Chapter 3

Elatroanalytical Methods
Voltammetry
What is Voltammetry?

• A group of analytical methods in which only a small portion of material is electrolytically reduced or less commonly oxidized
• Classification of voltammetric methods is based on:
  - Electrode type
  - How the potential is applied
  - How the current is measured
Characteristics

• Voltammetry is based upon the measurement of a current that develops in an electrochemical cell under conditions of complete concentration polarization.

• Potentiometric measurements are made at currents that approach zero and where polarization is absent.

• Furthermore, in voltammetry a minimal consumption of analyte takes place, whereas in electrogravimetry and coulometry essentially all of the analyte is converted to another state.

• Voltammetry (particularly classical polarography) was an important tool used by chemists for the determination of inorganic ions and certain organic species in aqueous solutions.
Current is a function of
• analyte concentration
• how fast analyte moves to electrode surface
• rate of electron transfer to sample
• voltage, time...
II. Excitation process

- A. What happens when a voltage is applied to an electrode in solution containing a redox species? Generic redox species O

\[ \text{O} + \text{e}^- \rightarrow \text{R} \quad \text{E} = -0.500 \text{ V v. SCE} \]

- Imagine that we have a Pt electrode in sol’n at an initial potential of 0.000 V v. SCE and we switch potential to -0.700 V.

- First:
B. Events that happen

1. supporting electrolyte forms an electrical double layer

\[ E_{\text{app}} = -0.7 \]

\[ \text{Pt} \]

\[ \text{double layer acts as a capacitor} \]

cation movement to electrode causes an initial spike in current

Formation of double layer is good because it ensures that no electric field exists across whole sol’n (requires 100:1 conc ratio of supporting elyte:redox species).
2. Electron transfer reaction

O is converted to R at electrode surface.

\[ E_{\text{app}} = -0.7 \]

A depletion region of O develops - a region in which conc of O is zero.

How does more O get to electrode surface? mass transport mechanisms
C. Mass transport to the electrode

1. Migration - movement in response to electric field. We add supporting electrolyte to make analyte’s migration nearly zero. (fraction of current carried by analyte $\rightarrow$ zero)

2. Convection
   • stirring

3. Diffusion
   In experiments relying upon diffusion, no convection is desired, sol’n is quiescent.
Solutions and electrodes

1. Solutions: redox couple + solvent + supporting electrolyte
   • supporting electrolyte: salt that migrates and carries current, and doesn’t do redox in your potential window of interest
   • a wide potential window is desirable
   • water - good for oxidations, not reductions except on Hg
   • supporting electrolytes: lots of salts
   • nonaqueous solvents: acetonitrile, dimethylformamide, etc.
   • supporting electrolytes: tetraalkylammonium BF\textsubscript{4}, PF\textsubscript{6}, ClO\textsubscript{4}
   • Oxygen is fairly easily reduced - we remove it by deoxygenating with an inert gas (N\textsubscript{2}, Ar).
2. Electrodes

- Working electrode (WE) is where redox activity occurs
- Auxiliary electrode (AE) catches current flow from WE
- Reference electrode (RE) establishes potential of WE
  - a. Working electrode materials:
    - Pt, Au, C, semiconductors
    - Hg - messy but good for reductions in water. Not good for oxidations.
  - b. Auxiliary electrodes: similar materials, large in area
  - c. Reference electrodes: real vs. quasi -
    - Real refs have an actual redox couple (e.g. Ag/AgCl)
    - Quasi refs (QRE) - a wire at which some (unknown) redox process occurs in sol’n. QREs OK if currents are needed but not potentials.
Voltammetric Techniques

- Polarography
- Square Wave Voltammetry
- Cyclic Voltammetry
- LSV
- Differential Pulse
- Normal Pulse
- Sampled DC
- Stripping Analysis
Differential Pulse Polarography

Fast Scan Polarography

A.C. Polarography
  Coulometry - (Constant I)
  Voltammetry - Solid Electrode

D.C. Polarography
  Amperometry

Potentiometry
  Coulometry - (Constant E)

Range of practical usefulness of electroanalytical techniques

[Graph shows concentration range in ng/ml, 100ng/ml, 1μg/ml, 10μg/ml, 100μg]
Polarography

The cell current is measured during electrolysis at various potentials.

Most common electrode type is a dropping mercury electrode (DME)

A current vs. potential curve is produced.
DC voltage source

Battery

G - galvanometer

V - voltammeter

Sample cell

Reference electrode

Cathode Working indicator electrode

ammeter

ammeter
Polarography

Summary

➢ Subject to high relative errors ( \( \geq +1\% \))

➢ Works best in the \(10^{-5} - 10^{-2}\) M range.

➢ Requires a calibration curve.

➢ Provides both qualitative and quantitative information.
Supporting Electrolyte

• Polaragrams are recorded in the presence of a relatively high concentration of a base electrolyte such as KCl.

• The base electrolyte will decrease the resistance for the movement of the metal ions to be determined thus, the IR drop throughout the cell will be negligible.

• It helps also the movement of ions towards the electrode surface by diffusion only.

• The discharge potential of the base electrolyte takes place at a very low negative potential therefore, most ions will be reduced before the base electrolyte species.

