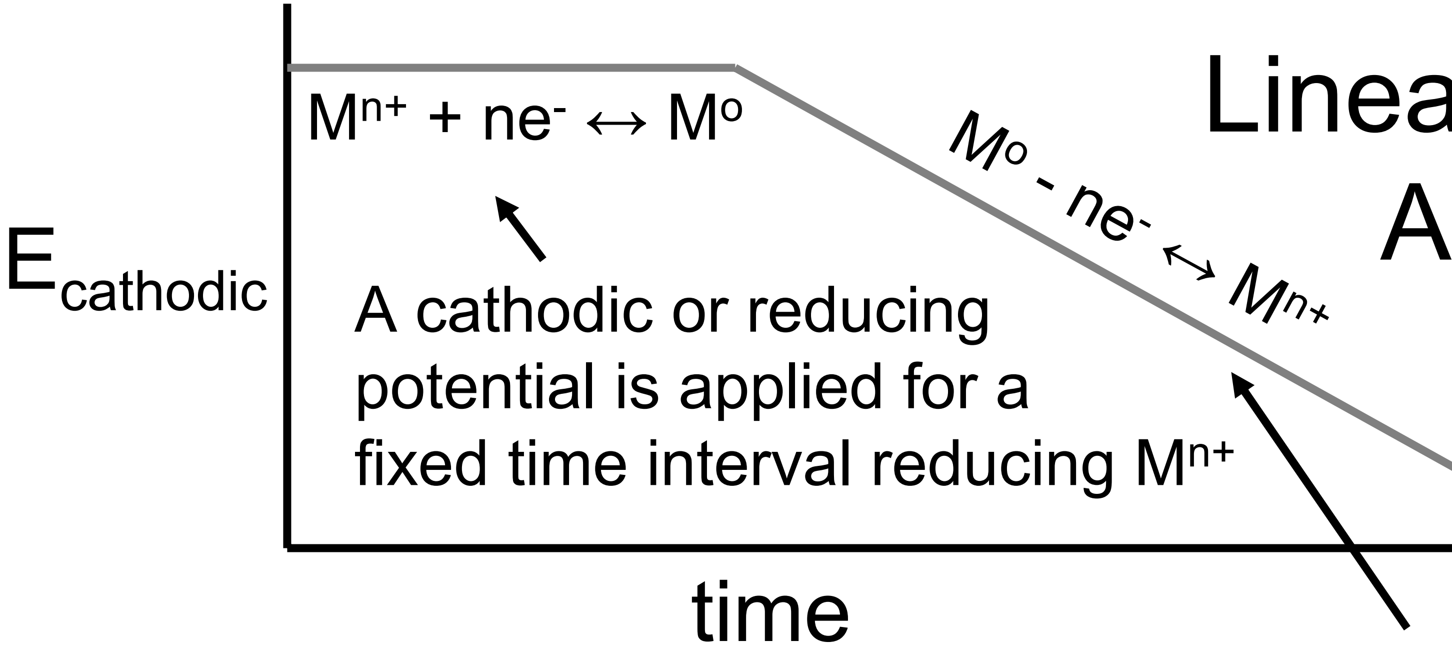
# Anodic Stripping Voltammetry (ASV)

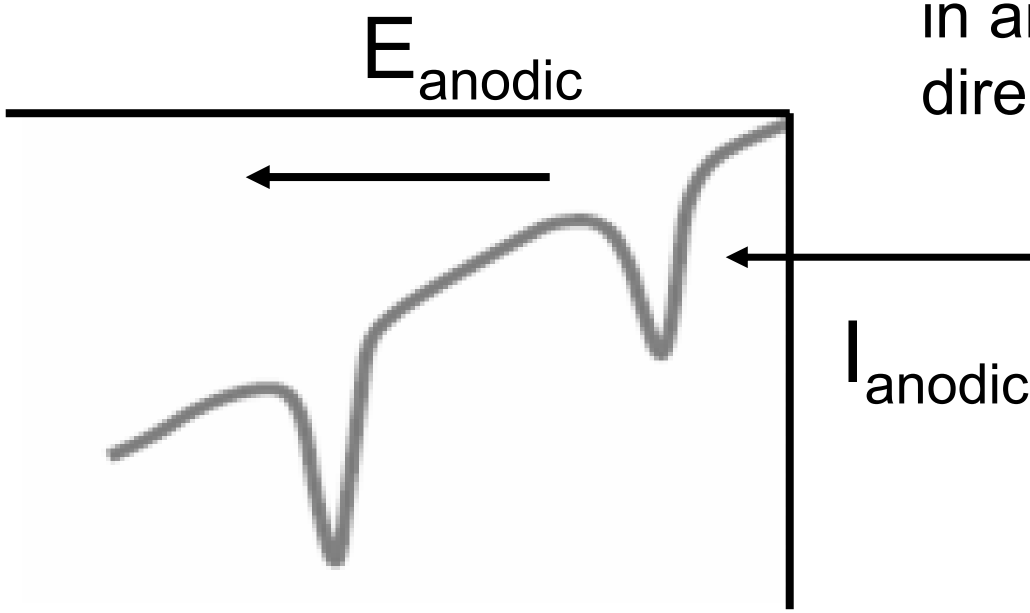
Combines two techniques discussed previously

