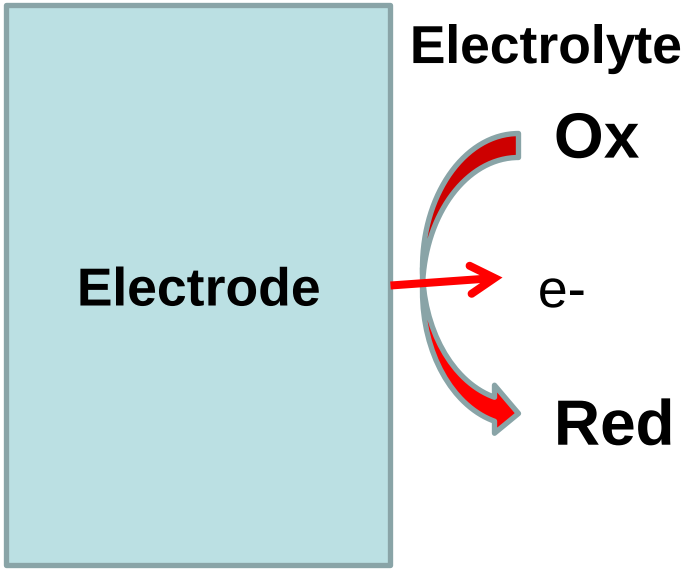
Electroanalytical Measurements

Electrochemical (analytical measurements) are *heterogeneous* in nature.



Electrolyte solution

$$i = kC$$

Current is also a direct measure of reaction rate.

Important factors: electrode material, electrolyte solution, surface cleanliness, and surface chemistry

Currents in Electrochemical Cells

Remember = all electrochemical reactions take place at the electrode-solution interface!!

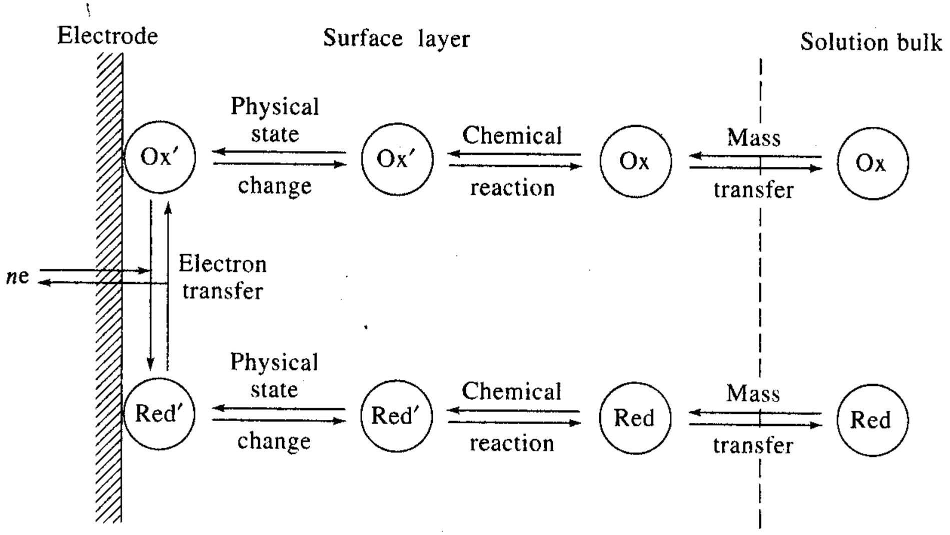


Figure 22-8 Steps in the reaction $Ox + ne^- \rightleftharpoons Red$ at an electrode. Note that the surface layer is only a few molecules thick. *(Adapted from A. J. Bard and L. R. Faulkner,* Electrochemical Methods, *p. 21. New York: Wiley, 1980. Reprinted by permission of John Wiley & Sons, Inc.)*

Current limited by (i) charge transfer resistance, (ii) mass transport resistance and ohmic solution resistance.

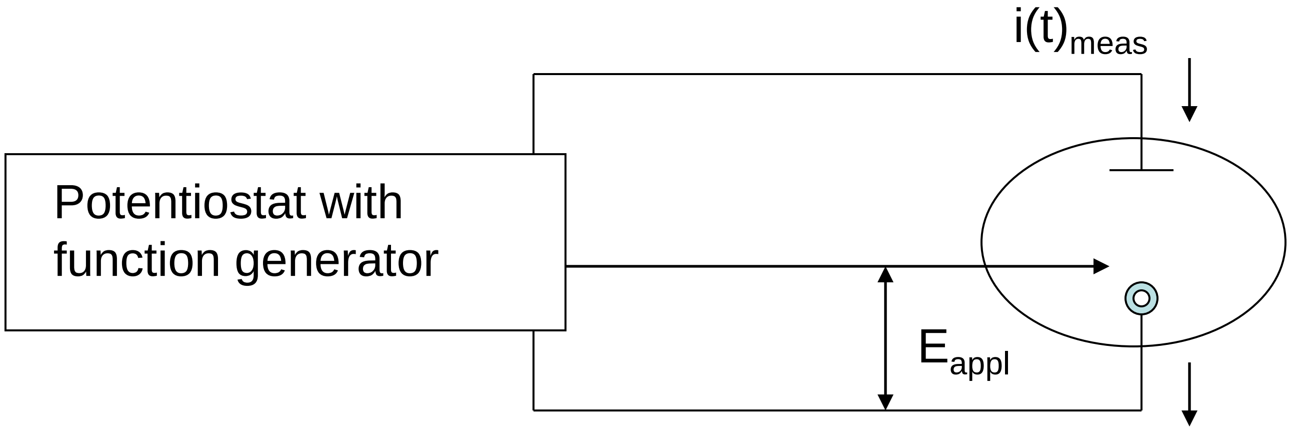
Modes of mass transport: (i) diffusion, (ii) convection and (iii) migration.