• Buffering & elimination of interferent by complexation
Sample cell

- Drop knocker
- Dropping Hg Electrode
- SCE reference electrode
- Inert gas purge
- Sample
Sample cell
Model 394 Voltammetric Analyzer

- Computer controlled polarographic and voltammetric analyzer
- PC compatible Windows software
- Can use existing 303A / 305
Wide Range of Techniques

• Square Wave Voltammetry
• Cyclic Voltammetry
• LSV
• Differential Pulse
• Normal Pulse
• Sampled DC
• Stripping Analysis
Pre-experiment selection

- Analyzer consol controls SMDE
- Automatic purging and stirring of sample
- Automatic conditioning of electrode
- Automatic control of deposition times
Standards

- Up to nine standards can be entered
- Selection of common reference electrode potentials
  - Electrolyte record

<table>
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<th>Component</th>
<th>Value</th>
<th>Unit</th>
<th>Reference Electrode</th>
<th>Reference Value</th>
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Multi-element Analysis
Advantages of HDME

1. Drops (4-6/s, 0.1-cm diam)
   - nearly spherical (nice mathematically)
   - highly reproducible surface area
   - each drop = new experiment
   - self-cleansing - adsorbed species carried away
   - eliminates passivation/poisoning
   - drops stir/refresh solution
Advantages of HDME (cont’d)

- High overpotential for H₂ evolution
  \[ \text{H}_2\text{O} + \text{e}^- = 0.5 \text{H}_2 + \text{OH}^- \quad -0.83 \text{ V} \]
  - Significance: HDME good for reductions

![Graph showing current (I) vs. energy (E) with HDME at -2.8 V and Most M at -0.83 V]
Advantages of HDME (cont’d)

- A lot of M's form amalgams with Hg
  - Significance: M(Hg) more easily reduced, e.g.,
    - $K^+ + e^- = K(s)$
    - $K^+ + e^- + Hg \rightarrow K(Hg)$
    - $E' = -2.936 \text{ V}$
    - $E' = -1.975 \text{ V}$
Disadvantages of HDME

- Oxidation of Hg occurs at low E (\(+0.4\) V vs. SCE)
  - Significance: HDME is a poor anode
  - Potential range: \(+0.4\) V \(\rightarrow\) \(-2.8\) V

- HDME has appreciable residual current (0.2 \(\mu\)A)
  - Significance: cannot study [Analyte] < 0.1 mM
Polarography - LSV at DME

- Response called polarogram
  - limiting current
  - residual current
- $E_{1/2}$ potential where $I = 0.5 i_d$
- Sawtooth pattern
  - Hg drop grows - $I$ grows
  - Hg drop falls, $I$ drops sharply
LSV Nernstian Response

\[ E_{DME} = E_{1/2} - \frac{RT}{nF} \ln \left( \frac{i}{i_d - i} \right) \]

- Q: when \( i = i_d/2 \), \( E_{DME} \) equals ______

- \( E_{1/2} = E^0 - (RT/2nF) \ln(D_\alpha/D_{\text{red}}) \)

- Q: if \( D_\alpha = D_R \), \( E_{1/2} = ____ \)
Advantages and Disadvantages of the Dropping Mercury Electrode

- High overvoltage associated with the reduction of hydrogen ions. As a consequence, metal ions such as zinc and cadmium can be deposited from acidic solution even though their thermodynamic potentials suggest that deposition of these metals without hydrogen formation is impossible.

- A second advantage is that a new metal surface is generated continuously; thus, the behavior of the electrode is independent of its past history. In contrast, solid metal electrodes are notorious for their irregular behavior, which is related to adsorbed or deposited impurities.

- A third unusual feature of the dropping electrode, which has already been described, is that reproducible average currents are immediately realized at any given potential whether this potential is approached from lower or higher settings.
• One serious limitation of the dropping electrode is the ease with which mercury is oxidized: this property severely limits the use of the electrode as an anode. At
• potentials greater than about + 0.4 V, formation of mercury(I) gives a wave that masks the curves of other oxidizable species.
• In the presence of ions that form precipitates or complexes with mercury(I), this behavior occurs at even lower potentials. For example, in the Figure, the beginning of an anodic wave can be seen at 0 V due to the reaction
• $2\text{Hg} + 2\text{Cl}^- \leftrightarrow \text{Hg}_2\text{Cl}_2(s) + 2\text{e}^-$
• Incidentally, this anodic wave can be used for the determination of chloride ion.
- **Fig. 18**: Residual current curve for a 0.1M solution of HCl
Another important disadvantage of the dropping mercury electrode is the nonfaradaic residual or charging current, which limits the sensitivity of the classical method to concentrations of about 10^{-5} M.

At lower concentrations, the residual current is likely to be greater than the diffusion current, a situation that prohibits accurate measurement of the latter.

Finally, the dropping mercury electrode is cumbersome to use and tends to malfunction as a result of clogging.
Effect of Dissolved Oxygen

- Oxygen dissolved in the solution will be reduced at the DME leading to two well defined waves which were attributed to the following reactions:
  
  \[
  \begin{align*}
  \text{O}_2(g) + 2\text{H}^+ + 2e^- & \quad \leftrightarrow \quad \text{H}_2\text{O}_2 \\
  \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- & \quad \leftrightarrow \quad 2\text{H}_2\text{O}
  \end{align*}
  \]

- $E_{1/2}$ values for these reductions in acid solution correspond to -0.05V and -0.8V versus SCE.
How it works

- The applied voltage is gradually increased, typically by going to a more positive $E$.
- A small residual current is observed.
- When the voltage becomes great enough, reduction occurs at the analytical electrode causing a current.
- The electrode is rapidly saturated so current production is limited - based on diffusion of the analyte to the small electrode.
How it works

The reduced species alters the surface of the mercury electrode.