1) The first step is Electrodeposition at constant potential for the purpose of preconcentrating species of interest
   - Done in stirred solution to enhance mass transfer
   - Either plate 100% of material (usually a metal) onto or into the electrode
   - Or plate with reproducible stirring for a known time interval to plate a constant fraction each run (most common approach)
2) The second step is a linear potential sweep in the anodic direction to reoxidize or strip out the plated material
   - Unstirred solution during stripping step

# Linear Scan ASV




Potential is scanned in anodic or oxidizing direction to strip out $M^o$

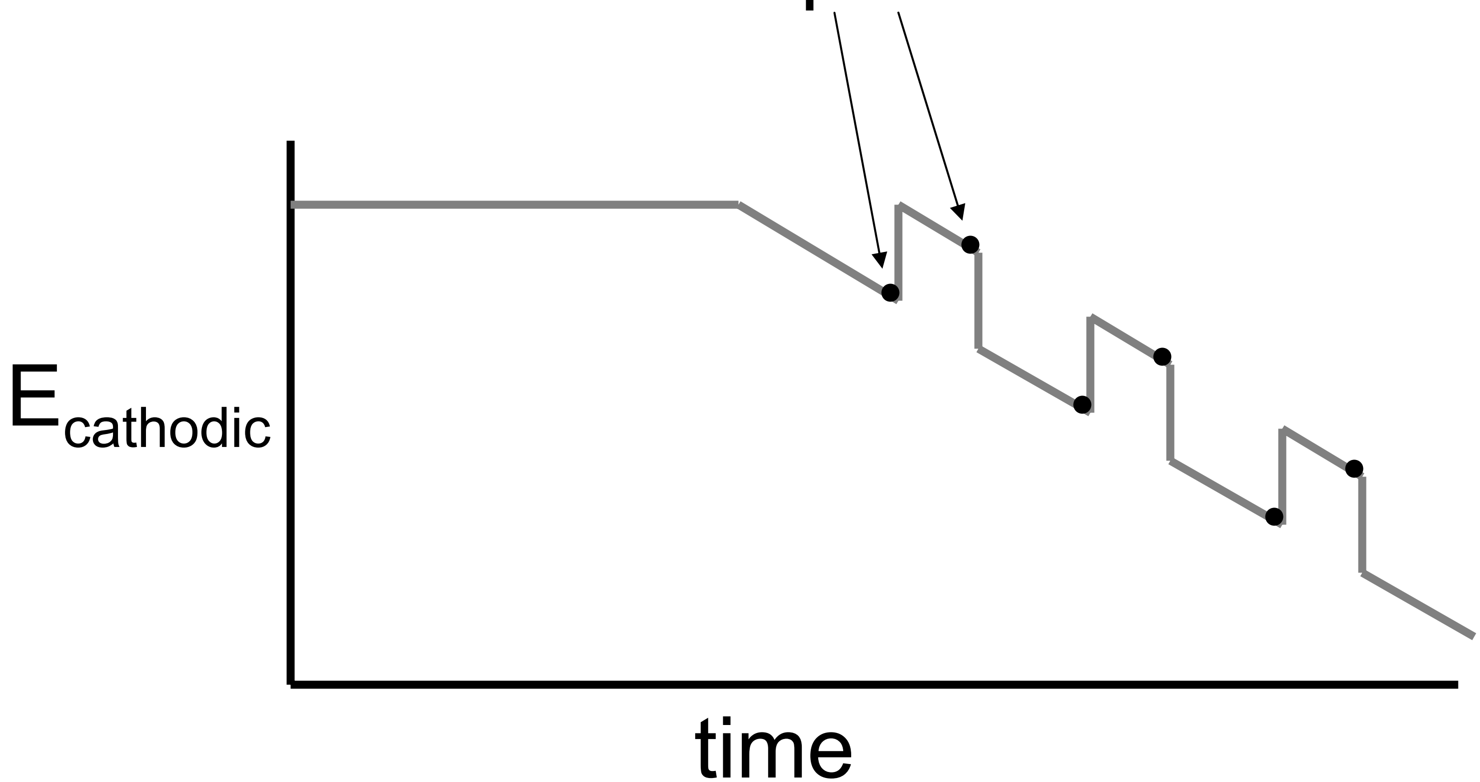


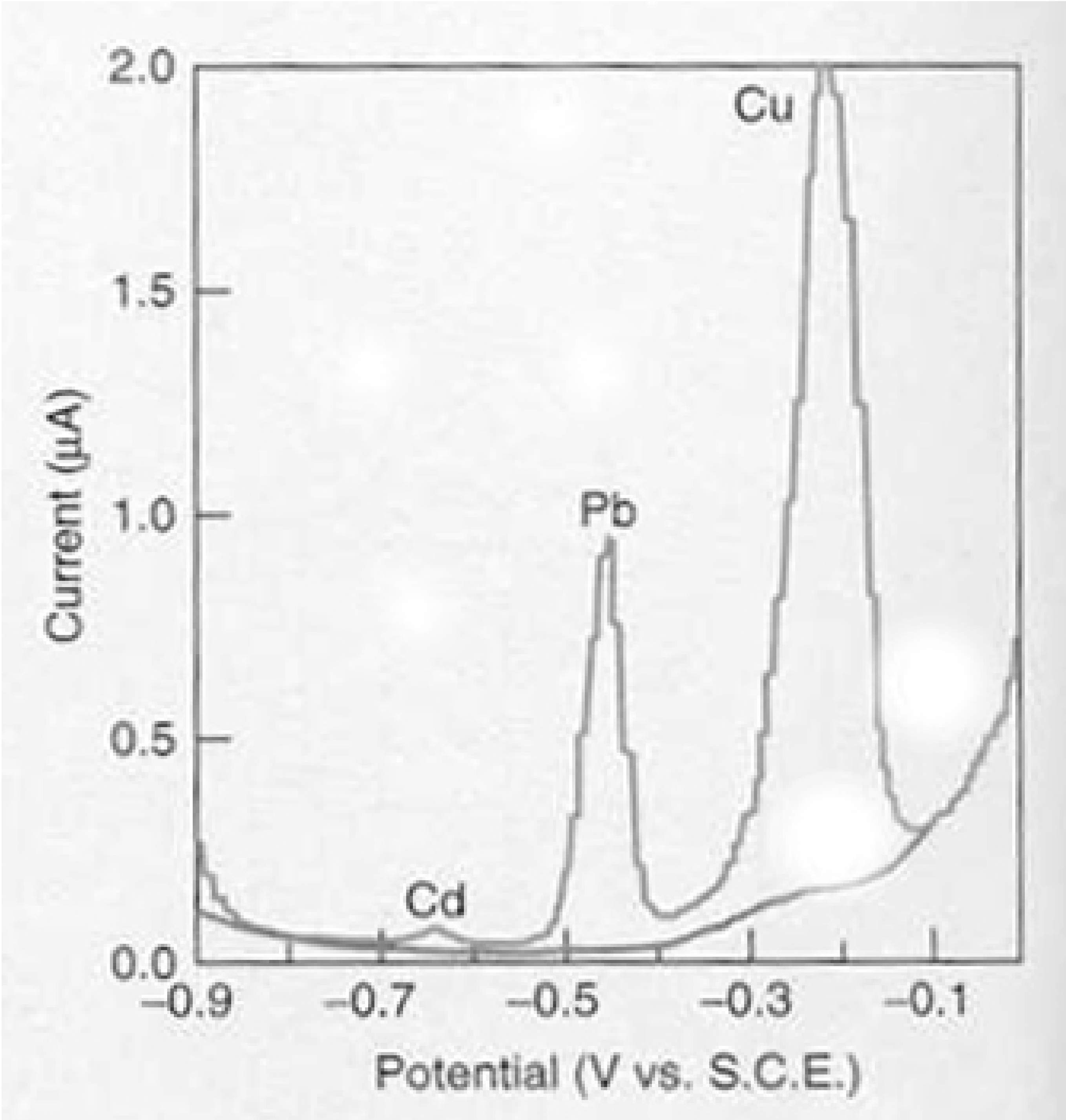

Convention requires plotting upside down peaks with backward scan

- ASV can be done with any electrode, however, once again mercury provides a very good surface for reduction & oxidation of metals
- The Hanging Mercury Drop Electrode (HMDE) has been used extensively
- A single drop is used throughout the experiment


Hanging
Mercury
Drop

- Can improve by use differential pulse waveform during anodic scan (i.e., stripping step)
- Measure current at points indicated



