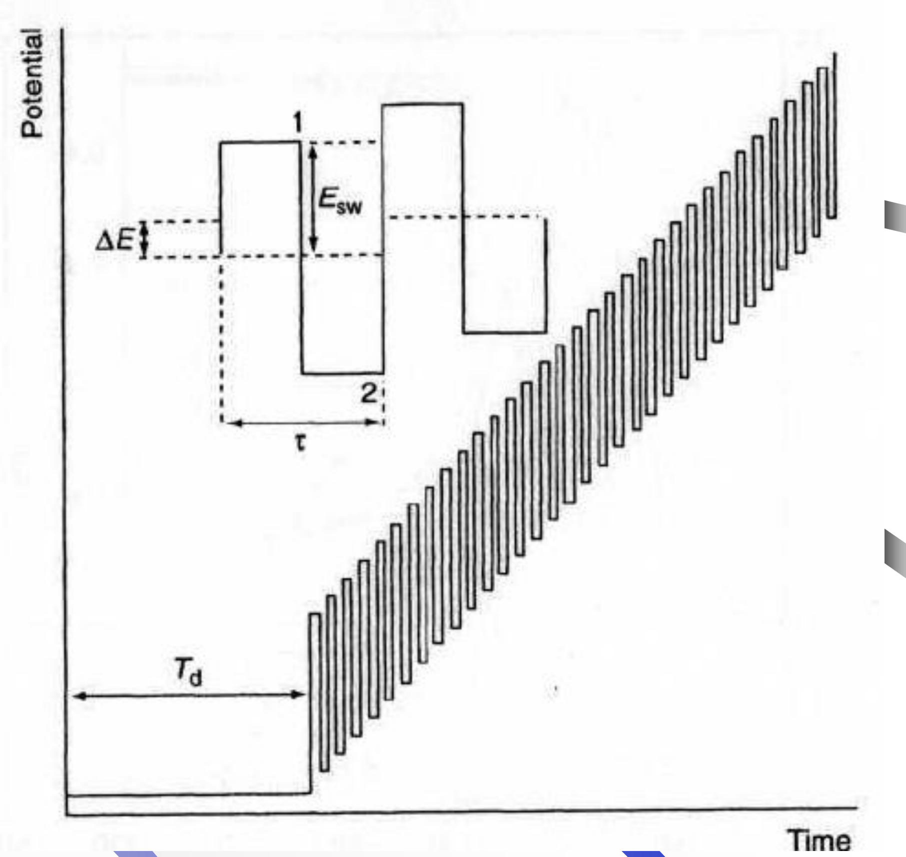
Square Wave Voltammetry

Square-wave is characterized by a pulse height or amplitude ΔE_p, the staircase height, ΔE_s, the pulse time, t_p, and the cycle period, t_s.

The square wave frequency:

$f = 1/2t_p$

The staircase shifts by ΔE_s at the start of each cycle so the scan rate is: $f\Delta E_s = \dfrac{\Delta E_s}{2t_p}$



Potential Step Methods

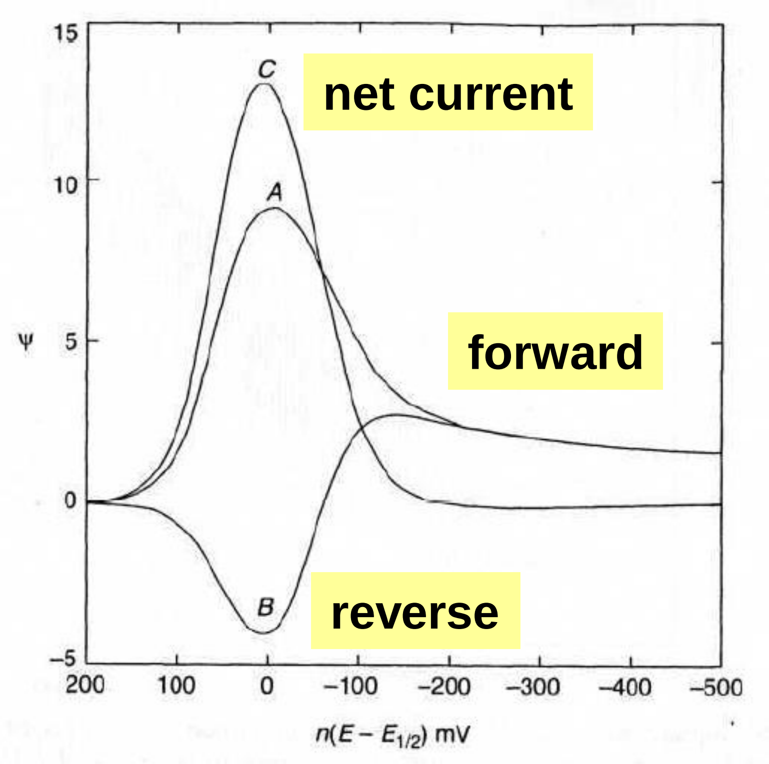
Square Wave Voltammetry

Major advantage – speed, complete voltammogram can be recorded within a couple of seconds. Runs at speeds of 1 V/sec versus 1-10 mV/s for normal and differential pulse.

Advantageous in batch and flow analytical operations, can resolve neighboring peaks in chromatography and capillary electrophoresis.

$\Delta I = I_2 - I_1$

C = B-A



Potential Step Methods

Square Wave Voltammetry

Notice that the SWV is much more sensitive than the DPV.

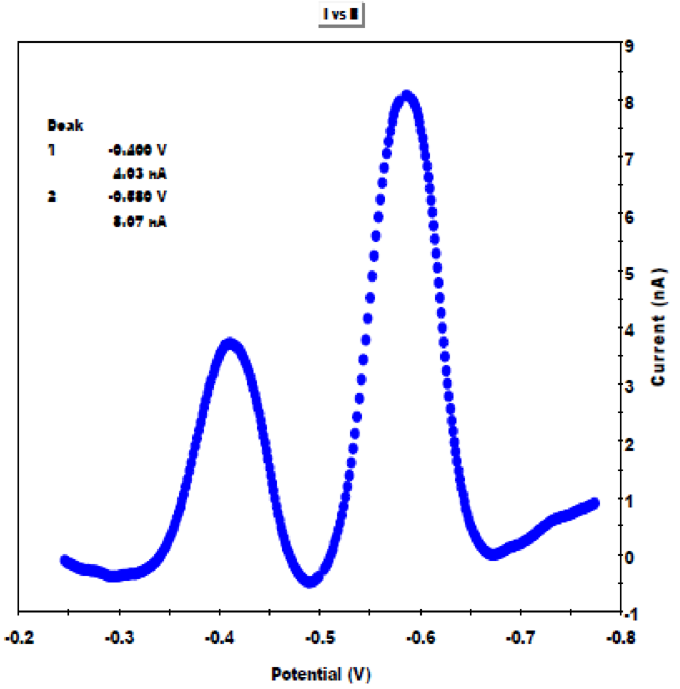


FIGURE 3A: Differential pulse polarogram of lead and cadmium.

