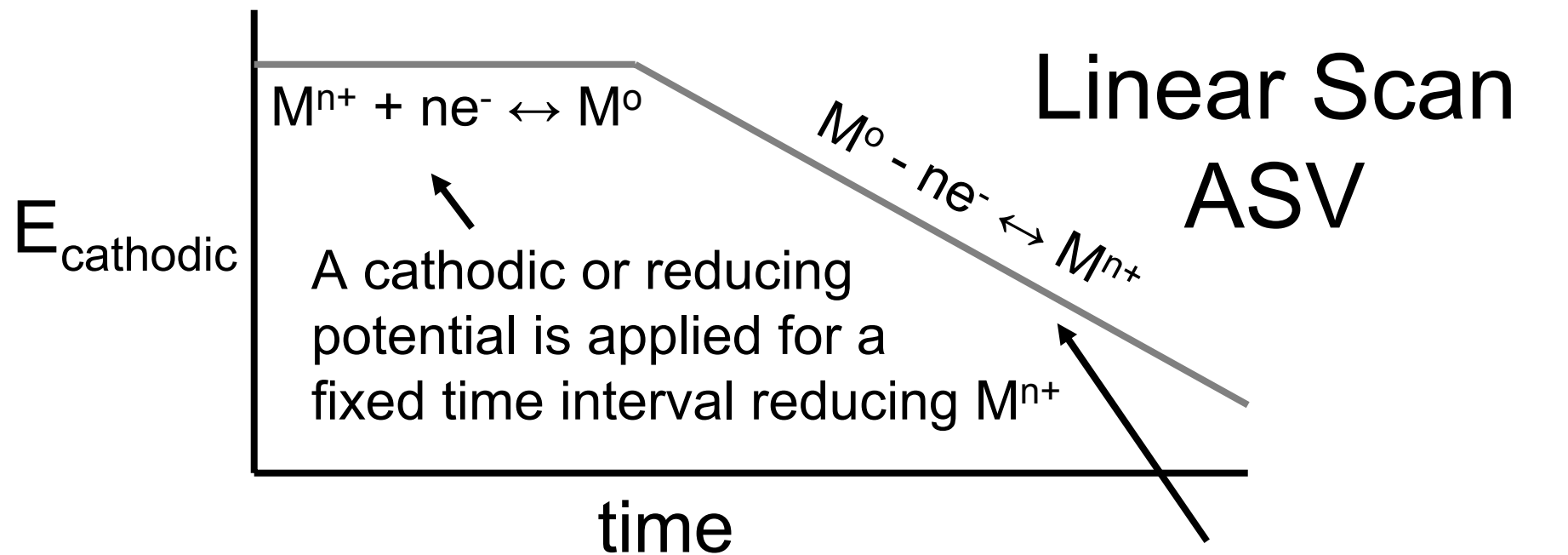


# Anodic Stripping Voltammetry (ASV)

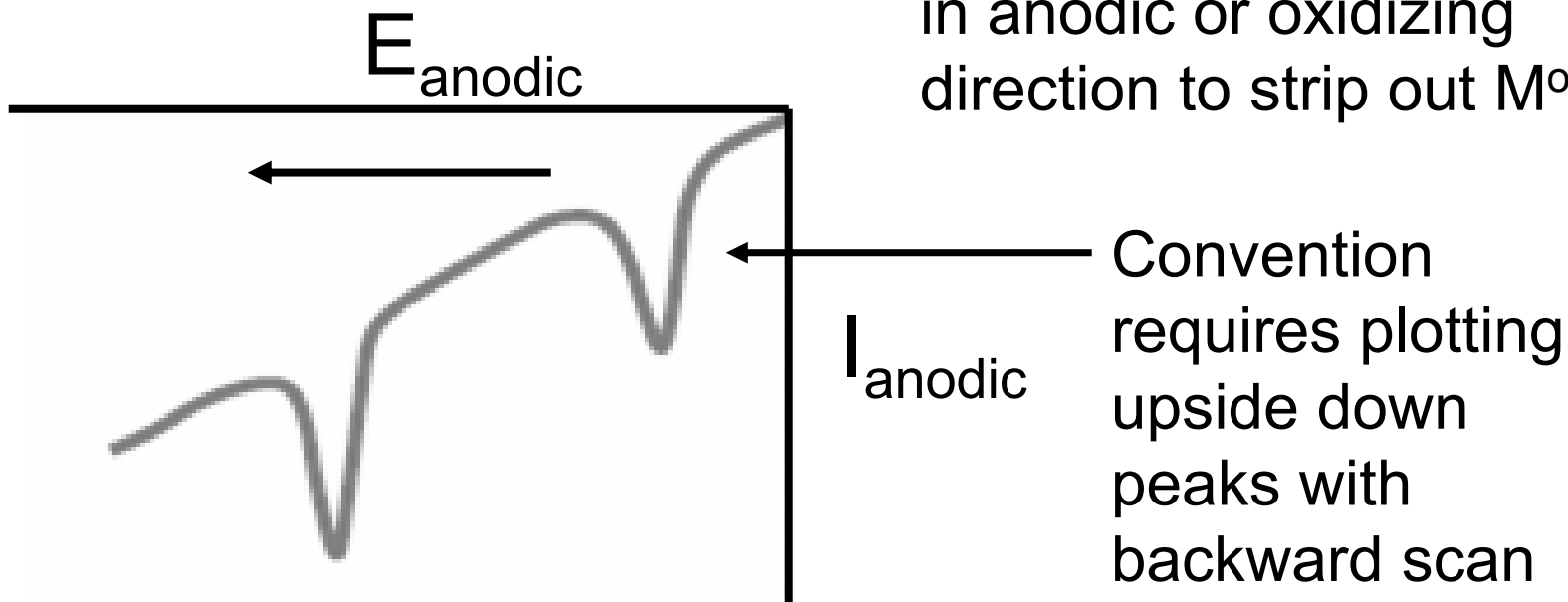
Combines two techniques discussed previously