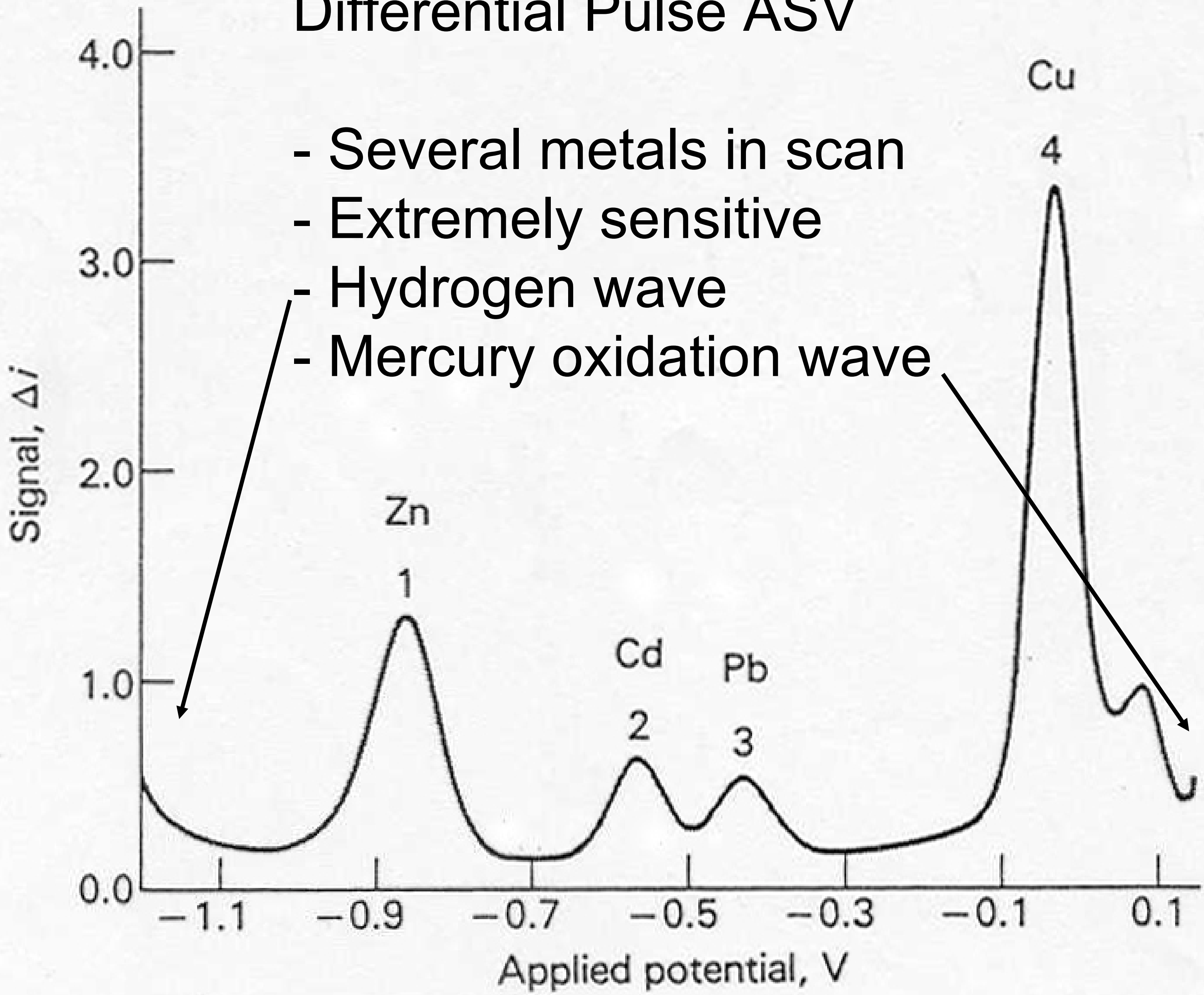



DPASV peaks showing steps caused by pulses

- A thin film mercury electrode (TFME or MFE) can also be prepared by plating mercury onto the surface of a carbon electrode
- This is usually accomplished by adding a solution of mercury ions to the sample and plating out the mercury simultaneously with the analyte ions
- The other metals strip out first and mercury last

# Differential Pulse ASV

- Several metals in scan
- Extremely sensitive
- Hydrogen wave
- Mercury oxidation wave