To prevent problems, the mercury surface is renewed by ‘knocking off’ a drop - providing a fresh surface.

This results in an oscillation of the data as it is collected.
How it works
How it works
How it works

The average response is then used for subsequent data analysis.
Polarographic data

Two types of information are obtained.

$i_d$

diffusion current

$E_{1/2}$

halfwave potential
Polarogram for (A) $5 \times 10^{-4}$ M Cd$^{2+}$ in 1 M HCl. (B) 1 M HCl
In the absence of migration (eliminated by addition of supporting electrolyte) and convection (prevented by keeping the electrolyzed solution unstirred), diffusion is the only mode of transport involved. Therefore, the limiting current is proportional to the rate of diffusion, and

\[ i_l = nFAD \left( \frac{\partial c}{\partial x} \right)_{x=0} \tag{3.1} \]

where

- \( A \) = area of the electrode
- \( D \) = diffusion coefficient of the electroactive species
- \( (\partial c/\partial x)_{x=0} \) = concentration gradient of the electroactive species at the electrode surface
- \( x \) = distance from the electrode surface

The DME is virtually spherical; its volume can be calculated from the rate of flow of mercury, \( m \) (in mg/sec), the time \( t \) (in sec) measured from the beginning of drop growth, and the density of mercury. This gives the radius of the drop, from which the surface area, \( A \) (in mm\(^2\)), is

\[ A = 0.852(mt)^{2/3} \tag{3.2} \]
Polarographic data

Diffusion current The rate of diffusion to our electrode is concentration dependent based on the Ilkovich equation

\[ i_d = 706 \, n \, C \, D^{1/2} \, m^{2/3} \, t^{1/6} \]

\[ i_d = \text{current in } \mu\text{A} \quad n = \# \text{ e$^{-}$ in transfer} \]

\[ C = \text{concentration} \quad D = \text{diffusion coefficient} \]

\[ m = \text{mass of drop} \quad t = \text{drop time} \]

\[ i_d \text{ (average)} = 6/7 \, (708) \, n \, D^{1/2}m^{2/3}t^{1/6}C \]
Polarographic data

Diffusion current

If \( t, m, D \) and \( n \) are constant, then we can simplify things by using a standard.

Then

\[
\frac{i_{d_{\text{STD}}}}{i_{d_{\text{UNK}}}} = \frac{C_{\text{STD}}}{C_{\text{UNK}}}
\]
Polarographic data

Halfwave potential

Where our reaction occurs (what $E$) can tell us what the species is.

Using the starting point for the wave would give poor results since it is concentration dependent.

The potential at half height is more reliable.
Polarographic data

Halfwave potential

The $E_{1/2}$ value is the inflection point of the curve. It can be found by taking the derivative of the curve or by determining the $E$ at one half of the $i_d$. 
Polarographic data

$E_{1/2}$ values are listed versus the SCE.

Not the same as $E^\circ$ values

Are also dependent on the supporting electrolyte used for the analysis.

Typical range is -1.9 to +0.2 V vs SCE.
### Polarographic data

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_{1/2}$ vs SCE</th>
<th>Supporting electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu}^{2+} \rightarrow \text{Cu}$</td>
<td>0.04</td>
<td>0.1 M KCl</td>
</tr>
<tr>
<td>$\text{Sn}^{4+} \rightarrow \text{Sn}^{2+}$</td>
<td>-0.25</td>
<td>4 M $\text{NH}_4\text{Cl}, 1$ M HCl</td>
</tr>
<tr>
<td>$\text{Pb}^{2+} \rightarrow \text{Pb}$</td>
<td>-0.40</td>
<td>0.1 M KCl</td>
</tr>
<tr>
<td>$\text{Pb}^{2+} \rightarrow \text{Pb}$</td>
<td>-0.50</td>
<td>0.4 M Na tartrate</td>
</tr>
<tr>
<td>$\text{Pb}^{2+} \rightarrow \text{Pb}$</td>
<td>-0.76</td>
<td>1 M NaOH</td>
</tr>
</tbody>
</table>

Note how the $E_{1/2}$ value can be shifted by changing the supporting electrolyte.
Polarographic data

If more than a single species is present, the curves will add on top of each other.
Currents controlled by factors other than diffusion

- Processes other than diffusion are involved on the electrode surface:
  1. Chemical reactions involving oxidation or reduction
  2. Adsorption of electroactive species
Kinetic Currents

• Currents whose magnitudes are controlled by the rates of chemical reactions

\[ A \ (\text{not electroactive}) + X \rightleftharpoons Ox \]

\[ CH_2O(H_2O) \rightleftharpoons CH_2O + H_2O \]

\[ CH_2O + 2H^+ + 2e \rightleftharpoons CH_3OH \]

\[ i_l = i_d + i_k \]
Catalytic Current

- It is controlled by a catalytic process
- Either the electroactive substance is regenerated by a chemical reaction
  \[ \text{Fe}^{3+} + e \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2 \leftrightarrow \text{Fe}^{3+} \]
- The electroreduction of a species is shifted to a more +ve potential
- Proteins catalyze the reduction of H+ and shift the corresponding wave to a more +ve potential
- \( i_k \) is a nonlinear function of concentration or linear over a limited concentration range
Adsorption Currents

- If oxidized form is adsorbed its reduction will take place at a more −ve potential than the diffusion current.