i (current) = $\partial Q/\partial t$ = nFA(area, cm^2)$\partial C/\partial t$ (flux, mol/s-cm^2)

Chapter 25 – Cyclic Voltammetry

Read pp. 716 - 729   748-750   Problems: 25-2, 3, 4, 7, 10, 13

- Control the applied potential and measure the current that flows. Often performed under mass transport limited conditions.

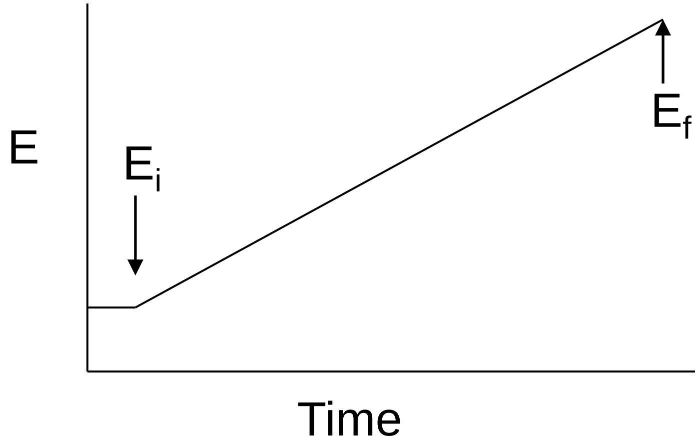


Working – Au, Pt, carbon (pretreated to clean and smooth the surface)
Counter – large area carbon placed normal to the working electrode

Instrument allows for a controlled potential to be applied between the working and reference electrodes that can be maintained regardless of the current flowing between the counter and working electrodes.