- 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



A cathodic or reducing potential is applied for a fixed time interval reducing  $M^{n+}$

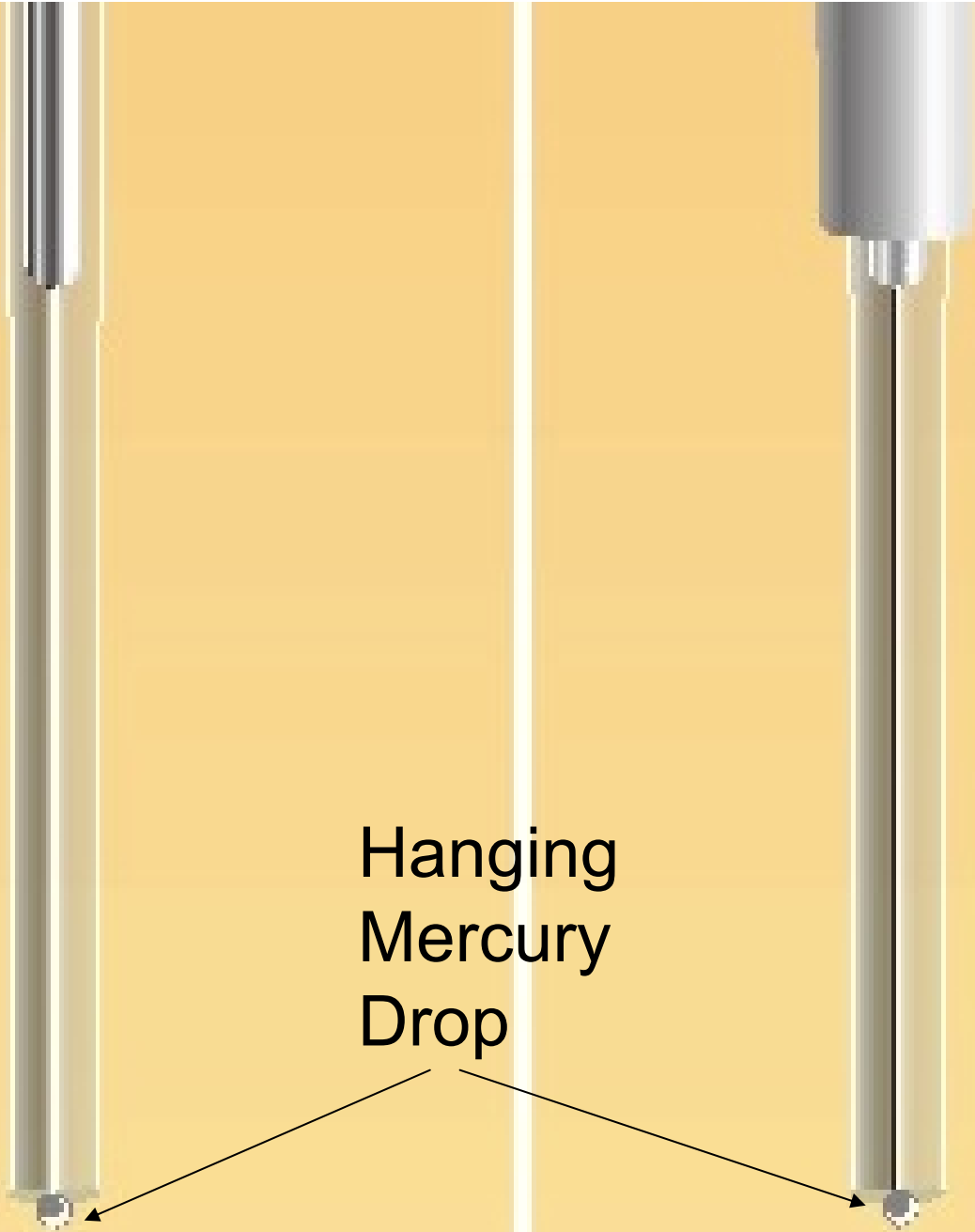
Potential is scanned in anodic or oxidizing direction to strip out  $M^{\circ}$