- If reduced form (product) is adsorbed its reduction will take place at a more +ve (prior) potential than the diffusion current.
Polarographic Maxima

- Currents that are at a certain point of potential higher (about 2 order of magnitude) than the diffusion current
- Be removed by addition of surfactant (triton-100) or gelatin
Tests of Current Limiting Processes

- Usually the currents are distinguished from each other by the changes that take place when the following parameters are varied:
  - Concentration of electroactive species
  - Mercury column height
  - pH
  - Buffer concentration
  - Temperature
Figure 3.5. Relation of limiting current to concentration. Curve A: Linear dependence observed for diffusion currents and for some kinetic and catalytic currents. Curves B and C: Limiting dependences observed for adsorption and some catalytic currents.
Figure 3.6. Variation of the limiting current with mercury-column height for various types of polarographic currents. Curves A and D: Variation of diffusion current, $i_d$. Curves B and E: Variation of kinetic current, $i_k$. Curves C and F: Variation of adsorption current, $i_a$. 
Figure 3.7. Illustration of the relative importance of faradaic and charging current as the concentration of the electroactive species is reduced during the life of a single mercury drop. Solid lines—faradaic current; dashed lines—charging current. Curve A: For a 1 mM solution, the contribution of the charging current is small and can be neglected. Curve B: For a 0.2 mM solution, the contribution of the charging current is still small but not negligible and should be corrected for. Curve C: For 0.03 mM solution, the charging current becomes larger than the faradaic current, and the separation of the two currents becomes necessary. The y-axes on the three curves have been normalized so that the faradaic-current curves (solid lines) are the same size.
Polarographic wave shapes

Consider the following reversible equilibrium reaction at the electrode surface:

\[ A + ne \rightleftharpoons B \]

\[ E_{\text{applied}} = E^0 - \frac{0.059}{n} \log \frac{[B]_0}{[A]_0} \quad (3.10) \]

where \([B]_0\) and \([A]_0\) = concentrations at the DME surface

If species B is absent from the bulk (prepared) solution and can be formed only by the reduction of A, then

\[ [B]_0 \propto i = ki \quad (3.11) \]

where \(i\) = current at the DME

It follows that the concentration of A at the electrode surface is

\[ [A]_0 \propto (i_d - i) = k'(i_d - i) \quad (3.12) \]
since \([A]_0\) is the difference between the amount of A that was initially at the electrode (an amount that would produce the limiting current, \(i_d\), if entirely reduced) and the amount remaining after the formation of \([B]_0\). By analogy to the constants in the Ilkovic equation, the proportionality constants \(k\) and \(k'\) are identical except for the diffusion coefficients of A and B, and so Equation 3.10 becomes

\[
E_{\text{applied}} = E^{0'} - 0.059 \frac{n}{i} \log \left( \frac{D_A}{D_B} \right)^{1/2} - 0.059 \frac{n}{i_d} \log \frac{i}{i_d - i}
\]

(3.13)

Since the half-wave potential, \(E_{1/2}\), is defined as the potential at which \(i = 0.5i_d\),

\[
E_{1/2} = E^{0'} - 0.059 \frac{n}{i} \log \left( \frac{D_A}{D_B} \right)^{1/2}
\]

(3.14)

or

\[
E_{\text{applied}} = E_{1/2} - 0.059 \frac{n}{i_d} \log \frac{i}{i_d - i}
\]

(3.15)
Polarography - LSV at DME

- Response called polarogram
  - limiting current
  - residual current
- $E_{1/2}$ potential where $I = 0.5 i_d$
- Sawtooth pattern
  - Hg drop grows - $I$ grows
  - Hg drop falls, $I$ drops sharply
LSV Nernstian Response

\[ E_{DME} = E_{1/2} - \frac{RT}{nF} \ln \left( \frac{i}{i_d - i} \right) \]

- Q: when \( i = i_d/2 \), \( E_{DME} \) equals _____

- \( E_{1/2} = E^\circ - (RT/2nF) \ln(D_{ox}/D_{red}) \)

- Q: If \( D_{ox} = D_{red} \), \( E_{1/2} = ____ \)
• Equation 3.15 holds for reversible, diffusion-controlled electrochemical reactions where the electrolysis product is initially absent in the bulk solution, and is soluble in the solution or in the electrode itself (as an amalgam, which is the case for reduction of many metal ions).

• A plot of $E_{\text{applied}}$ versus $\log[i/(i_d - i)]$ can be used as a test for these conditions (a straight line would be obtained).

• It is also a means of determining $n$ (from the slope) and $E_{1/2}$.

• The interpretation requires that in addition to a straight line, a reasonable, integral $n$-value be obtained before reversibility can be claimed.

• The $E_{1/2}$-value is useful because it provides an estimate of $E^\circ'$; the term $\log(D_A/D_B)^{1/2}$ is generally small.