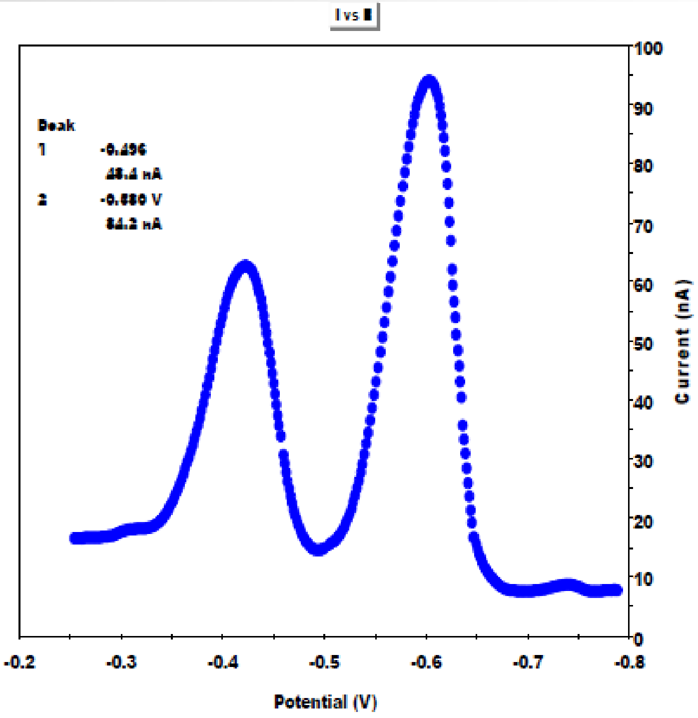
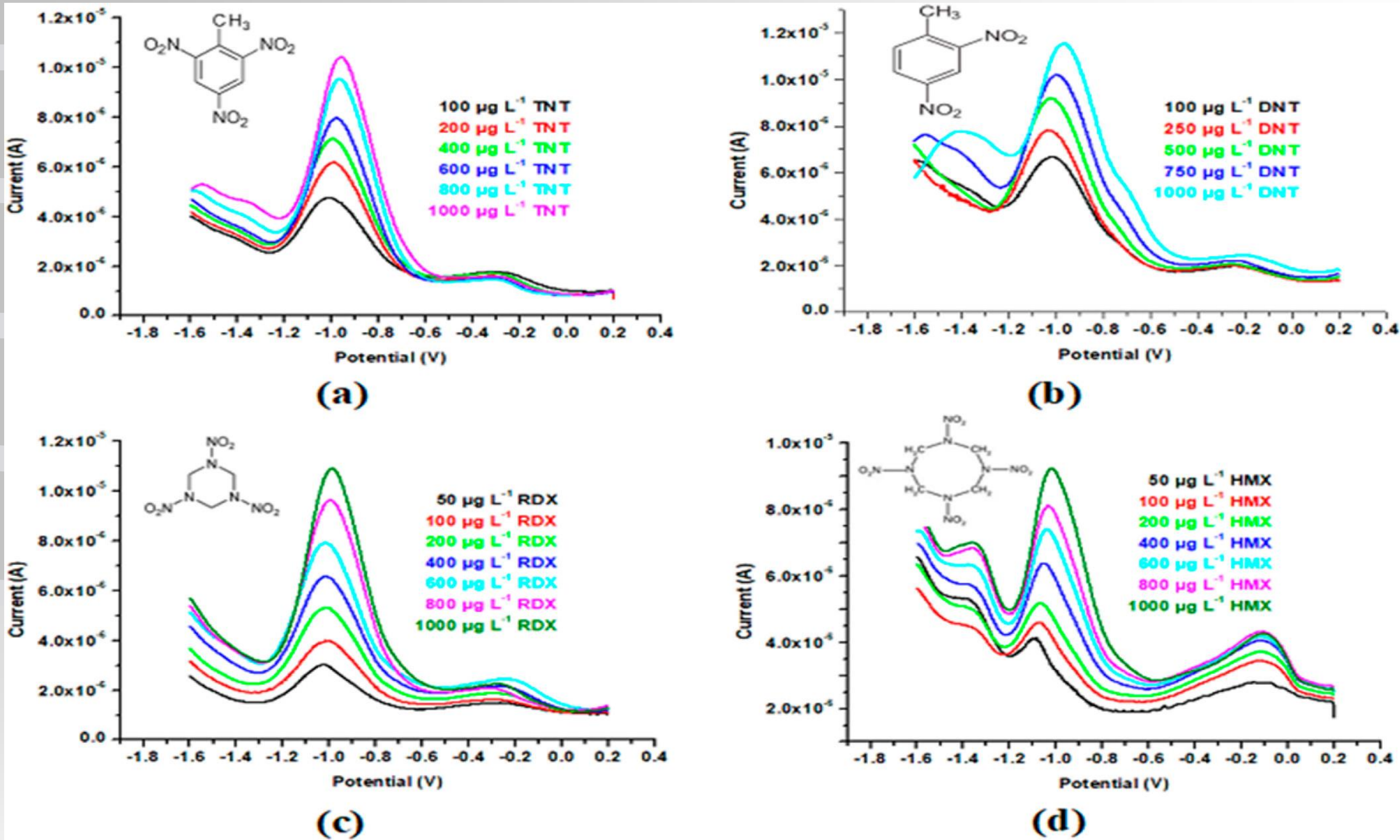


FIGURE 3B: Square wave voltammogram of lead and cadmium.

