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 $M^{o}$.

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.
ASV can be done with any electrode.
- 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

\[ I = n F A D^{1/2} C \pi^{1/2} \tau^{1/2} \psi(E_s, E_p) \]
Square wave voltammetry combines a square wave and a staircase wave.

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

Measure current at 1 and 2.
A = cathodic current
B = anodic current
C = difference

\[ \Delta i = i_1 - i_2 \]
- 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 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