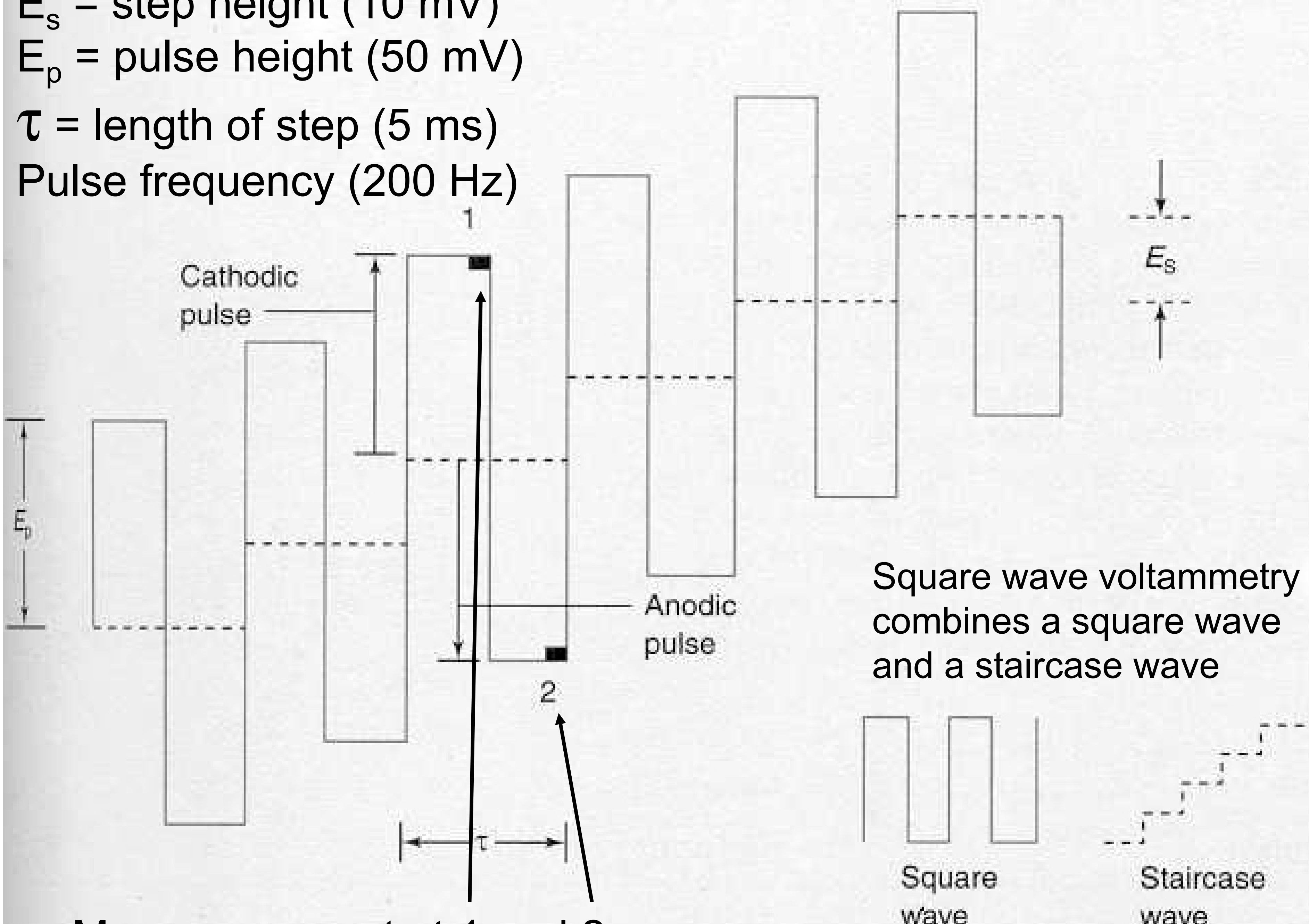
- ASV or DPASV are widely used especially where high sensitivity is necessary
- Use longer plating times (electrolysis step) to preconcentrate more metal
- Nanomolar ($10^{-9}$ M) or part per trillion (ppt) detection is achievable
- e.g., metals in seawater, Pb in blood, etc.
- Instrumentation inexpensive and portable
- As with most electrochemistry, a skilled operator is required
- Inert metal complexes are not be measured – free metal ion only

- Can also do cathodic stripping voltammetry (CSV) or adsorptive stripping voltammetry using an anodic potential to adsorb anionic species on the surface of the electrode
- Ions like $MoO_4^{2-}$ and $CrO_4^{2-}$
- Stripping step is a cathodic scan