Chapter 25 – Potential Sweep Methods

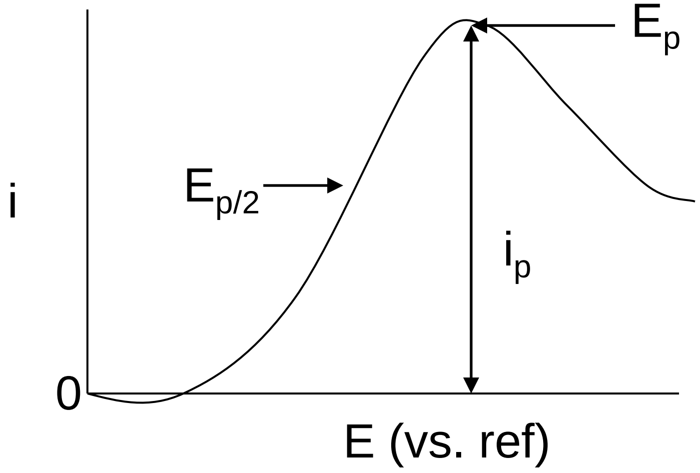
Linear Sweep Voltammetry



Perturbation signal: $E(t) – E_i + \upsilon t$

υ = scan rate = ± V/s

$Ox + e^- \leftrightarrow Red$

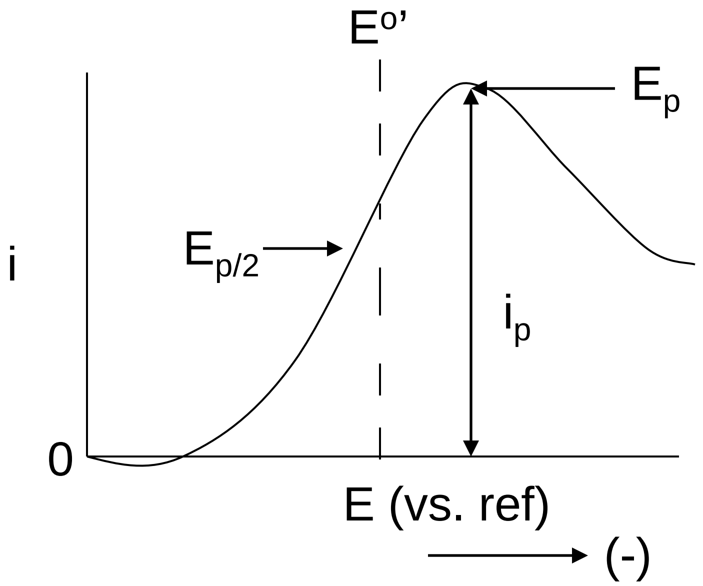


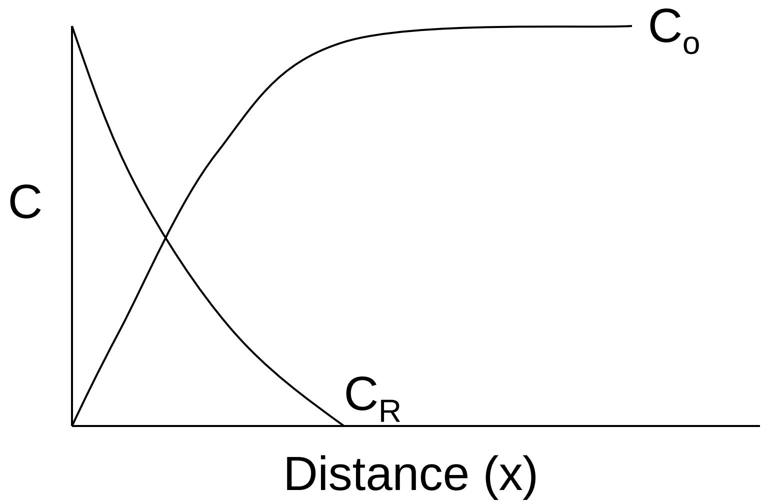
$i_p \; \alpha \; C_o$

Macroelectrodes: max. 1000 mV/s

Microelectrodes: max. 10^6 V/s

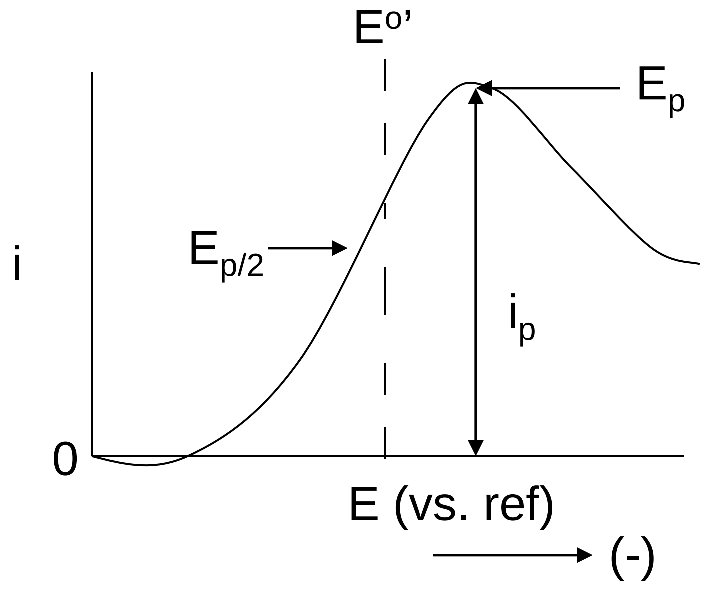
Chapter 25 – Potential Sweep Techniques

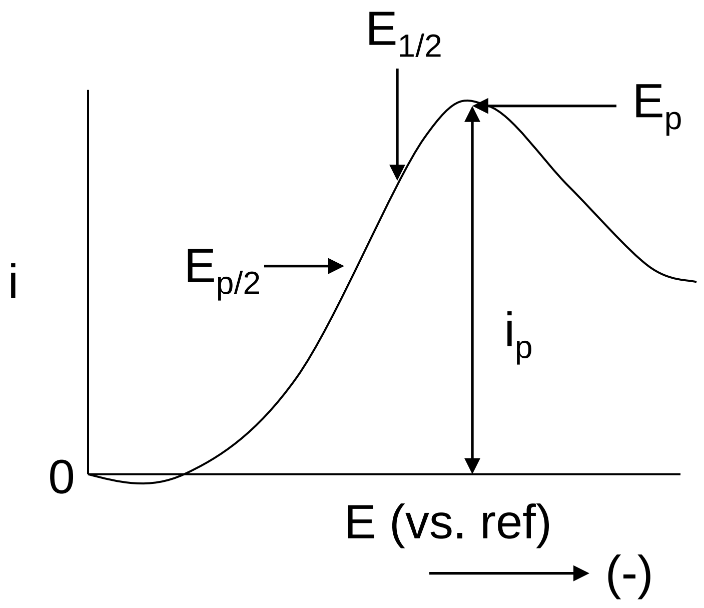




Potential reached vicinity of $E^{o'}$ and current begins to flow. As potential grows more negative surface concentration of Ox must drop hence the flux and current increase. Steep $\partial C/\partial x$! As potential moves past $E^{o'}$, the surface concentration drops to nearly zero and mass transport of Ox reaches a maximum rate. Current then declines as a depletion effect sets in.

Chapter 25 – Potential Sweep Techniques





Nernstian (Reversible) System

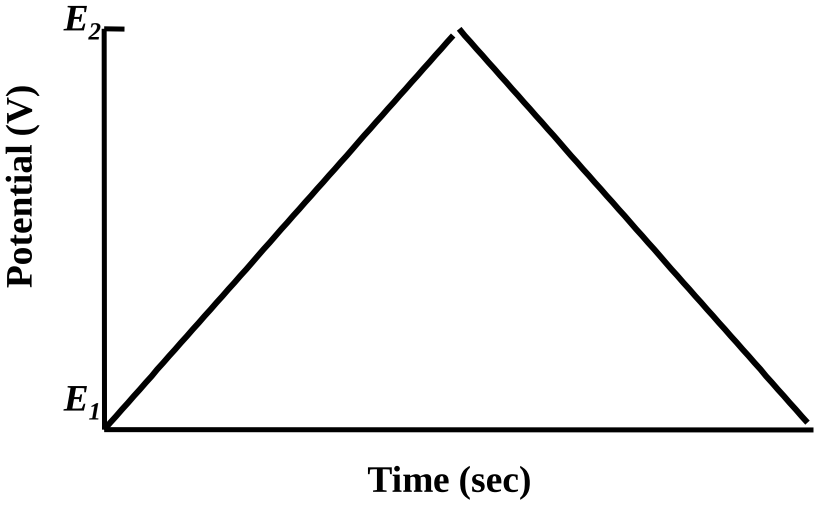
$$C_o(0,t)/C_R(0,t) = f(t) = \exp\,[nF/RT(E_i+\upsilon t - E^{o\prime})$$