• If the electrode reaction is not reversible, the rising portion of the polarographic wave is drawn out. This occurs when the rate constants near $E^\circ'$ are too small to allow equilibrium to be reached on the time scale of the experiment.
Effect of complex formation on polarographic waves

• When the metal ion forms a complex with a ligand, a shift in the $E_{1/2}$ takes place. This shift goes towards more –ve potential.

• The magnitude of this shift is proportional to the stability of the complex as well as to the concentration of the ligand.

• Formation constants can be estimated from the magnitude of the shift in the $E_{1/2}$.
• Previous equation (3.15) is not applicable if either species A or B is adsorbed on the electrode or is involved in a chemical reaction other than simple electron transfer.

• A common example of the latter is the case where A is a metal ion that is in equilibrium with p molecules of a ligand, L, and a metal complex, $AL_p$:

\[
A + pL \rightleftharpoons AL_p
\]

\[
K_f = \frac{(AL_p)}{(A)(L)^p} \approx \frac{[AL_p]}{[A][L]^p}
\]

where
- the terms in parentheses = activities
- the terms in brackets = molarities
- $K_f$ = formational constant of the complex
When the term $[A]_0$ in Equation 3.10 is replaced by $[AL_p]_0/K_f[L]_0$, and, if the concentration of the ligand is in large excess over that of $A$, the following expression can be written

\[(E_{1/2})_{\text{cplx}} = (E_{1/2})_{\text{free ion}} - \frac{0.059}{n} \log K_f - \frac{0.059}{n} \log [L] \quad (3.18)\]

where $\quad (E_{1/2})_{\text{cplx}} = \text{half-wave potential in the presence of excess L}$

$\quad (E_{1/2})_{\text{free ion}} = \text{half-wave potential for the reduction of the metal ion in the absence of L}$
• The slope of a plot of \((E_{1/2})_{\text{coplx}}\) versus log [L] yields "p" (if \(n\) is known)

• and the intercept, where [L] = 1 M, can be used to calculate \(K_f\) if \((E_{1/2})_{\text{free \ ion}}\) is known.
Analytical Applications

- Direct calibration method (external standards method)
- Standard addition method
- Internal standard method
- Examples of the electroactive species and applications can be found in the book p. 67-76
Polarograms of 3 mm Pb(II) and 0.25 mm Zn(II) in 2 m NaOH. (a) In the absence of a suppressor. (b) In the presence of 0.002% Triton X-100. [L. Meites, Polarographic Techniques, 2nd ed. (New York: Wiley, 1965).]
In the method of \textit{standard additions}, a known amount of analyte is added to the unknown. The increase in signal intensity tells us how much analyte was present prior to the standard addition.

\[ I_d(\text{unknown}) = k C_x \]

where \( k \) is a constant of proportionality. Let the concentration of standard solution be \( C_S \). When \( V_S \) mL of standard solution is added to \( V_x \) mL of unknown, the diffusion current is the sum of diffusion currents due to the unknown and the standard:

\[ I_d(\text{unknown} + \text{standard}) = k C_x \left( \frac{V_x}{V_x + V_s} \right) + k C_s \left( \frac{V_s}{V_x + V_s} \right) \]

\[ C_x = \frac{C_s V_s}{R \left( V_x + V_s \right) - V_x} \]
Illustration of standard addition. The increased signal (current) when standard is added tells us how much unknown was present initially.
Use of an internal standard. The relative size of the two signals tells us how much unknown is present.
Chloroform and the pesticide DDT exhibit the following half-wave potentials in a medium consisting of 0.05 m (CH₃)₄NBr in 3:1 (vol/vol) dioxane/water:

\[
\begin{align*}
\text{CHCl}_3 & \quad \text{DDT} \\
E_{1/2} & = -1.6 \text{ V} \quad E_{1/2} = -0.8 \text{ V}
\end{align*}
\]

Suppose that a polarogram of a mixture containing 0.500 mM chloroform and 0.800 mM DDT gives the following relative wave heights:

\[
\frac{\text{Wave height of CHCl}_3}{\text{Wave height of DDT}} = 1.53 \quad \text{when} \quad \frac{[\text{CHCl}_3]}{[\text{DDT}]} = \frac{0.500 \text{ mM}}{0.800 \text{ mM}} = 0.625
\]

To use chloroform as an internal standard for the analysis of DDT, a known concentration of chloroform is added to an unknown solution of DDT. Suppose that when the concentration of internal standard is 0.462 mM, the relative wave heights are

\[
\frac{\text{Wave height of CHCl}_3}{\text{Wave height of DDT}} = 1.11 \quad \text{when} \quad \frac{[\text{CHCl}_3]}{[\text{DDT}]} = \frac{0.462 \text{ mM}}{\text{unknown}} = x
\]

Find the concentration of DDT in the unknown.

To do this, we can set up a ratio. Let \( x \) be the quotient \([\text{CHCl}_3]/[\text{DDT}]\) in the mixture of unknown plus internal standard. When the relative wave heights were 1.53, the relative concentrations were 0.625. When the relative wave heights are 1.11, the relative concentrations, \( x \), must be given by

\[
\frac{\text{Relative concentrations in unknown}}{\text{Relative concentrations in known}} = \frac{\text{relative wave heights in unknown}}{\text{relative wave heights in known}}
\]

\[
\frac{x}{0.625} = \frac{1.11}{1.53} \quad \Rightarrow \quad x = 0.453 = \frac{[\text{CHCl}_3]}{[\text{DDT}]}
\]

Putting in \([\text{CHCl}_3] = 0.462 \text{ mM}\), we find

\[
[\text{DDT}] = \frac{[\text{CHCl}_3]}{x} = \frac{0.462}{0.453} = 1.02 \text{ mM}
\]
Modified voltammetric methods

To improve polarographic results or evaluate new phenomena, several modifications have been made to the classical approach.