# Square Wave Voltammetry

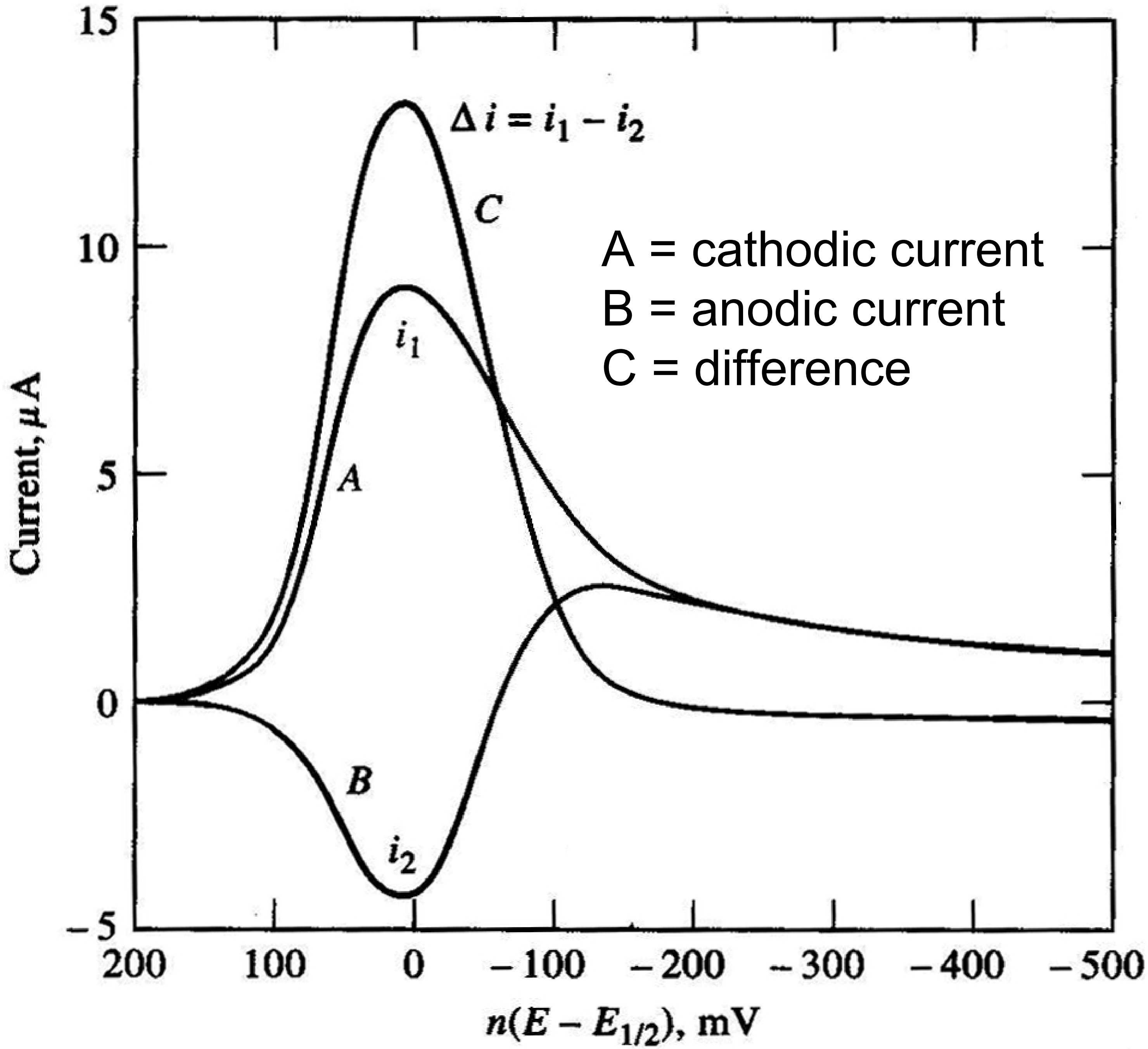
- One of the most modern electroanalytical techniques (approximately 20 years old)
- Very sensitive
- Very fast (1 Volt scan in 0.5 sec)
- Can be used with all types of electrodes
- Can be used with a preconcentration step as in ASV (square wave stripping)
- Uses large amplitude square wave
- $I = n F A D^{1/2} C \pi^{1/2} \tau^{1/2} \psi(E_s,E_p)$

$E_s$ = step height (10 mV)
$E_p$ = pulse height (50 mV)
$\tau$ = length of step (5 ms)
Pulse frequency (200 Hz)




Square wave voltammetry combines a square wave and a staircase wave

Measure current at 1 and 2


15
10
5
0
−5
Current, μA
200
100
0
−100
−200
−300
−400
−500
$n(E - E_{1/2})$, mV
$\Delta i = i_1 - i_2$
C
$i_1$
A
B
$i_2$
A = cathodic current
B = anodic current
C = difference

- Voltammogram is obtained in 0.5 to 3 sec depending on frequency
- If using DME, the entire scan is done in the last half of a single drop
- For a reversible reaction, size of pulse is large enough to cause reduction in one direction and oxidation on reverse pulse
- Get forward current (cathodic) and reverse current (anodic) combine to get 2 x current
- Gives peak at $E_{1/2}$
- Detection limits ~ $10^{-8}$ M, without plating

# Analytical Applications of Electrochemistry

- Quantitative analysis
  - Bulk analysis of samples in lab
  - Sensors for *in situ* measurements
    - Environmental
    - Clinical
    - Process
  - Flow through systems
    - HPLC
    - FIA
    - Pipelines
- Metal speciation
- Study mechanisms of reactions
- Reagent cleanup
- Preconcentration

FIA/HPLC flow cells – use low volume cell with working electrode upstream, reference and counter electrode downstream

Several possible types of measurements

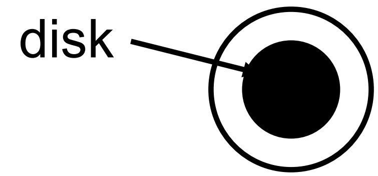
1) Conductance – measure conductivity of flow stream as in ion chromatography (IC)
2) Amperometry – like chronoamperometry with fixed potential measuring current as solutes reach electrode
3) Voltammetry – need fast method like SWV
4) Coulometry – fix E (or I) and count coulombs as solutes go by (not efficient)