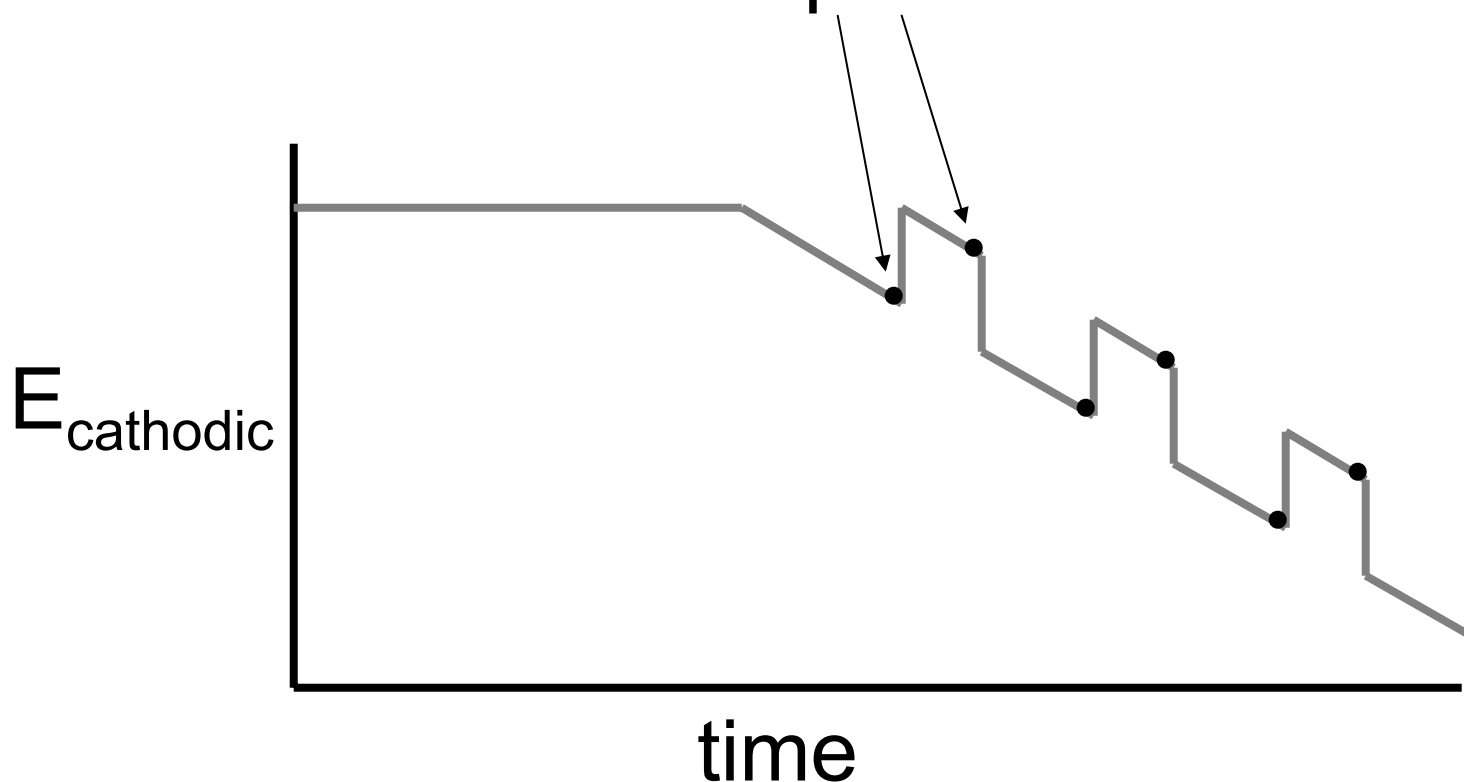
- ASV can be done with any electrode, however, once again mercury provides a very good surface for reduction & oxidation of metals
- The Hanging Mercury Drop Electrode (HMDE) has been used extensively
- A single drop is used throughout the experiment