Potential Step Methods

Square Wave Voltammetry



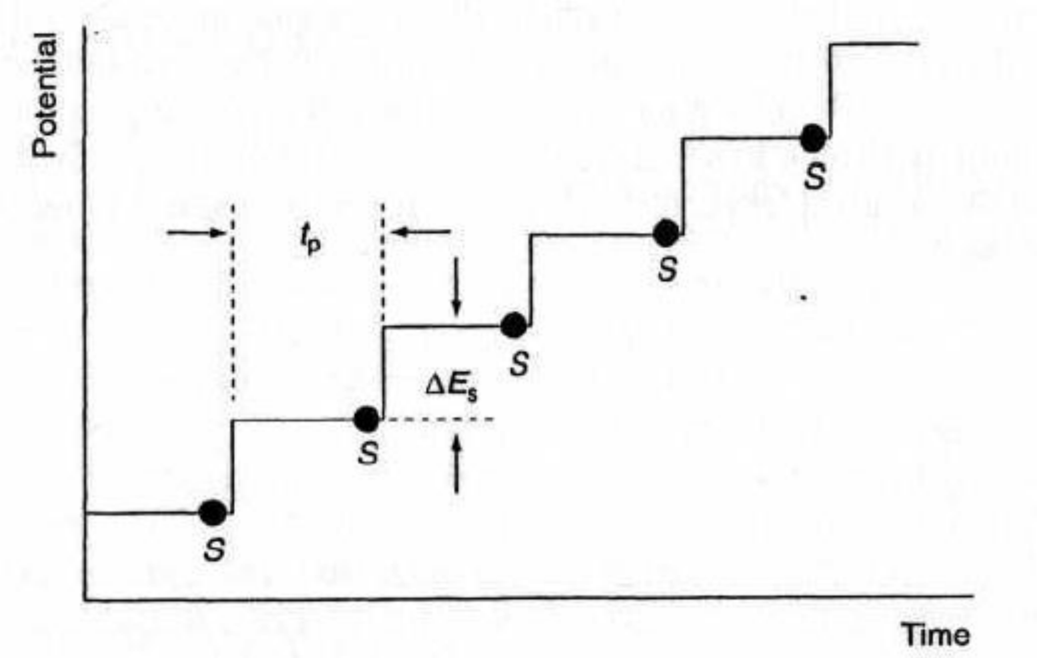
Square wave voltammograms and structures of (a) TNT, (b) DNT, (c) RDX, and (d) HMX recorded with energetic material memory–GC/P(Cz-*co*-ANI)-Au$_{nano}$ electrodes.

Potential Step Methods

Staircase Voltammetry

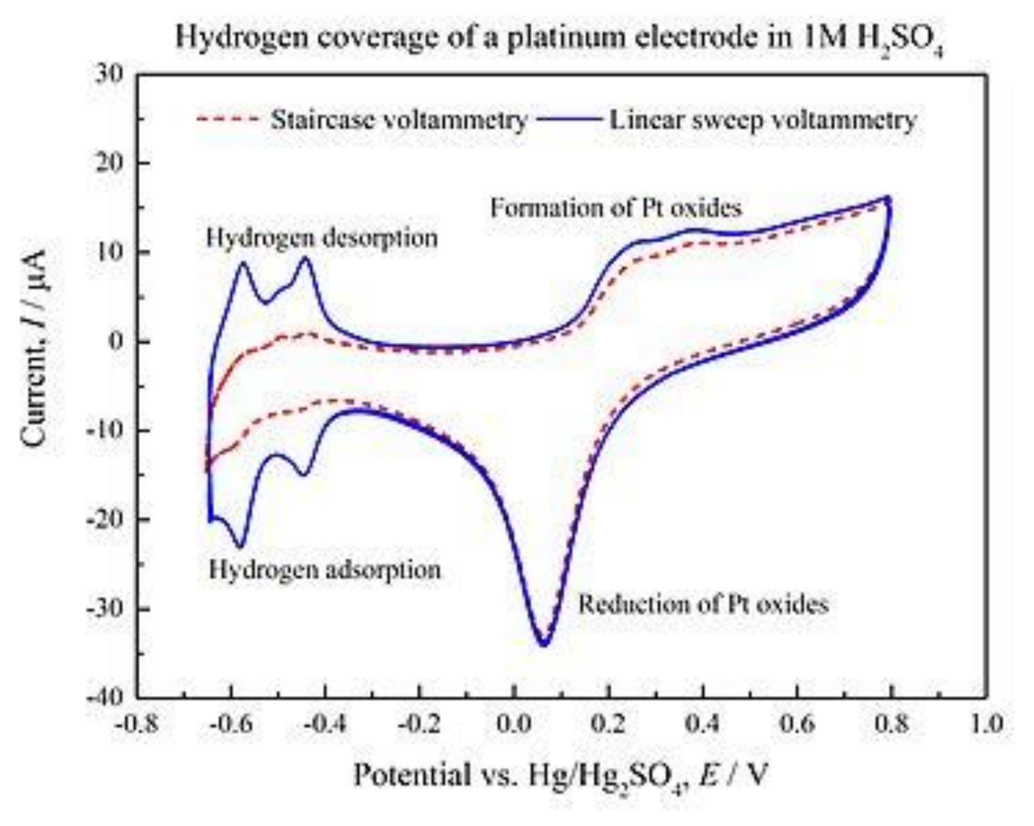
Derivative of linear sweep, voltage is increased in steps of ~10 mV with 50 ms delay.

Response similar to cyclic voltammetry but with reduced charging current. Has not been used that much.