# Frontiers in Electrochemistry

1) Hydrodynamic electrochemistry

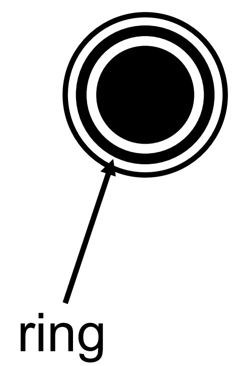
e.g. using Rotating Disk Electrode (RDE)

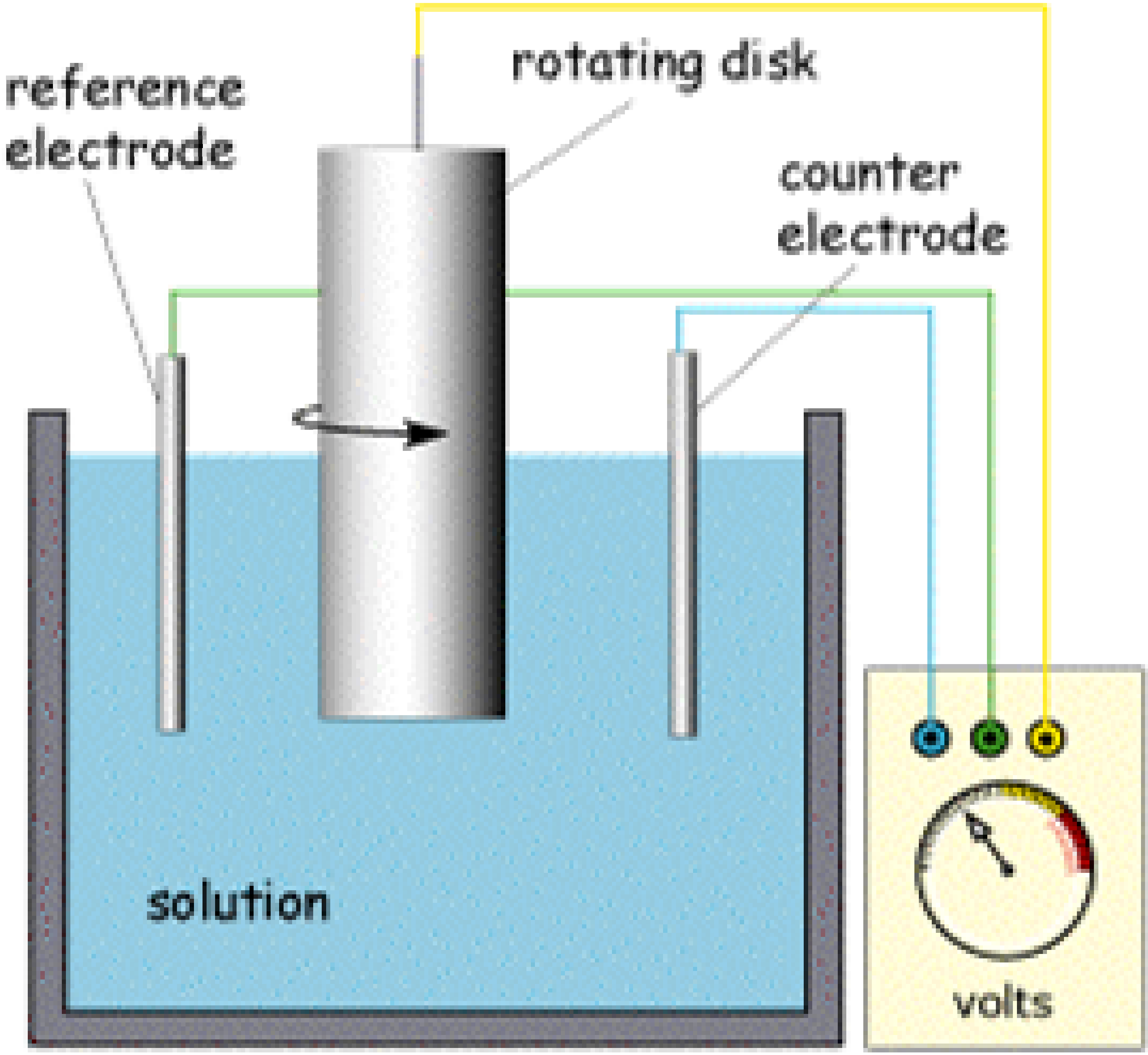
- improved mass transport
- reproducible convection