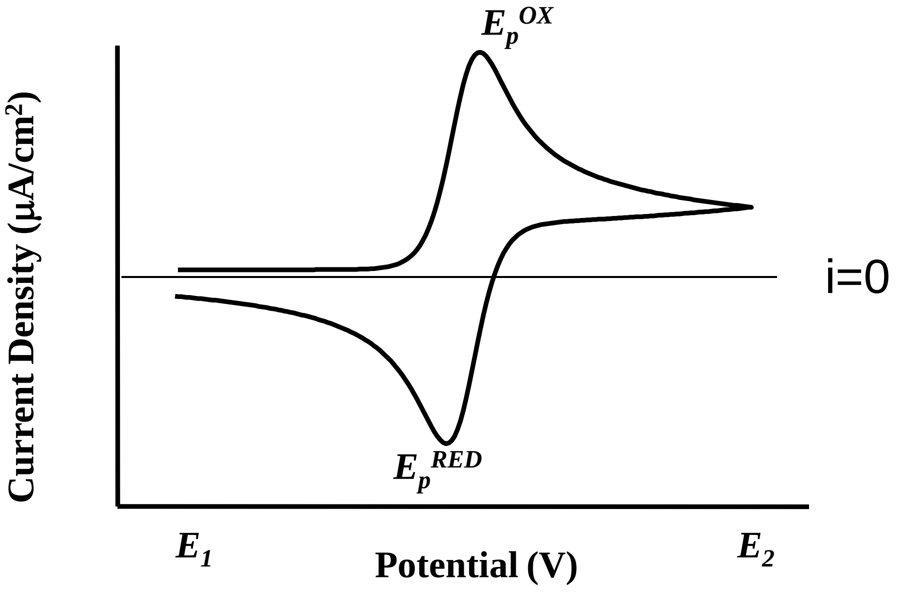
$$\boxed{i_p = (2.69\text{x}10^5)n^{3/2}AD_o^{1/2}C_o{}^{*}\upsilon^{1/2}}$$

Chapter 25 – Potential Sweep Techniques

Cyclic Voltammetry

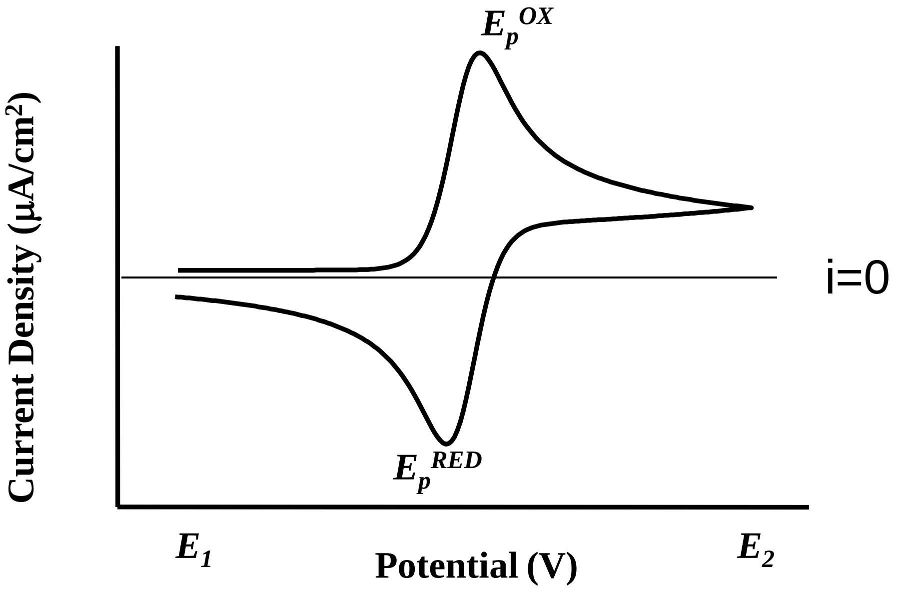
Reversal technique – Useful for determining k°, concentrations of analyte and studying electrode reaction mechanisms (generate a product at the electrode surface on the forward sweep and probe its fate on the rev. sweep