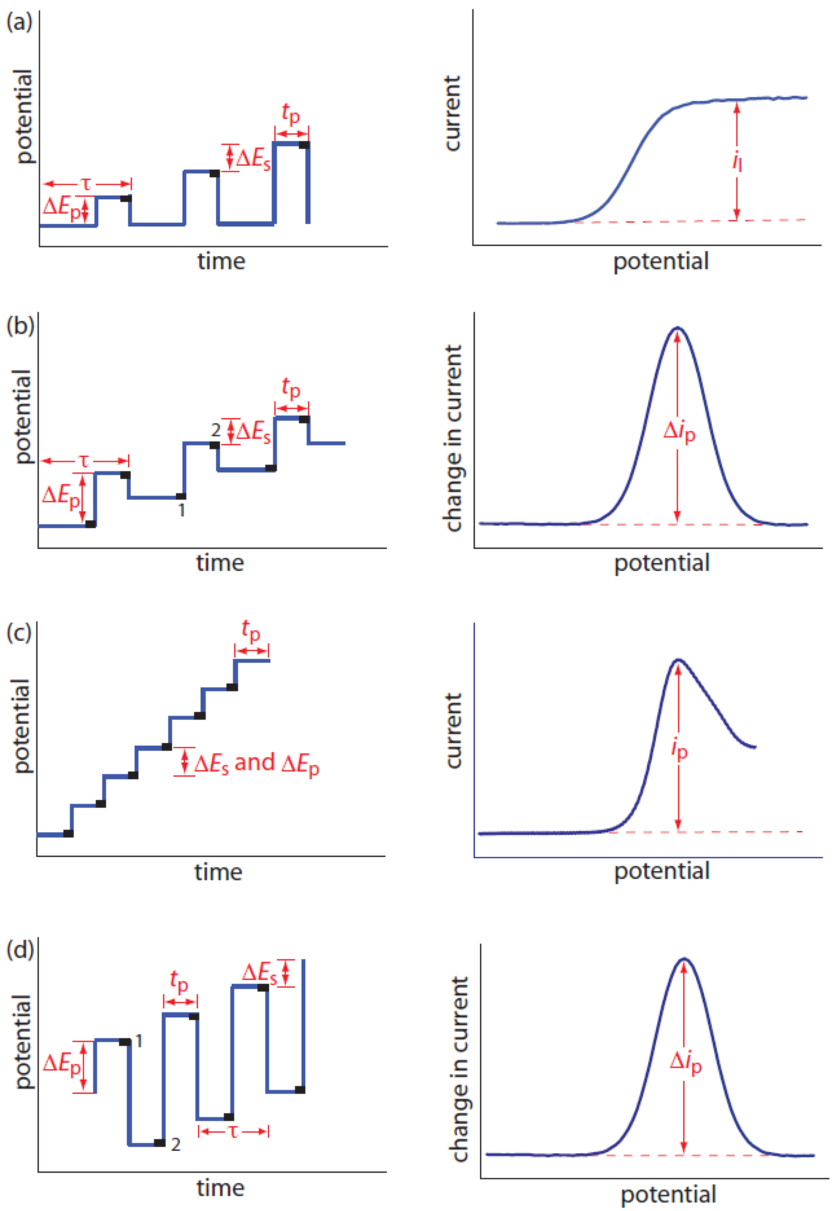


Potential Step Methods

Staircase Voltammetry



Potential Step Methods



(a) normal pulse voltammetry,

(b) differential pulse voltammetry,

(c) staircase voltammetry, and

(d) square-wave voltammetry.

The current is sampled at the time intervals shown by the black rectangles. When measuring a change in current, Δ*i*, the current at point 1 is subtracted from the current at point 2.

Potential Step Methods

Stripping Voltammetry

- first pre-concentrate the analyte on the surface of the electrode
- then strip (dissolve) the analyte and measure
- detection levels down to 10^{-10} M is feasible
- various variations exists:
  - anodic stripping voltammetry
  - potentiometric
  - adsorptive stripping
  - cathodic stripping
  - abrasive stripping

Potential Step Methods

Stripping Voltammetry

Historically:

Pre-concentration is done by amalgaming the metal in question in small volume mercury electrode.

$$M^{n+} + ne^{-} + Hg \rightarrow M(Hg)$$

The concentration can be calculated from the pre-concentration current measured.

$$C_{Hg} = \frac{i_1 t_d}{nFV_{Hg}}$$

During the anodic scan the metal is ‘stripped’ from the electrode.

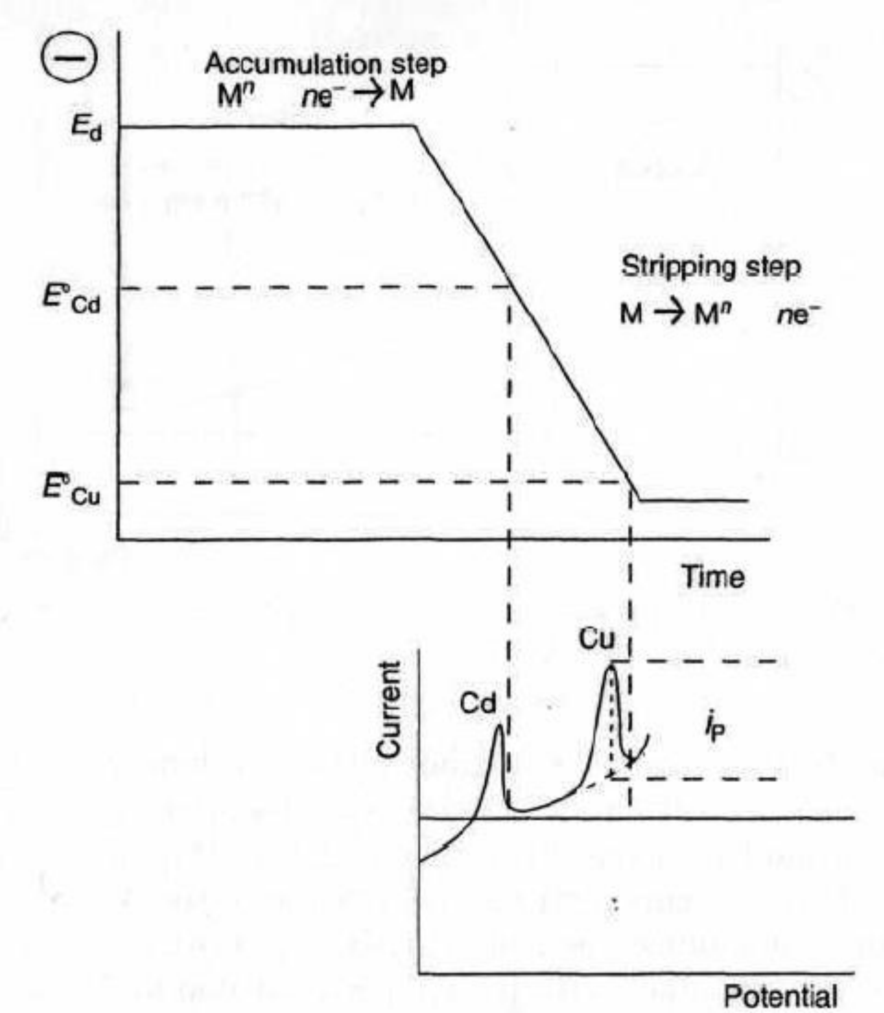
$$M(Hg) \rightarrow M^{n+} + ne^{-} + Hg$$