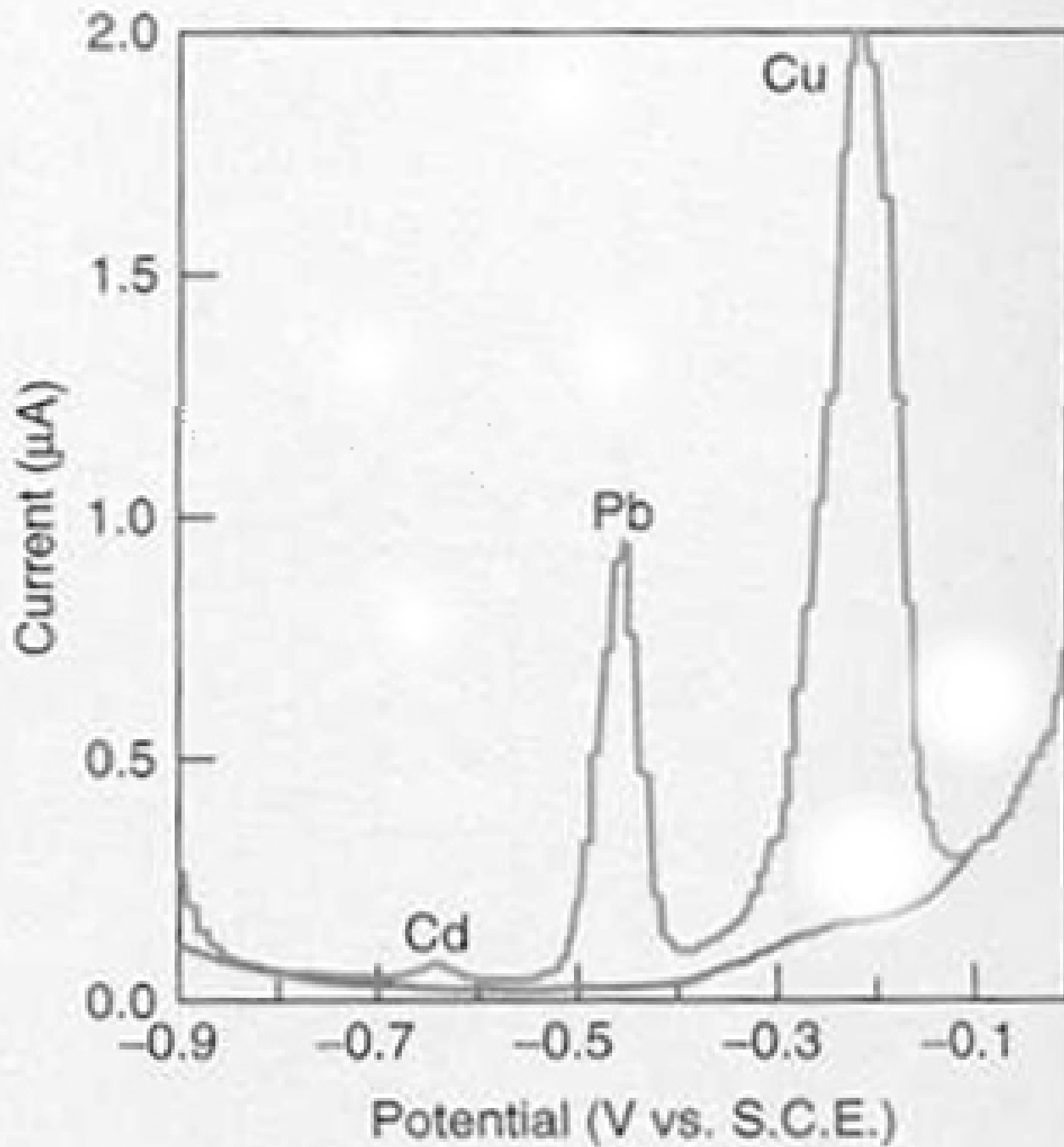


Hanging  
Mercury  
Drop



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



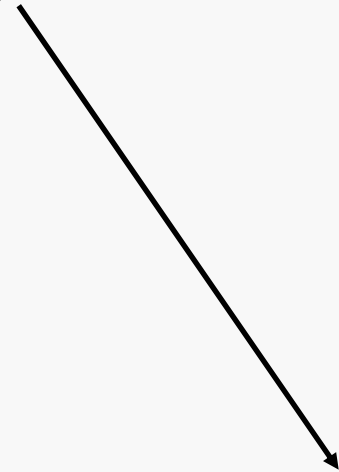
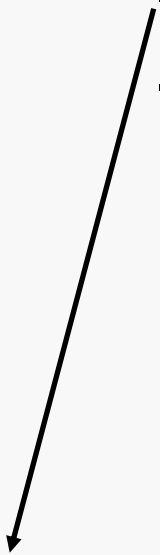