Classical - a voltage ramp is continuously applied and current constantly sampled.
The contribution of the charging current will be minimized and the spikes will disappear leading to a smoother polarogram (stair-shape polarogram).
Pulse Polarography

- **DC:** $i_{cha}$ almost equal $i_{far}$
- $i_{far}$/$i_{cha}$ ratio
- Change in the electrode area is very rapid in early stages and almost constant close to the end
- In pp the potential will not be applied until the area-time curve is flattened out
- $i_{far}$ and $i_{cha}$ decay in time but the decay of $i_{far}$ is much slower

1. Normal Pulse polarog.: gradual increase in the amplitude in the voltage pulse
2. Differential pulse polarog.: Voltage pulse of constant amplitude superimposed on a slowly increasing voltage
Series of pulses (40 ms duration) of increasing amplitude (potential) are applied to successive drops at a preselected time (60 ms) near the end of each drop lifetime. Between the pulses, the electrode is kept at a constant base potential where no reaction occurs.
• $i_c$ is very large at the beginning of the pulse; it then decays exponentially.
• $i$ is measured during the 20 ms of the second half of the pulse when $i_c$ is quite small
• The current is sampled once during each drop life and stored until next sample period, thus the polarogram shows a staircase appearance
• NPP is designed to block electrolysis prior to the measurement period
Differential Pulse Polarography

• A pulse (of constant amplitude of 5-100 mV) of 40-60 ms is applied during the last quarter of the drop life
• The pulse is superimposed on a slowly increasing linear voltage ramp.
• The current is measured twice: one immediately preceding the pulse and the other near the end of the pulse.
• Overall response plotted is the difference between the two currents sampled
Fixed magnitude pulses (50 mV each) superimposed on a linear potential ramp are applied to the working electrode at a time just before the drop falls (last 50 ms). The current is measured at 16.7 ms prior to the DC pulse and 16.7 ms before the end of the pulse.
Differential pulse polarography

Your data is recorded as a differential so the concentration is represented by peak area.

Because more data points are used, there is an increase in sensitivity.

With classical polarography, the diffusion current is determined by extrapolation of a single point.
(a) Linear voltage ramp used in direct current polarography. (b) Pulsed ramp of differential pulse polarography. Current is measured only during the intervals shown by heavy lines. (c) Behavior of faradaic and condenser currents during each pulse.
Voltamunogram for a differential pulse polarography experiment
(a) Differential pulse polarogram: 0.36 ppm tetracycline · HCl in 0.1 acetate buffer, pH 4, PAR Model 174 polarographic analyzer, dropping mercury electrode, 50-mV pulse amplitude, 1-s drop.

(b) DC polarogram: 180 ppm tetracycline · HCl in 0.1 M acetate buffer, pH 4, similar conditions.
The example above shows the simultaneous determination of Zn, Cd, Pb and Cu using standard addition.
Applications

- Determination of trace elements Pb, Cd, Cu, Fe, Ni, Co, Al, Cr, Hg ....
- Determination of nitrate, nitrite, chloride, iodiide, cyanide, oxygen ..... 
- Determination of numerous organic and toxic materials - surfactants, herbicides, pesticides, insecticides, nitro compounds, halogenous compounds
## Detection Limits in the ultra trace range

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Applications of DPP

Figure 3. DIFFERENTIAL PULSE POLAROGRAPHY OF CHROMIUM(VI) IN AMMONIACAL BUFFER, pH 10. MODEL 174, 2 mV/sec. SCAN RATE, 25 mV MODULATION, 1 sec/PULSE.

Figure 4. CALIBRATION CURVE FOR CHROMIUM(VI) IN pH 10 AMMONIACAL BUFFER. DIFFERENTIAL PULSE POLAROGRAPHY. PEAK CURRENT vs. CONCENTRATION.
Figure 5. DIFFERENTIAL PULSE POLAROGRAPHY OF CHROMIUM(III) IN 0.2 M KSCN/0.3 M HOAc, pH 3.2. MODEL 374, BLANK SUBTRACTED.

Determination of free Vanadium (i) formation of complex extractable from petroleum
(ii) wet or dry ashing of petroleum

Differential Pulse Polarography of Vanadium (V) in 0.1 M KSCN + 0.1 M H₂SO₄

- Modulation Amplitude: 50 mV
- Drop Time: 1 second
- Scan Rate: 2 mV/second

Signal

Peak Current vs Concentration for Vanadium (V) in 0.1 M KSCN + 0.1 M H₂SO₄
Peak Current Measured at -0.84 V vs SCE

Blank

Potential (E vs SCE)

80 ppb

40 ppb

160 ppb

120 ppb
Differential Pulse Polarography of bleach sample containing Fe(III)
A = Bleach sample
B = A + 4.0 ppm Zn, Ni and Fe(III)