Potential Step Methods

Anodic Stripping Voltammetry

- potential scan

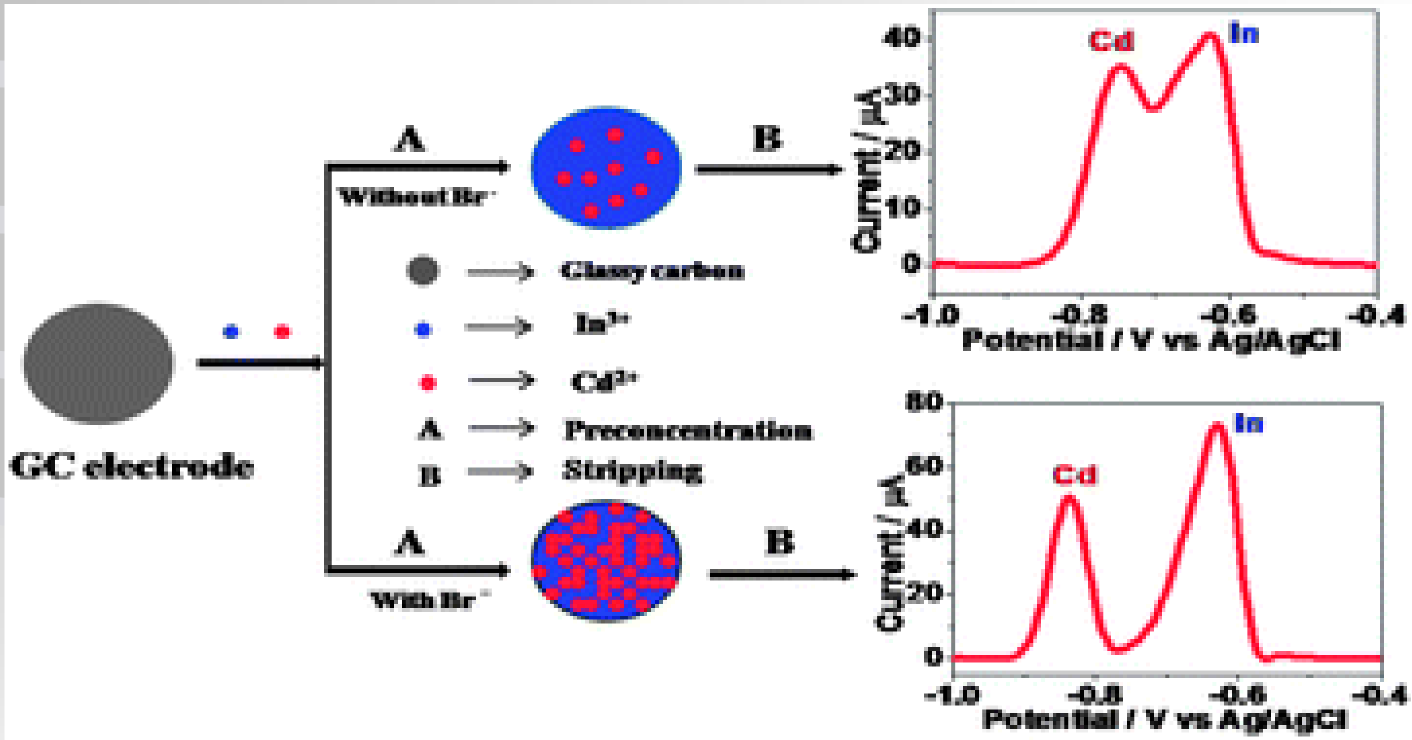
- voltammogram



Potential Step Methods

Anodic Stripping Voltammetry

Push to eliminate Hg

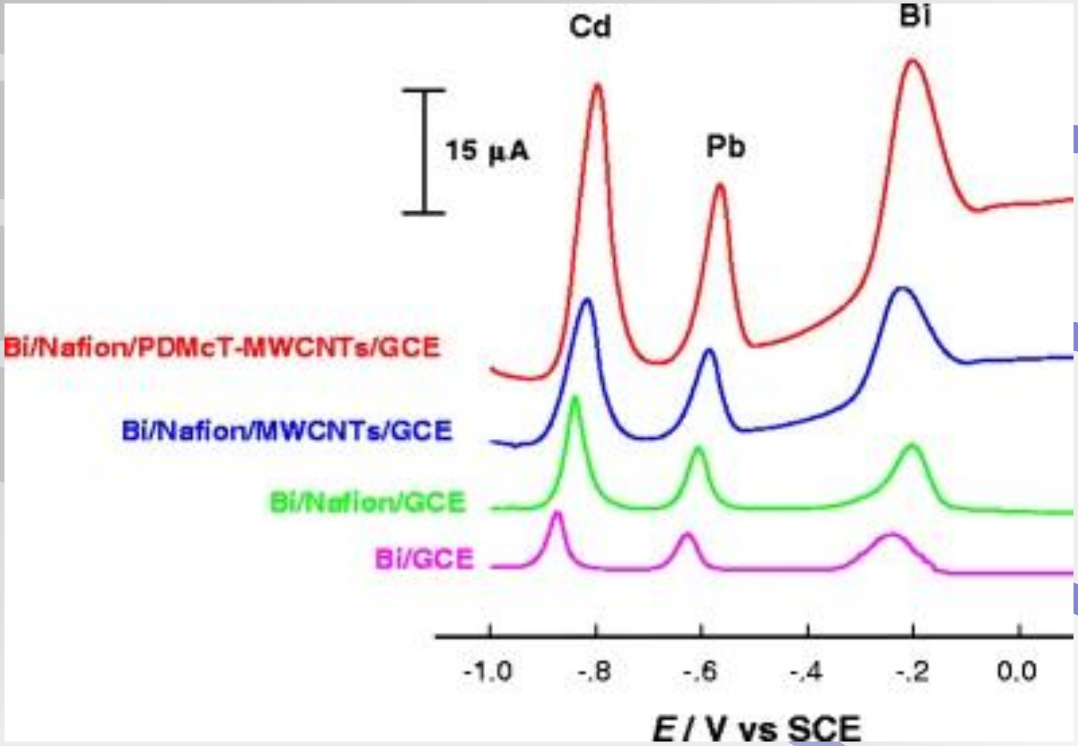


Anodic stripping voltammetric determination of cadmium using a "mercury free" indium film electrode

Potential Step Methods

Anodic Stripping Voltammetry

Push to eliminate Hg



Differential pulse anodic stripping voltammetric determination of Cd and Pb at a bismuth glassy carbon electrode modified with Nafion, poly(2,5-dimercapto-1,3,4-thiadiazole) and multiwalled carbon nanotubes