DPASV  
peaks  
showing  
steps  
caused  
by pulses

- 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



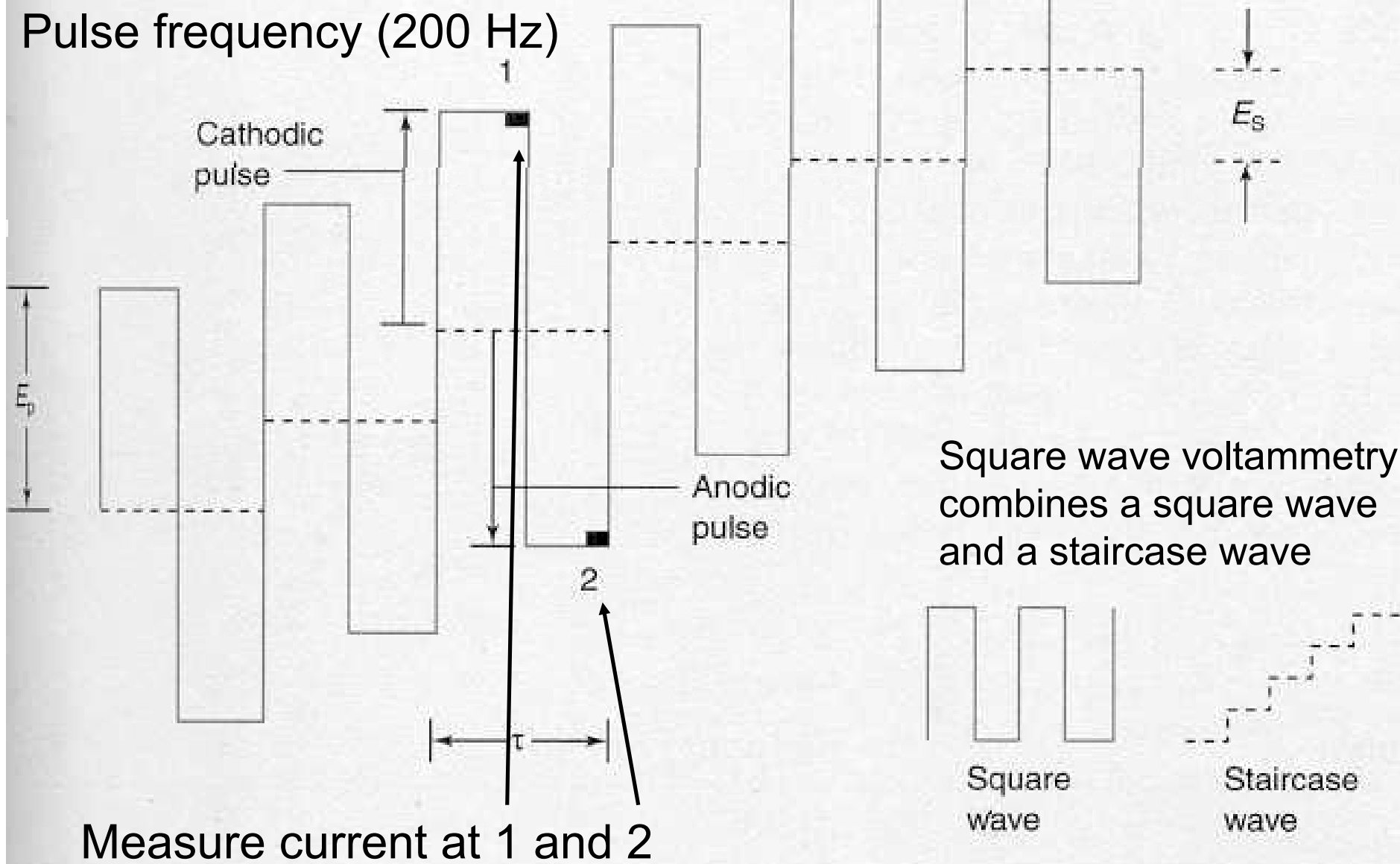
- ASV or DPASV are widely used especially where high sensitivity is necessary
- Use longer plating times (electrolysis step) to preconcentrate more metal
- Nanomolar ( $10^{-9}$  M) or part per trillion (ppt) detection is achievable
- e.g., metals in seawater, Pb in blood, etc.
- Instrumentation inexpensive 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  $\text{MoO}_4^{2-}$  and  $\text{CrO}_4^{2-}$
- Stripping step is a cathodic scan