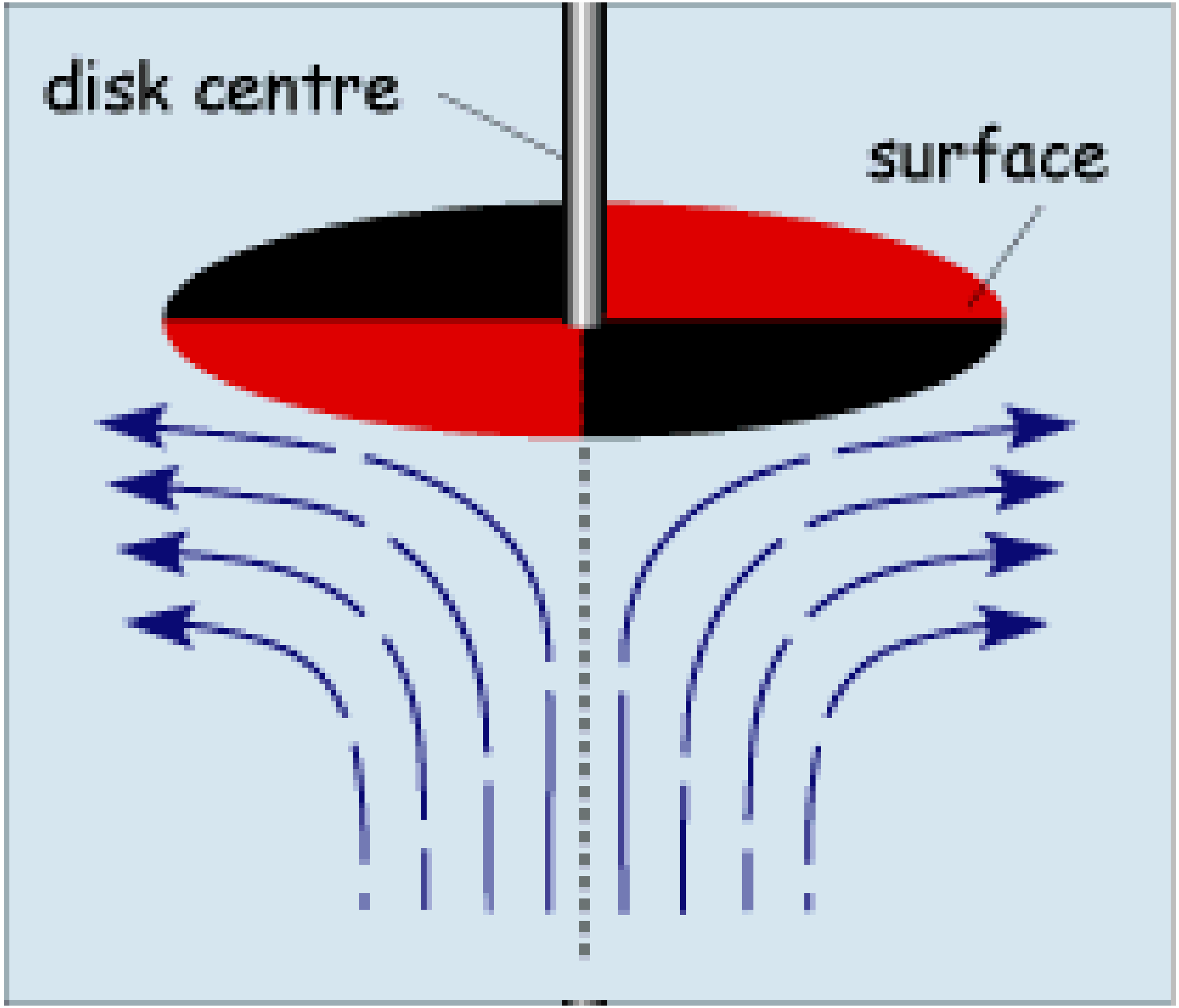



Rotating Ring Disk Electrode (RRDE)

- reduce something at the disk
- reoxidize it as it passes the ring
- similar to cyclic voltammetry




reference
electrode
rotating disk
counter
electrode
solution
volts


disk centre
surface

2) Membrane covered electrodes

- put dialysis membrane or other membrane over the surface of the electrode for selectivity
- mass transport is hindered

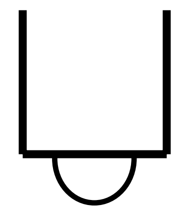
3) Chemically modified electrodes

- modify surface of electrode by attaching functional groups that are either oxidized or reduced themselves or that bind other species that are electroactive

4) Conducting polymers as electrodes

## 5) Ultramicroelectrodes (or microelectrodes)

- smaller than 20 um
- hemispherical shape (usually Hg or Ir)



- several unique characteristics
  - Short diffusion path
  - Faster rate of mass transport
  - Steady state conditions established in < 1 μs
  - No need for convection
  - IR drop low
  - Capacitive current low
  - Can use low ionic strength