PROCEDURE:
1. Mix 10 ml bleach sample and 15 ml conc. HCl
2. Boil 10 minutes
3. Add 2 ml of 1 M NH₄ tartrate buffer and adjust to pH 9.0
4. Run by Differential Pulse Polarography
5. Quantitate by standard additions
Differential Pulse Polarography of water sample containing Fe(III)
A = Sample
B = A + 400 ppb Zn, Ni, Fe(III), Mn

PROCEDURE:
1. Take 5 ml water sample and 5 ml conc. HNO₃
2. Add 400 ppb each of Zn, Ni, Fe and Mn
3. Digest to dryness
4. Reconstitute in 5 ml NH₄ tartrate buffer, pH 9. Warm for 10 minutes.
5. Run by Differential Pulse Polarography
6. Quantitate by standard additions
Nitrite

Differential Pulse Polarography of Nitrite in 2 M Citrate Buffer, pH 2.8

Signal vs Potential (E vs SCE)
PEAK CURRENT vs CONCENTRATION
FOR NITRITE IN 2 M CITRATE BUFFER, pH 2.5

[Graph showing peak current vs concentration]
Figure 1. POLAROGRAMS OBTAINED USING THE RECOMMENDED PROCEDURE. PHOSPHATE CONCENTRATION: (i) to (vi); 0, 5.7, 11.4, 17.1, 22.8, 28.5 ppb, RESPECTIVELY.

Phosphate

PO₄³⁻ is extracted by molybdenum blue in isoamyl alcohol then back extracted into tetranitrate buffer.
Linear Scan Voltammetry

• The whole potential (0 – 2 V or any other pot. range) is carried out on a constant electrode surface; one Hg drop in a rapid manner, 50 to 50,000 mV/sec (Fast Linear scan/sweep voltammetry)

• In polarog. i-E relationship is independent of scan rate since the voltage is almost constant during the drop life; it is in the order of mV or less.

• Mechanistic studies require the high end of scan rates and analytical studies require the slower end

• Hanging mercury drop electrode is used. Pt, graphite or others could be used when more +ve potential is required
• As the potential goes more –Ve below $E^o$ an increase in the electeolytic process takes place until the surface concentration drops to almost zero and the rate of transfer of the electroactive species reaches max. A peaked $i-E$ is then observed.

• As the potential goes more -Ve than $E^o$ a depletion of the electroactive species in the electrode vicinity takes place. The rate of replenishment is slow as a result of the fast scan rate. The surface concentration and the current will then decrease.

• Randles-Sevcik Eq.: 

\[ i_p = kn^{3/2}AD^{1/2}C v^{1/2} \]

\[ i_p \propto v^{1/2} \text{ and } i_c \propto v. \text{ Thus } i_p/i_c \text{ ratio decreases with scan rate.} \]
Figure 3.14. Typical linear-scan voltammograms for reductions. Curve A: Reduction of a single species. The peak potential ($E_p$), and the magnitude of the peak current ($i_p$) are marked. The dashed line represents the “background” current obtained in the absence of the electroactive species. Curve B: Reduction of two species, with some overlap of peaks. Note that the peak current for the second wave, $i'_p$, is measured from the (extrapolated) current due to the first peak.
Fast linear sweep

The current is rapidly ramped (2 sec) over approximately a 0.5 V range - one drop.

This results in larger drops and smaller residual currents.
Fast linear sweep

Diffusion currents are about ten times greater than with classical polarography.

Residual currents are sufficiently small that peak height can be used for quantification.
Stripping voltammetry

Very sensitive method of analysis $10^6 - 10^9$ M

Summary

Step one

A single Hg drop is hung from the electrode

Go through an electrodeposition step:
5 min for $10^7$ M, 60 min for $10^9$ M

This removes all metal from the sample - all will be present in a single Hg drop.
Anodic Stripping voltammetry

Step two.
Voltammetric/stripping step
The potential is reduced at a known rate and anodic current measured.

The oxidation of our metals from mercury is monitored in this step.
**Deposition.**
Solution was stirred while the electrode potential was held at -1V for 2 minutes. The stirring was stopped and the solution was allowed to come to rest for thirty seconds before beginning the stripping experiment.

**Stripping Experiment.**
The scan was started at -1V and swept to 0.3V at a linear ramp of 2V/sec.
Example of ASV:
Determination of Pb at HDME

- Deposition (cathodic) reduce Pb\(^{2+}\)
  - Stir (maximize convection)
    - Concentrate analyte

- Stop stirring = equilibration/rest period

- Scan E in anodic sense and record voltammogram
  - Oxidize analyte (so redissolution occurs)
Applications of HDME ASV

• Usually study M with $E^\circ$ more negative than Hg
  – EX: Cd$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Pb$^{2+}$

• Study M with $E^\circ$ more positive than Hg at Glassy carbon electrode
  – EX: Ag$^+$, Au$^+$, Hg

  • Can analyze mixture with $\Delta E^\circ \approx 100$ mV
Anodic Stripping Voltammetry
Differential-pulse anodic stripping voltammogram of 25 ppm zinc, cadmium, lead, and copper.
Cathodic Stripping voltammetry

- Anodic deposition
  - Form insoluble, oxidized Hg salt of analyte anion
  - Stir (maximize convection)
- Equilibrate (stop stirring)
- Scan potential in opposite sense (cathodic)
  - Reducing salt/film and forming soluble anion
Cathodic Stripping Voltammetry