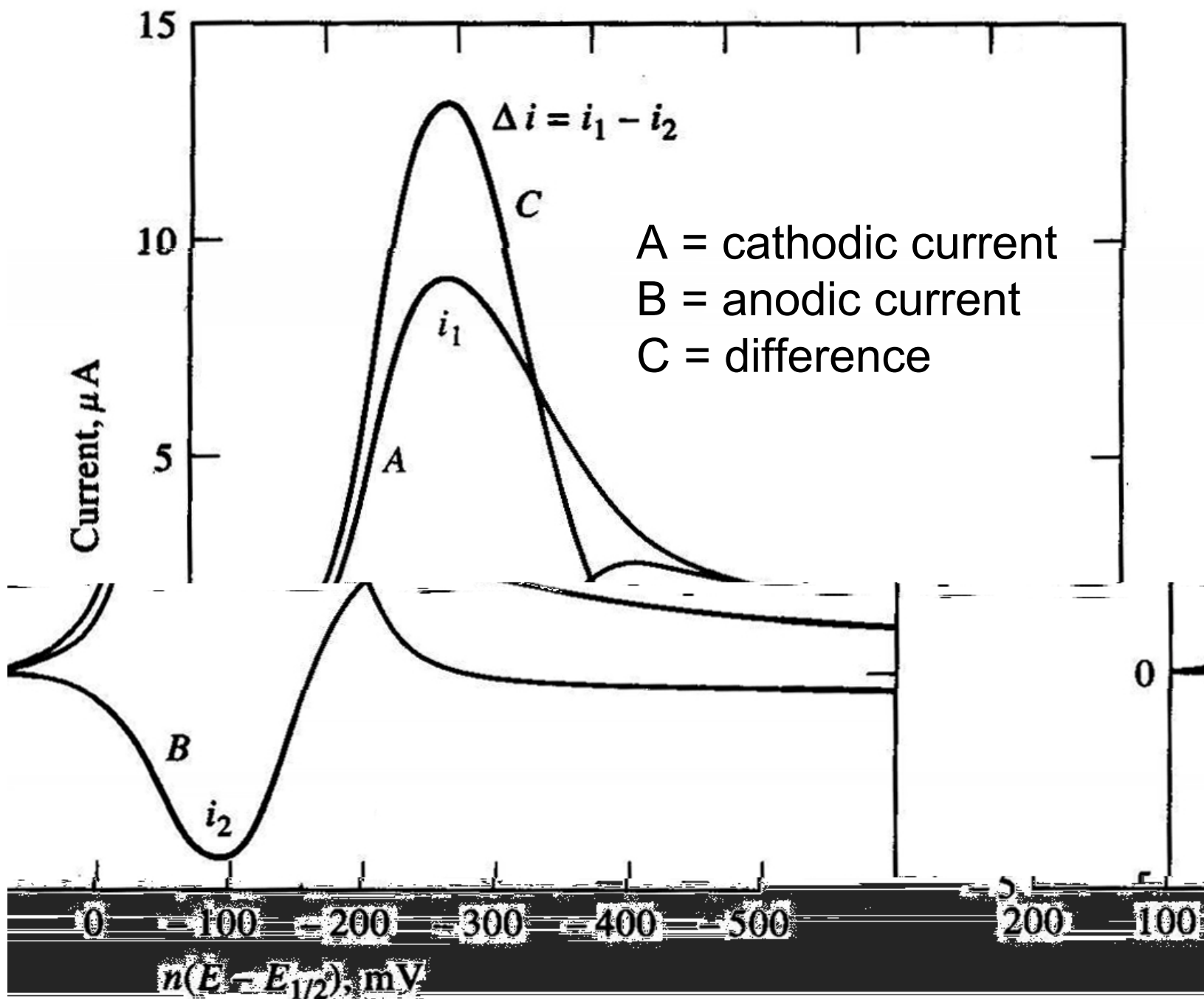
# Square Wave Voltammetry

- 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



- 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  $\sim 10^{-8}$  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