Chapter 25 – Potential Sweep Techniques

Important Diagnostics

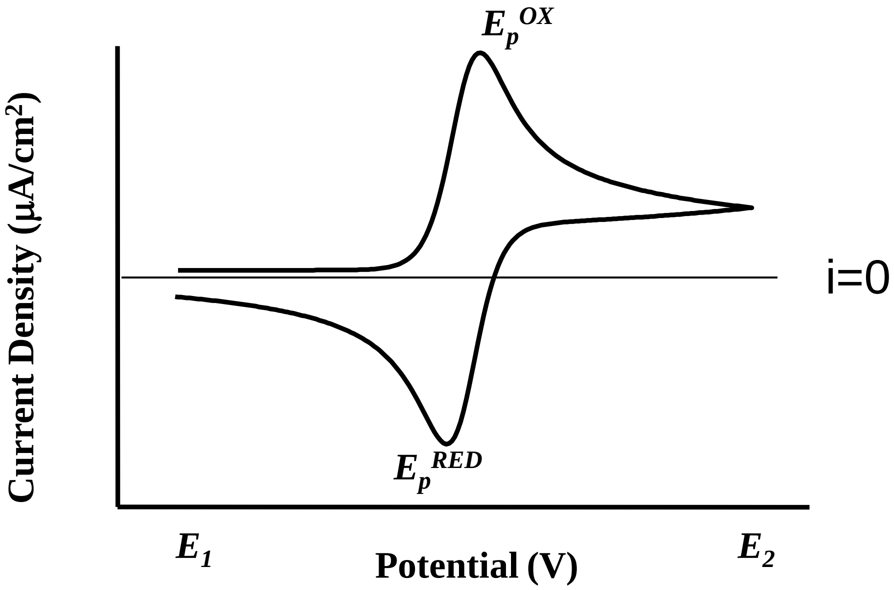


- E_p^{ox} and E_p^{red}
- $\Delta E_p = E_p^{ox} - E_p^{red}$
- i_{pox} and i_p^{red}
- i_p^{ox}/i_p^{red} ratio
- Q_p^{ox} and Q_p^{red}
- $E_{p/2}$

Remember: the perturbation signal is a time dependent potential sweep. Where the wave shows up on the potential axis (time!) depends on the time dependence of the electrode reaction (reaction kinetics).

Chapter 25 - Potential Sweep Techniques

Reversible or Nernstian Kinetics



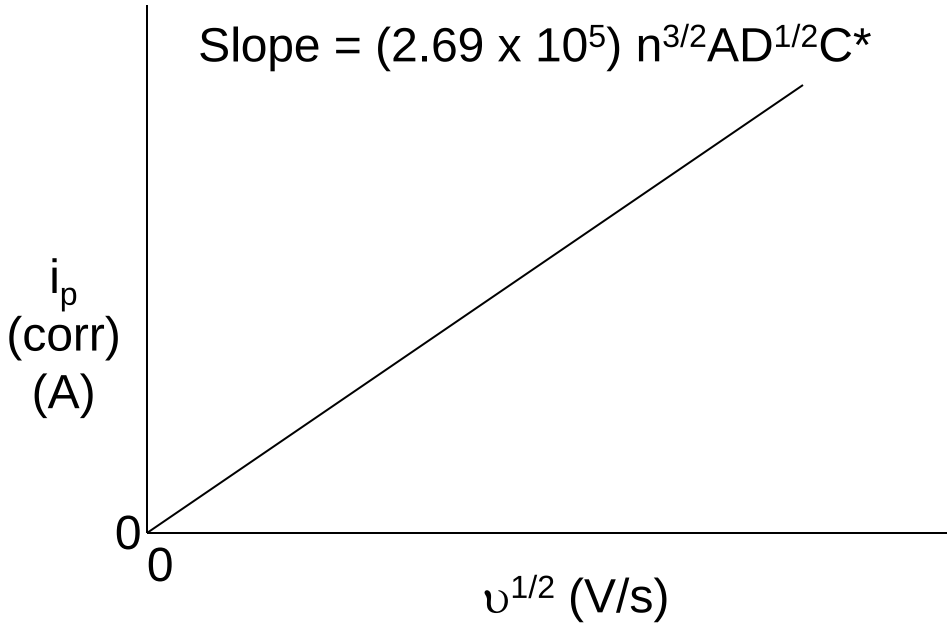
- $\Delta E_p = E_p^{ox} - E_p^{red} = 0.059/n$ V
- $\Delta E_p \neq f(\upsilon)$
- $i_{pox} / i_p^{red} = 1$
- i_p^{ox} and $i_p^{red} = f(\upsilon^{1/2})$
- $Q_p^{ox}/Q_p^{red} = 1$
- $\left| E_p - E_{p/2} \right| = 2.20\ RT/nF = 56.5/n$ mV

$E^{o\prime} = (E_p^{ox} + E_p^{red})/2$

Standard vs. Formal Potential

$$\boxed{i_p = (2.69 \times 10^5)\, n^{3/2} A D^{1/2} C^* \upsilon^{1/2}}$$

Chapter 25 – Potential Sweep Techniques



Linearity indicates:

- Semi-infinite linear diffusion controls the reaction rate.
- Electrochemical reversibility or irreversibility.
- Non-complicated redox reaction (can be reflective of this).