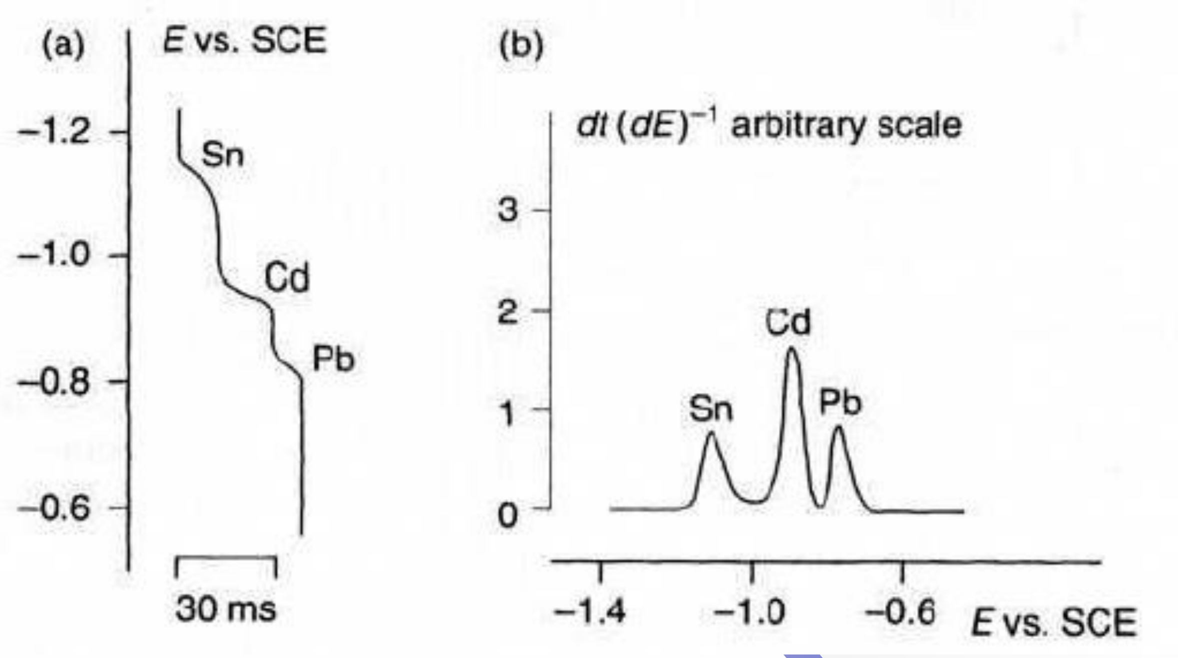
Potential Step Methods

Potentiometric Stripping Voltammetry

The oxidation step is done using an oxidation agent (O2, Hg(II) etc.) present in the solution.

$$M(Hg) + oxidant \rightarrow M^{n+}$$

Potential of the electrode is measured vs time.



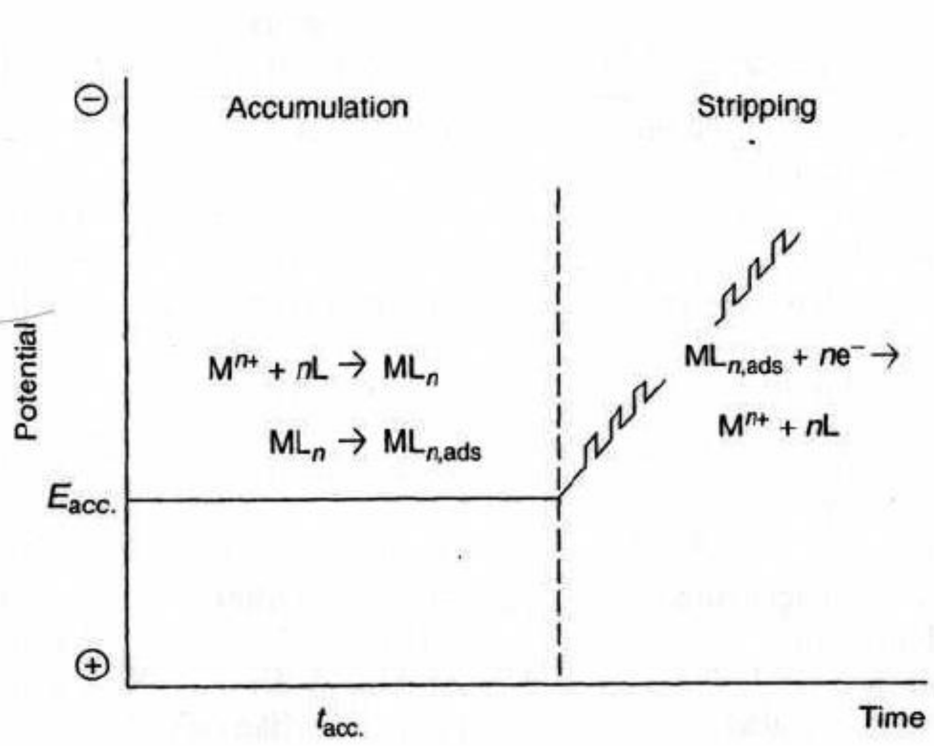
Potential Step Methods

Adsorptive Stripping Voltammetry

Pre-concentration goes via adsorption of a metal ion in a surface bound complex (instead of amalgam).

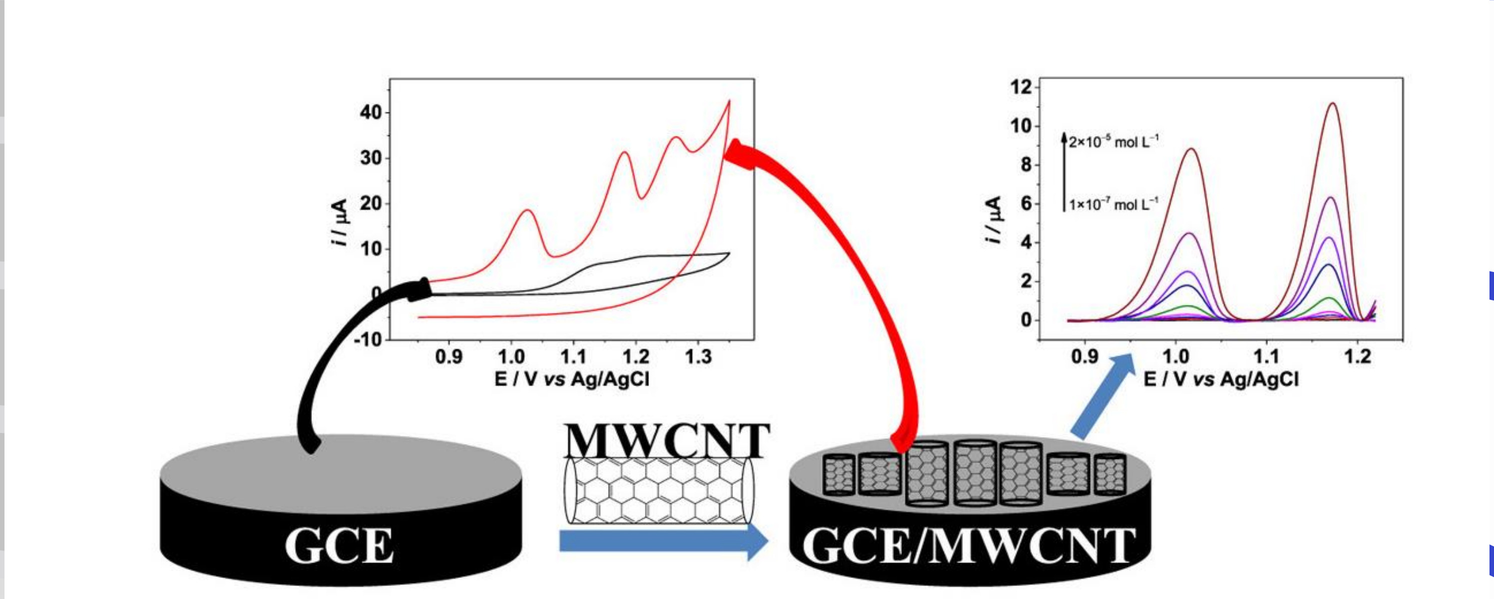
Langmuir kinetics of adsorption vs time

Extremely low detection limits can be achieved (down to 10^{-12} M)