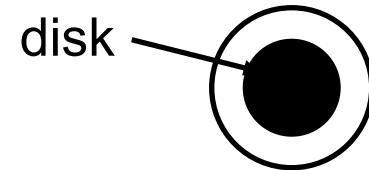
- 1) Conductance – measure conductivity of flow stream as in ion chromatography (IC)
- 2) Amperometry – like chronoamperometry with fixed potential measuring current as solutes reach electrode
- 3) Voltammetry – need fast method like SWV
- 4) Coulometry – fix E (or I) and count coulombs as solutes go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

# Frontiers in Electrochemistry

## 1) Hydrodynamic electrochemistry

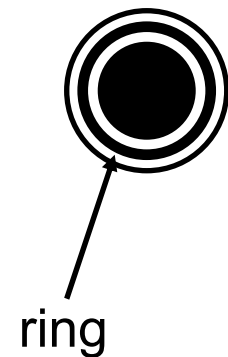
e.g. using Rotating Disk Electrode (RDE)

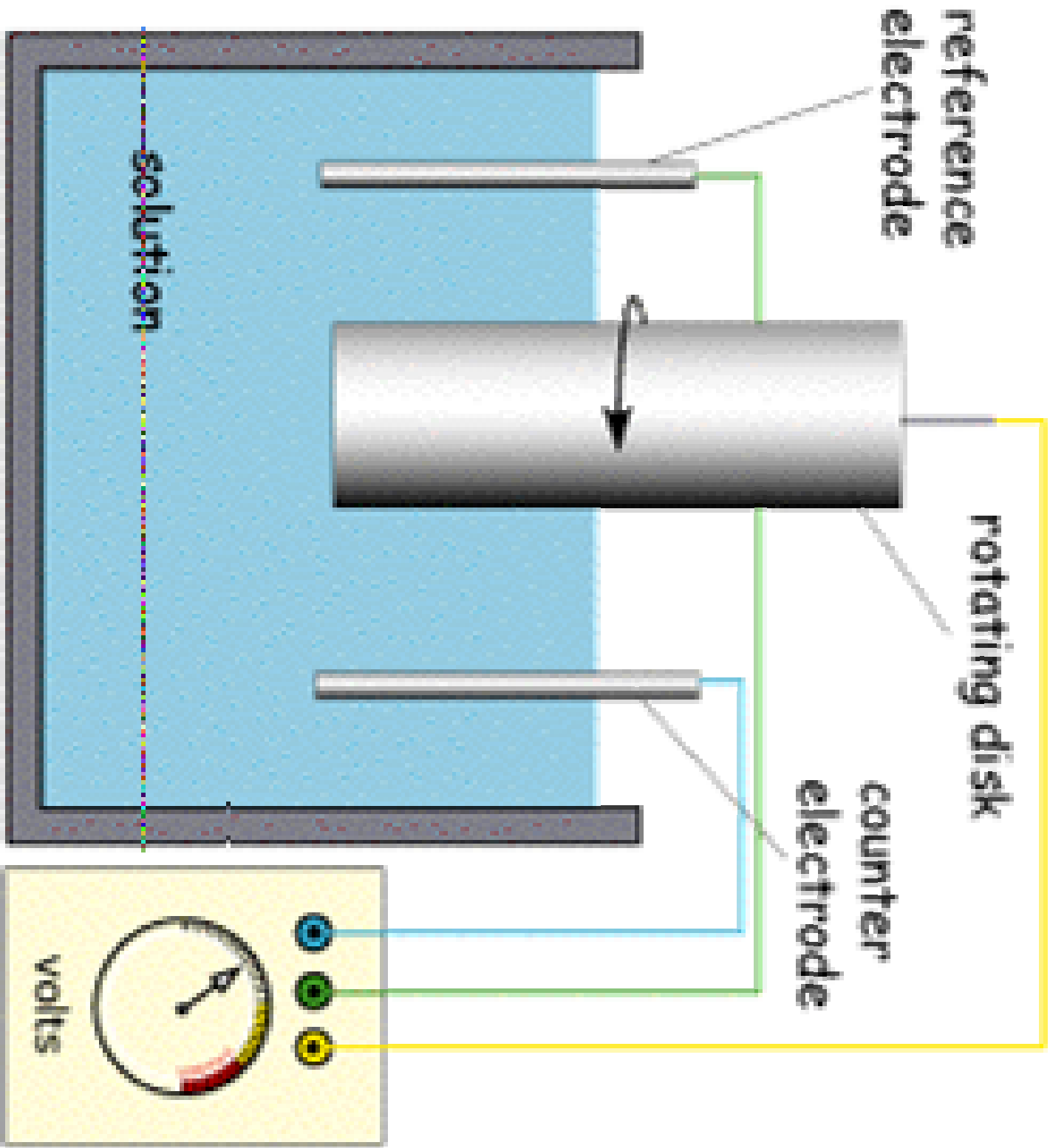
- improved mass transport
- reproducible convection