$$i_p = (2.69 \times 10^5)\, n^{3/2} A D^{1/2} C^* \upsilon^{1/2}$$

Anodic Stripping Voltammetry

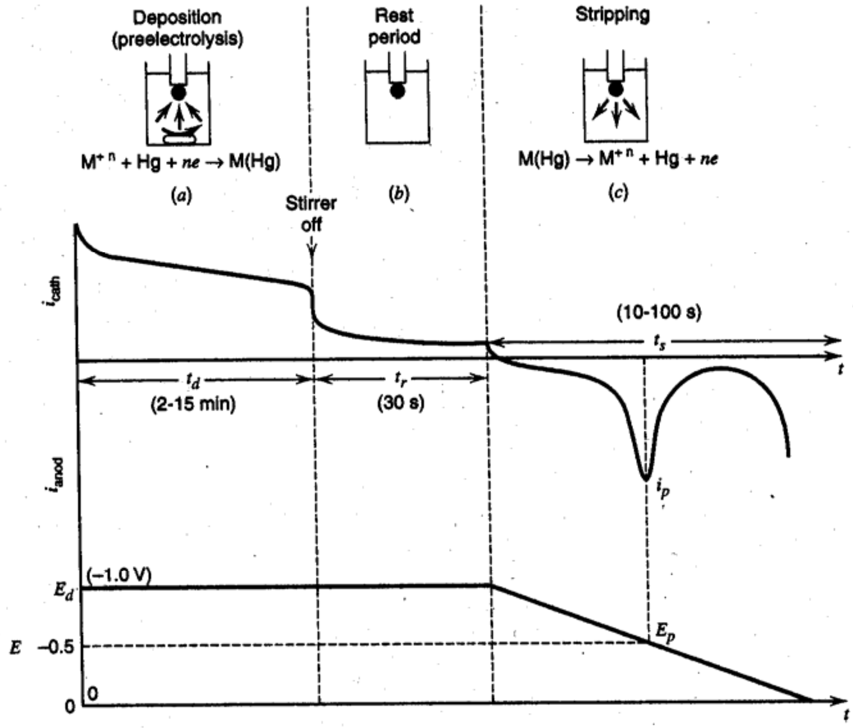


Figure 11.8.1 Principle of anodic stripping. Values shown are typical ones used; potentials and E_p are typical of Cu^{2+} analysis. (*a*) Preelectrolysis at E_d; stirred solution. (*b*) Rest period; stirrer off. (*c*) Anodic scan (v = 10–100 mV/s). [Adapted from E. Barendrecht, *Electroanal. Chem.*, **2**, 53 (1967), by courtesy of Marcel Dekker, Inc.]

Stripping analysis is an analytical technique that involves (i) *preconcentration* of a metal phase onto a solid electrode surface or into Hg (liquid) at negative potentials and (ii) selective *oxidation* of each metal phase species during an anodic potential sweep.

Excellent technique for trace metal ion analysis!

Preconcentration leads to low detection limits!

Anodic Stripping Voltammetry

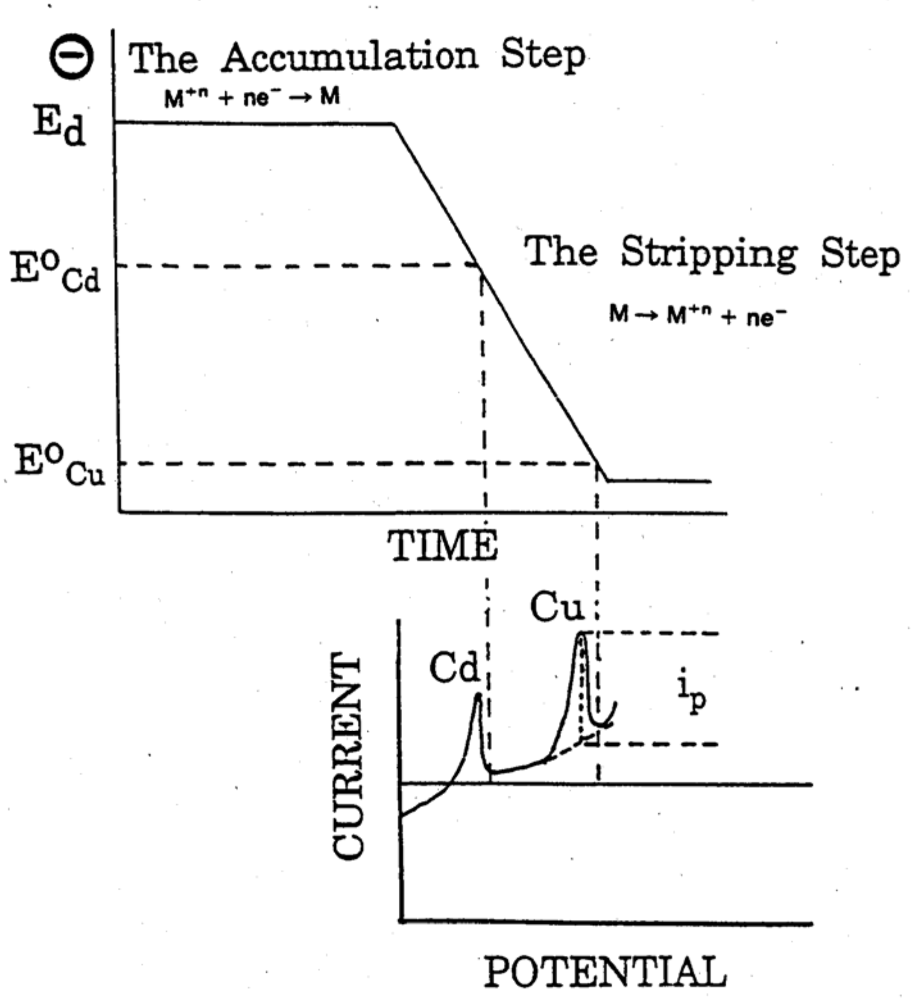


Figure 2.12 Anodic stripping voltammetry: the potential-time waveform (top), along with the resulting voltammogram (bottom).