Potential Step Methods

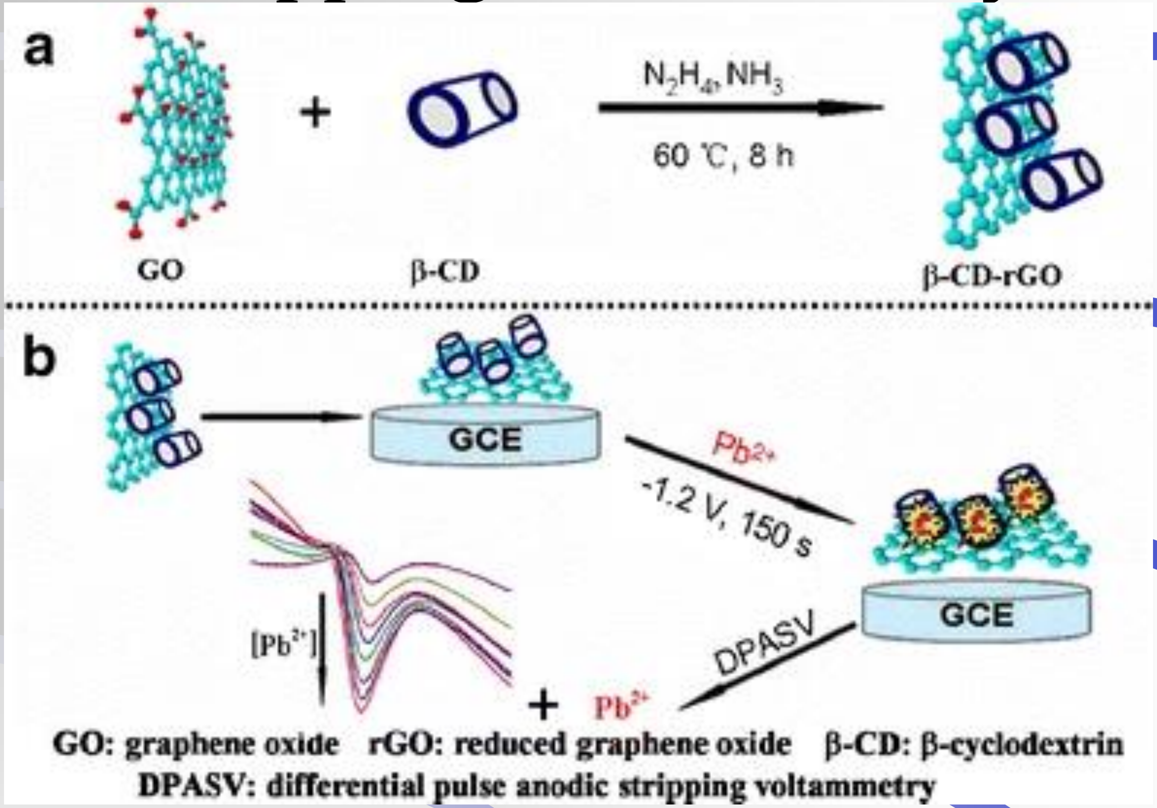
Adsorptive Stripping Voltammetry



Adsorptive stripping voltammetry for simultaneous determination of hydrochlorothiazide and triamterene in hemodialysis samples using a multi-walled carbon nanotube-modified glassy carbon electrode

Potential Step Methods

Adsorptive Stripping Voltammetry



Determination of lead(II) by adsorptive stripping voltammetry using a glassy carbon electrode modified with β-cyclodextrin and chemically reduced graphene oxide composite.

Potential Step Methods

Cathodic Stripping Voltammetry

Involves anodic deposition of analyte followed by negative-going potential scan for detection of anions in the solution.

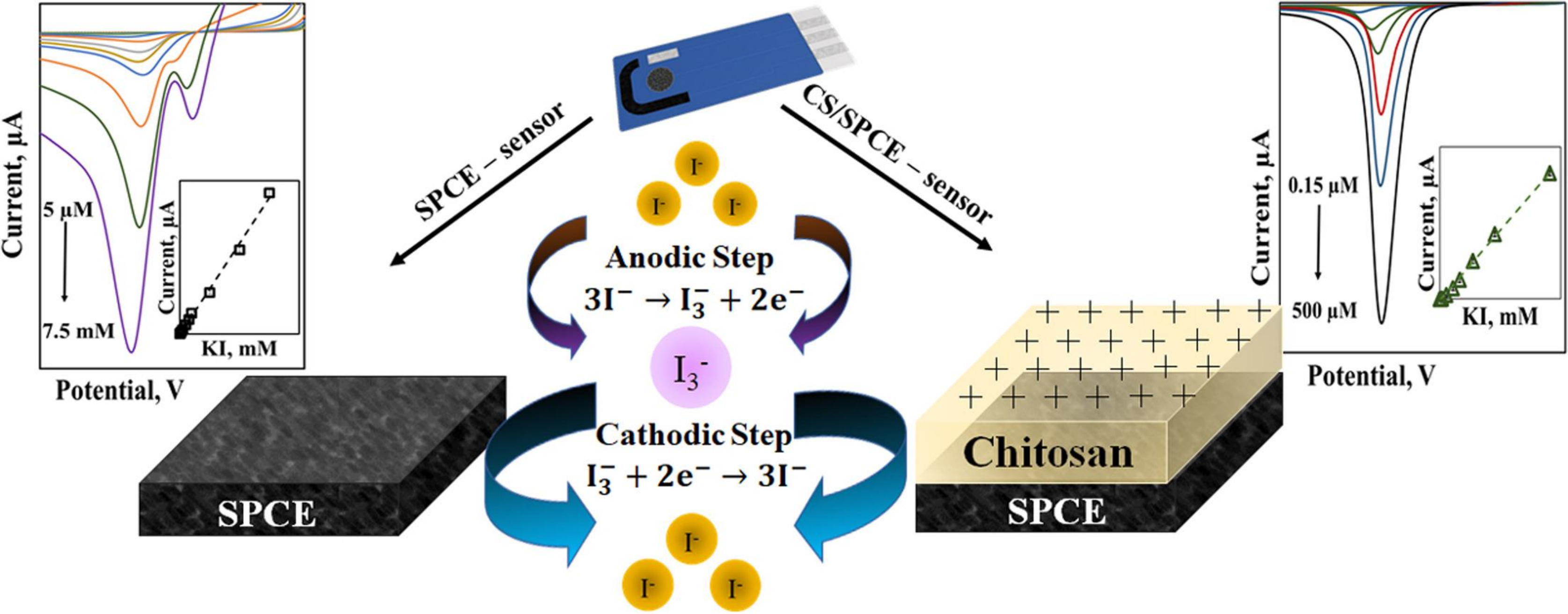
$$A^{n-} + Hg \underset{stripping}{\overset{deposition}{\rightleftarrows}} HgA + ne^-$$

Suitable for a wide range of compounds forming insoluble salts with mercury (halide ions, thiols, penicillins etc.).