Rotating Ring Disk Electrode (RRDE)

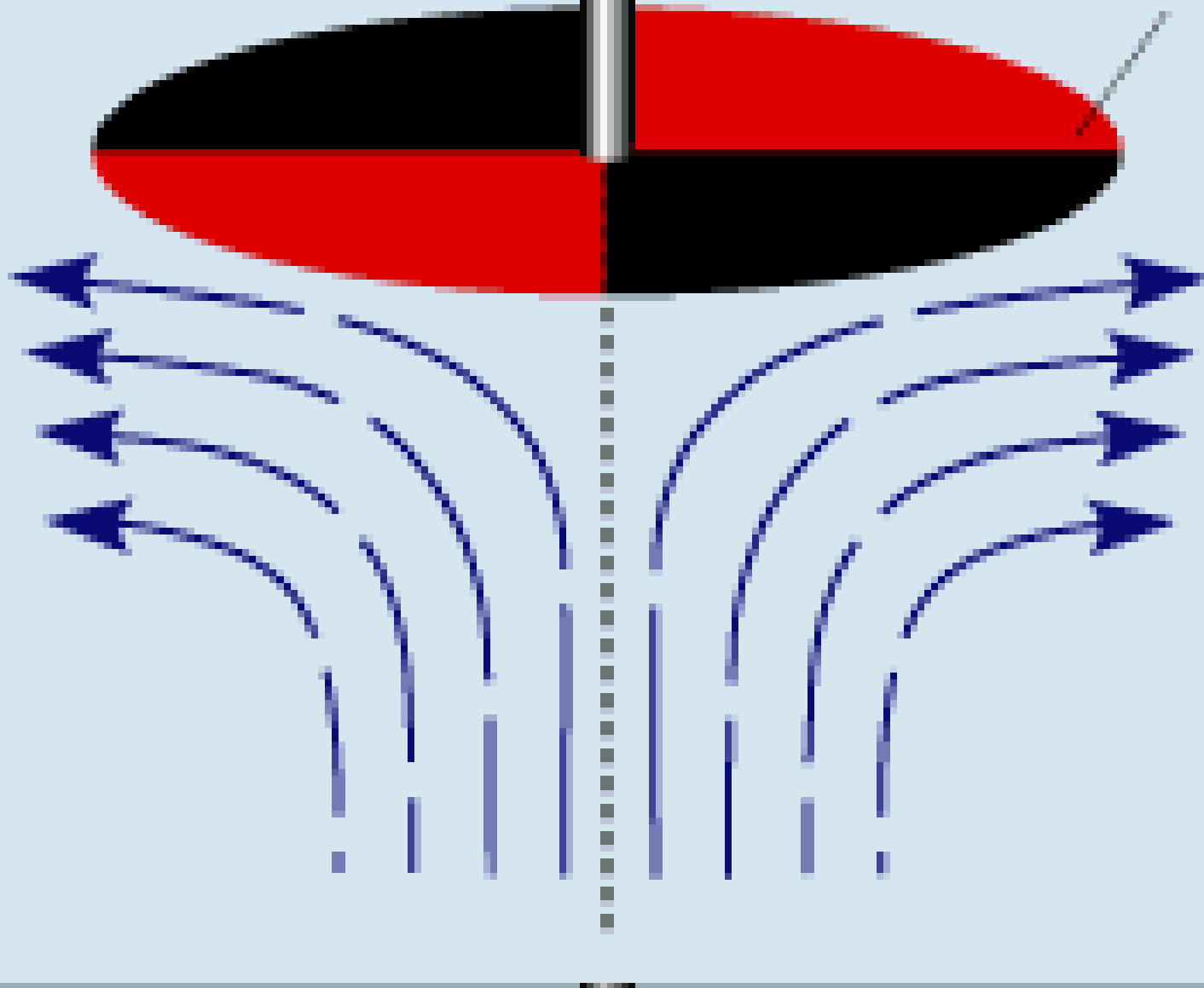
- reduce something at the disk
- reoxidize it as it passes the ring
- similar to cyclic voltammetry





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  $\mu\text{m}$
- hemispherical shape (usually Hg or Ir)
- several unique characteristics
  - Short diffusion path
  - Faster rate of mass transport
  - Steady state conditions established in  $< 1 \mu\text{s}$
  - No need for convection
  - IR drop low
  - Capacitive current low
  - Can use low ionic strength