1. HMDE
2. MFE
3. Bare carbon, Au, etc.

10^{-4} to 10^{-5} Hg^{+2} added for co-metal deposition.

Electrodeposition step, E_d, carried out in a stirred solution at a potential several tenths of a volt more negative that the E^o for the least easily reduced metal ion.

Anodic Stripping Voltammetry

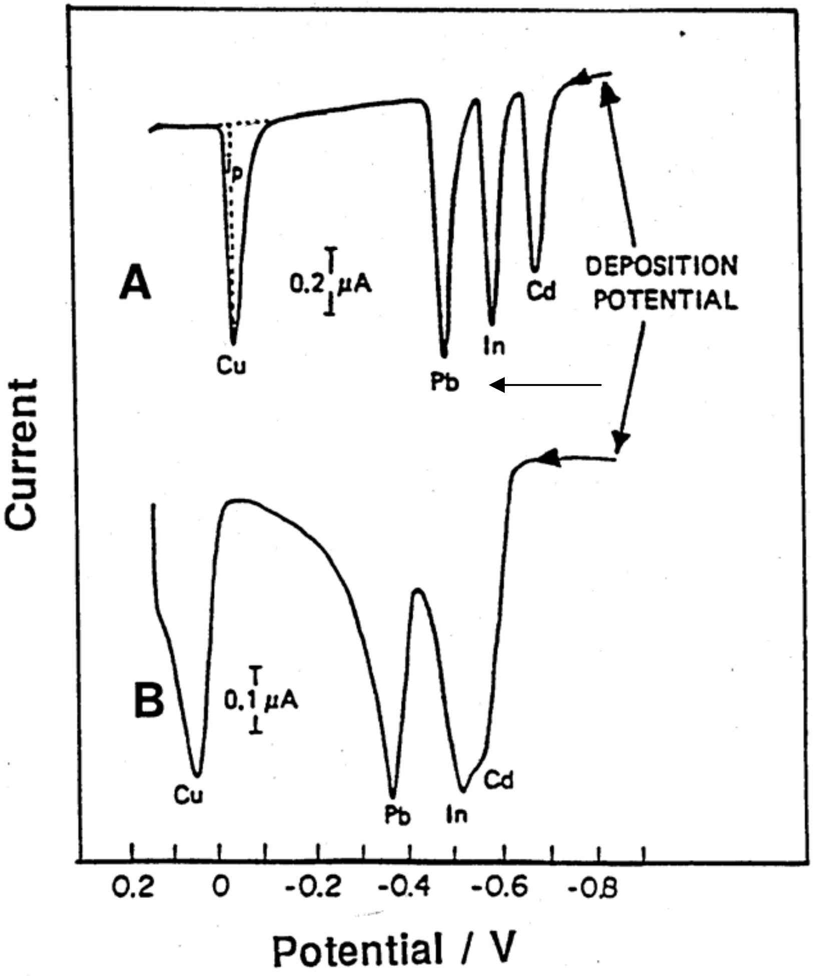


Figure 2.14 Stripping voltammograms for 2×10^{-7} M Cu^{+2}, Pb^{+2}, In^{+3}, and Cd^{+2} at the (A) mercury film and (B) hanging mercury drop electrodes. [Reproduced with permission (20).]

CONTROLLED POTENTIAL TECHNIQUES 55

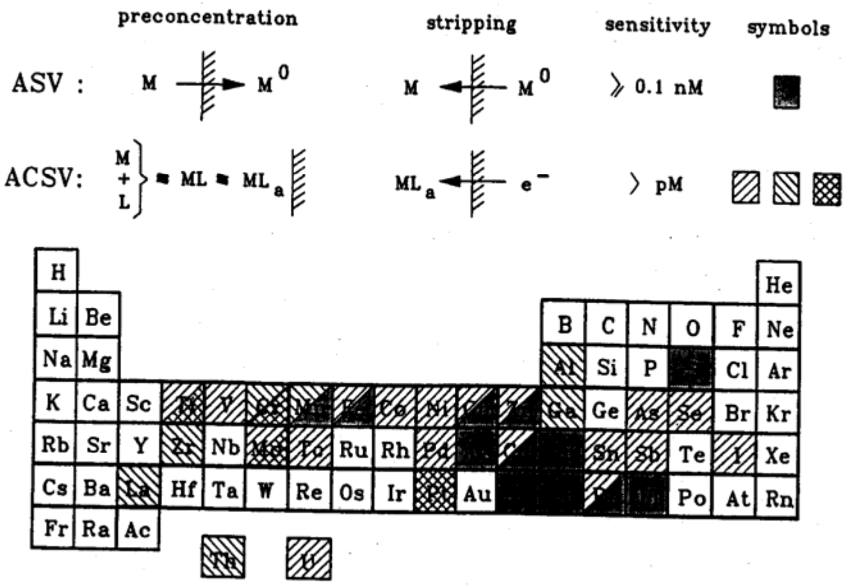


Figure 2.19 Elements measured by conventional ASV ■, adsorptive stripping schemes with reduction of the element in the complex ▨, reduction of the ligand ▧, or catalytic process ▩. [Reproduced with permision (39).]