Silver and copper can be used in a similar manner.

Potential Step Methods

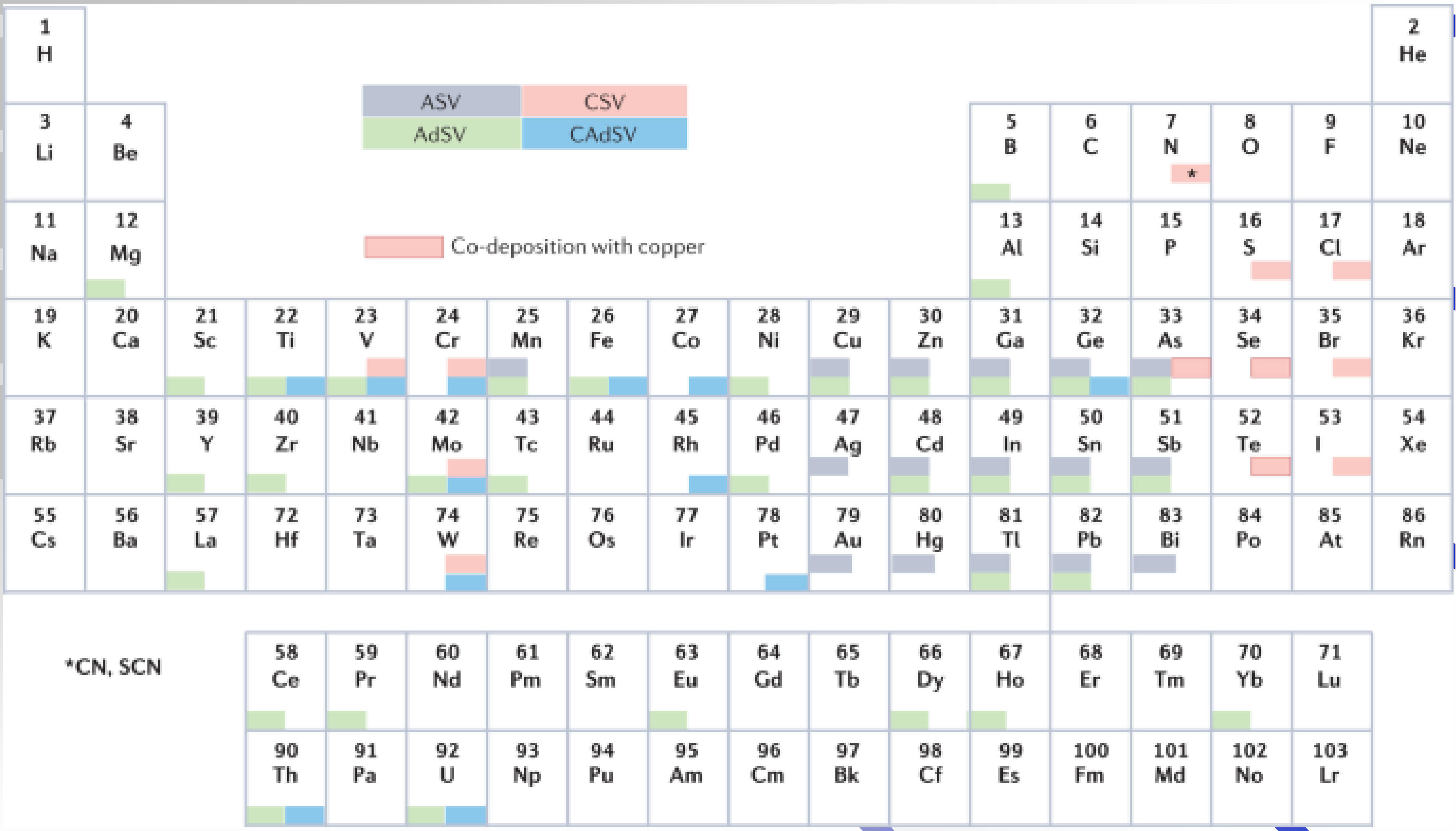
Cathodic Stripping Voltammetry



Cathodic stripping voltammetric determination of iodide using disposable sensors (screen printed).

Potential Step Methods

Stripping Voltammetry



🟪 ASV	🟥 CSV
🟩 AdSV	🟦 CAdSV

▣ Co-deposition with copper

1 H																	2 He
3 Li	4 Be											5 B 🟩	6 C	7 N 🟥 *	8 O	9 F	10 Ne
11 Na	12 Mg 🟩											13 Al 🟩	14 Si	15 P	16 S 🟥	17 Cl 🟥	18 Ar
19 K	20 Ca	21 Sc 🟩	22 Ti 🟩🟦	23 V 🟥 🟩🟦	24 Cr 🟥 🟦	25 Mn 🟪 🟩	26 Fe 🟩🟦	27 Co 🟦	28 Ni 🟩	29 Cu 🟪 🟩	30 Zn 🟪 🟩	31 Ga 🟪 🟩	32 Ge 🟪 🟩🟦	33 As 🟪▣ 🟩	34 Se ▣	35 Br 🟥	36 Kr
37 Rb	38 Sr	39 Y 🟩	40 Zr 🟩	41 Nb	42 Mo 🟥 🟩🟦	43 Tc 🟩	44 Ru	45 Rh 🟦	46 Pd 🟩	47 Ag 🟪	48 Cd 🟪 🟩	49 In 🟪 🟩	50 Sn 🟪 🟩	51 Sb 🟪 🟩	52 Te ▣	53 I 🟥	54 Xe
55 Cs	56 Ba	57 La 🟩	72 Hf	73 Ta	74 W 🟥 🟦	75 Re	76 Os	77 Ir	78 Pt 🟦	79 Au 🟪	80 Hg 🟪	81 Tl 🟪 🟩	82 Pb 🟪 🟩	83 Bi 🟪	84 Po	85 At	86 Rn

*CN, SCN	58 Ce 🟩	59 Pr 🟩	60 Nd	61 Pm	62 Sm	63 Eu 🟩	64 Gd	65 Tb	66 Dy 🟩	67 Ho 🟩	68 Er	69 Tm	70 Yb 🟩	71 Lu
	90 Th 🟩🟦	91 Pa	92 U 🟩🟦	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Class Assignment

- Abstract Due
- Read Chapters 1, 2, 4, 5, 6, 7, 12, 13, and 15 “Electrochemical Methods” Bard

Potential Step Methods

Abrasive Stripping Voltammetry

Mechanical (abrasive) transfer of solid material onto an electrode surface (e.g. paraffin coated graphite)