**THEORY**
If a relatively positive potential is applied to an HMDE, the mercurous ions produced by the oxidation of the mercury immediately react with chloride ions in the bulk solution to form an insoluble mercurous chloride film on the surface of the HMDE.

\[
\text{Hg} \quad \rightarrow \quad \text{Hg}^+ + \text{e}^- \quad \quad (1)
\]

\[
2\text{Hg}^+ + 2\text{Cl}^- \quad \rightarrow \quad \text{Hg}_2\text{Cl}_2 \quad \quad (2)
\]

If a negative-going potential scan is then applied to the HMDE, a cathodic current is observed due to the reduction of the mercurous chloride (from the mercurous chloride film).

\[
\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \quad \rightarrow \quad 2\text{Hg} + 2\text{Cl}^- \quad \quad (3)
\]
Figure 1. DIFFERENTIAL PULSE CATHODIC STRIPPING VOLTAMMETRY OF CHLORIDE IN 0.1 M HNO₃, IN 50% METHANOL. 75 SEC. DEPOSITION.
CATHODIC STRIPPING OF SELENIUM IN 0.2 M HCl

Figure 1
Cathodic Stripping Voltammogram for trace iodine in Sea Water

\[ \text{Reposition} \]

\[ I^- + \text{Hg} \rightleftharpoons \text{Hg}_2\text{I}_2 + 2e \]

\[ \text{Hg}_2\text{I}_2 + 2e \rightleftharpoons 2\text{Hg} + 2I^- \text{ stripping} \]

nanoampere (x10) vs. going pot. scan
Applications of HDME CSV

• Can study halides, sulfides, selenides, cyanides, molybdates, vanadates

• EX: FDA 1982-1986 used to confirm CN$^{-}$ (-0.1 V) in Tylenol Crisis
### Representative Applications of Stripping Analysis

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Sensitivity of Voltammetry

• Voltammetric techniques are ranked amongst one of the most sensitive analytical techniques.

• Concentrations of certain metals can be determined at sub-part per billion level.

• Many trace and ultra-trace organic determinations can be conveniently made.
Speed of Voltammetric Techniques

• Analysis using multiple electrodes possible
• Fast techniques such as square wave voltammetry possible
• For liquid and gaseous samples dilution in appropriate liquid may be sufficient

• Polarographic or voltammetric analyzer console controls complete process of analysis.
Multi-component capability

• Simultaneous determination of several analytes by a single scan.
• Voltammetry can determine metals, organics and anions in one procedure.
Real Benefits

• Conventional methods of analysis may require long, involved preparative techniques to concentrate the species of interest or remove contaminating or interfering ions.

• These preparations risk contaminating the sample. Polarography and voltammetry can offer a more effective, reliable tool for speciation analysis of natural water where the analyte of interest is in the sub ppm range.

• Without the long preparation you'll have more free time
The sensitivity of the instrument is comparable with AAS and in many cases it is even better.
Amperometric Titrations

- $i_l$ is measured during the titration to detect the end point.
- $i_l$ is proportional to concentration and can be detected due to titrant, analyte, product or any two of them.

1. Amperometric Titration Using one Polarized or Indicator Electrode

Example: Titration of Pb$^{2+}$ versus SO$_4^{2-}$
- Lead is reducible at about $-0.4$ V but sulfate is not.
- Constant voltage (-1 V) that has any value on the $i_d$-E curve is applied.
- The $i_d$-volume of titrant curve will depend upon the electroactivity of the species.
Figure 3.16. Current-versus-voltage curves and amperometric titration curve for the titration of Pb$^{2+}$ with Na$_2$SO$_4$ solution. A: Successive current-versus-voltage curves for the reduction of Pb$^{2+}$ ion at a mercury electrode, made after increments of SO$_4$$^{2-}$ were added. B: Resulting amperometric titration curve for currents ($i_0$, $i_1$, $i_2$, ...) measured at an applied potential of $-1$ V versus SCE.
Two Polarized or Indicator Electrodes
Bi-amperometric Titrations

• A small fixed potential difference (20-250 mV) is applied across two identical (Pt) indicator electrodes. The current is measured during the titration.

* Example: Titration of Fe$^{2+}$ vs Ce$^{4+}$
Figure 3.18. Titration curves for amperometric titrations with two polarized or indicator electrodes. A: Both the titrant and the substance titrated have reversible voltammetric curves. B: The substance titrated displays irreversibility, and the titrant reversibility. C: The substance titrated displays reversibility, and the titrant irreversibility.
Cyclic voltammetry

Similar to fast linear sweep method.

Voltage is swept in both directions during a drop (typically < 1 second).

DME, glassy carbon or Pt electrodes may be used.

Method looks at oxidation, reduction and if the reaction is reversible.

The method is used to study the REDOX process - organics and organometallics.
Cyclic voltammetry
Cyclic voltammetry

If the process is not reversible, you get a non-symmetrical plot.
Cyclic voltammetry

Reversible reaction

Glassy carbon electrode

5 mM Ferrocyanide in 50 mM KNO₃

Scan rate 100 mV/sec
Cyclic voltammetry

Quasi-reversible reaction.

As the reaction approaches irreversibility the peak separation becomes greater.

1 mM hydroquinone in pH 7 phosphate buffer

Scan rate of 500mV/sec