Anodic Stripping Voltammetry

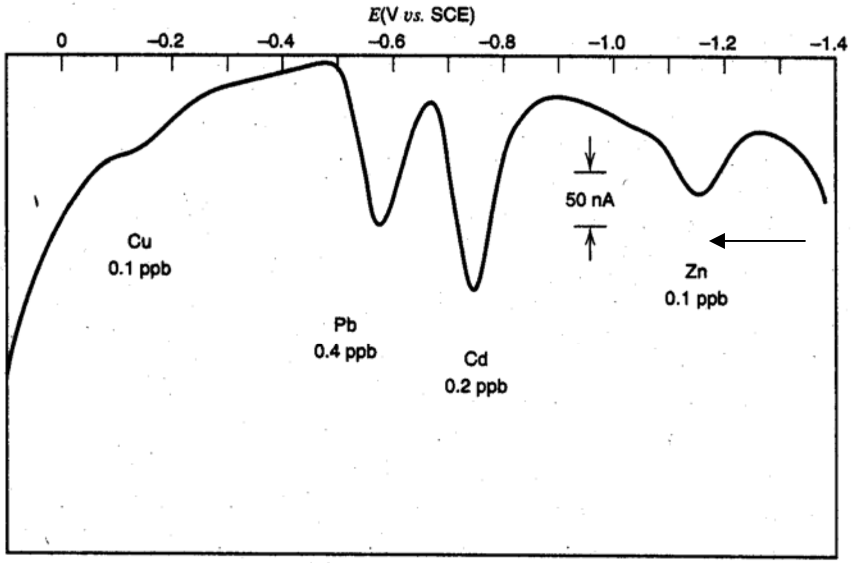
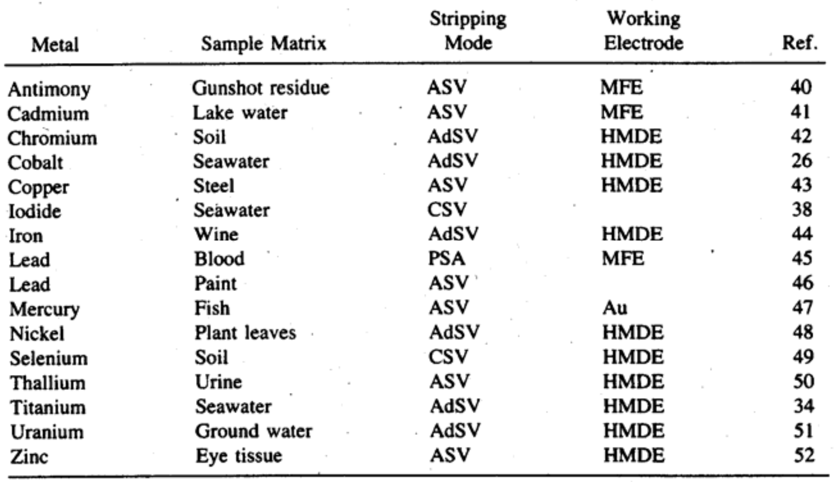


Figure 11.8.5 Anodic stripping analysis of a solution containing 2×10^{-9} *M* Zn, Cd, Pb, and Cu at an MFE (mercury-plated, wax-impregnated graphite electrode). Stripping carried out by differential pulse voltammetry.

Table 2.3 Representative Applications of Stripping Analysis



Metal	Sample Matrix	Stripping Mode	Working Electrode	Ref.
Antimony	Gunshot residue	ASV	MFE	40
Cadmium	Lake water	ASV	MFE	41
Chromium	Soil	AdSV	HMDE	42
Cobalt	Seawater	AdSV	HMDE	26
Copper	Steel	ASV	HMDE	43
Iodide	Seawater	CSV		38
Iron	Wine	AdSV	HMDE	44
Lead	Blood	PSA	MFE	45
Lead	Paint	ASV		46
Mercury	Fish	ASV	Au	47
Nickel	Plant leaves	AdSV	HMDE	48
Selenium	Soil	CSV	HMDE	49
Thallium	Urine	ASV	HMDE	50
Titanium	Seawater	AdSV	HMDE	34
Uranium	Ground water	AdSV	HMDE	51
Zinc	Eye tissue	ASV	HMDE	52

ASV = anodic stripping voltammetry
CSV = cathodic stripping voltammetry
AdSV = adsorptive stripping voltammetry

ppb and even ppt detection limits are possible (s/n =3) with ASV!

Anodic Stripping Voltammetry

- Very sensitive and reproducible (RSD<5%) method for trace metal ion analysis in aqueous media.
- Concentration limits of detection for many metals are in the low ppb to high ppt range (S/N=3) and this compares favorably with AAS or ICP analysis.
- Field deployable instrumentation that is inexpensive.
- Approximately 12-15 metal ions can be analyzed for by this method.
- The stripping peak currents and peak widths are a function of the size, coverage and distribution of the metal phase on the electrode surface (Hg or alternate).