Electro-Analytical Techniques

Dynamic

Potentiometric methods measure the potentials at electrodes by a suitable coupling with a reference electrode; as a potential difference $E$ ($E_{cell}$). At the electrode the redox reaction has reached equilibrium. Under such a situation there is no net transfer of charge (current) across the electrode interface. Thus as the measurement is made very little or no current drawn by the measuring device (potentiometer).

Example (electrode):

$\text{Pt/Sn}^{2+}(a_{\text{Sn}^{2+}}), \text{Sn}^{4+}(a_{\text{Sn}^{4+}}) \quad E_{el}$

$\text{Sn}^{4+} + 2e = \text{Sn}^{2+}$

The concentrations at the electrode surface are nearly the same as that in the bulk solution.

Disturbing the equilibrium (drives a reaction):

$\text{Pt/Sn}^{2+}(a_{\text{Sn}^{2+}}), \text{Sn}^{4+}(a_{\text{Sn}^{4+}}) \quad E < E_{el}$ (E sufficiently negative)

$\text{Sn}^{4+} + 2e \rightarrow \text{Sn}^{2+}$

The concentrations at the electrode surface are different from that in the bulk solution – polarization.

Working electrode (WE)
Electrode at which reaction of interest occur.

Electrochemistry in Stirred Solutions

Metal electrodes are generally polarizable.

To make them non-polarized, stir the solution so that the concentration at the surface is the same as in the bulk.

Reference electrodes are generally non-polarizable.

Current is a measure of the reaction rate at the electrode(s).

Charge is a measure of the extent of the reaction occurred at the electrode(s).
Application of a potential sufficiently different from the equilibrium potential would drive the half reaction in one direction. This would lead to a flow of charge (electrons) i.e. a current, \( i \).

\[
\frac{dq}{dt} = i
\]

And quantity of charge \( q = it \); \( t \) = time; \( i \) is held constant;

More precisely:

\[
q = \int_0^t idt
\]

Moles of material electro-generated:

\[
\frac{q}{nF} = \frac{\int_0^t idt}{nF}
\]

However, potential at a single electrode cannot be changed solitarily, two electrodes are required.

The second electrode – **Auxiliary (or counter) electrode**.

A redox reaction (complementary) would occur at the counter electrode simultaneously.

**Electrolysis**

**Electro-deposition of Copper.**

Non-spontaneous process.

The energy required to effect the reaction is drawn from the external power source.

\[
\text{Cu}^{2+} + 2e \rightarrow \text{Cu}
\]

\[
\text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e
\]

Note: **electrolysis** is not an equilibrium situation.

1. Redox reaction occur at the electrode interfaces, interchange of electrons occur. The reaction is ‘forced’; it is a energetically uphill, non-spontaneous process.

2. Oxidation reaction occur at the anode,

3. Reduction reaction occur at the cathode,
Minimal applied potential (difference) required to effect Electrolysis.

Overcoming activation energy requires input of energy. Achieved by increasing the **negativeness** of the cathode. i.e. \( E_{app,\text{cathode}} < E_{eq,\text{cathode}} \)

\[
\begin{align*}
&\text{a. Reduction: } \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \\
&\text{Overcoming activation energy requires input of energy.}
\end{align*}
\]

\[
\begin{align*}
&\text{b. Oxidation: } \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- \\
&\text{To overcome the activation energy required an input of energy, increasing the **positivity** of the anode.}
\end{align*}
\]

\[
V_{app} = E_{app,\text{anode}} - E_{app,\text{cathode}} > E_{cell} \text{ just to start electrolysis}
\]

\[
V_{app} - E_{cell} = \text{Cell overvoltage}
\]

In addition, to drive a current the resistance of the cell must be overcome as well; IR drop, Ohmic potential.

\[
V_{app} = E_{\text{cathode}} - E_{\text{anode}} + \text{overpotentials} + iR
\]

Further, the depletion of material at the electrodes would require the movement of material from the bulk of the solution (diffusion – if solution is unstirred) and that involves some energy as well - **concentration overpotential**.
i–V Plot, stirred solutions

\[ E_{\text{app}} = E_{\text{cathode}} - E_{\text{anode}} + \text{overpotentials} + iR \]

**Table 1.** Overpotential (V) for gas evolution at various current densities at 30°C

<table>
<thead>
<tr>
<th>Electrode</th>
<th>10 A/m²</th>
<th>100 A/m²</th>
<th>1000 A/m²</th>
<th>10000 A/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished A</td>
<td>0.95</td>
<td>0.68</td>
<td>0.60</td>
<td>0.54</td>
</tr>
<tr>
<td>Smooth B</td>
<td>0.95</td>
<td>0.71</td>
<td>0.65</td>
<td>0.58</td>
</tr>
<tr>
<td>Cu</td>
<td>0.93</td>
<td>0.73</td>
<td>0.64</td>
<td>0.57</td>
</tr>
<tr>
<td>Ag</td>
<td>0.96</td>
<td>0.74</td>
<td>0.66</td>
<td>0.58</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.99</td>
<td>0.77</td>
<td>0.77</td>
<td>0.77</td>
</tr>
<tr>
<td>Pb</td>
<td>0.97</td>
<td>0.78</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
<td>Zn</td>
<td>0.96</td>
<td>0.78</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
<td>Hg</td>
<td>0.95</td>
<td>0.78</td>
<td>0.79</td>
<td>0.79</td>
</tr>
</tbody>
</table>

*Note: International Critical Tables, 1929, 6, 159. This reference also gives overpotentials for E_0, B_0, and i.*
How the applied potential difference distributes itself between the two electrodes is harder to decipher.

Often it is necessary to find the actual potential on the working electrode.

The working electrode is the electrode in an electrochemical system on which the reaction of interest is occurring.

Strategy – three electrode cell.

Three electrode cell

Controlled potential analysis

Electrogravimetric Analysis

This method employs an electric current to deposit a solid on an electrode from a solution.

Two or three electrode circuit used, either a constant current or a constant potential is applied to the pre-weighed working electrode.


Coulometry:

Coulometry determines the unknown concentration of an analyte in solution by completely converting the analyte from one oxidation state to another.

Coulometry is an absolute measurement similar to gravimetry or titrimetry and requires no chemical standards or calibration.

Useful for determining absolute concentration of standards.

**Coulometry**

\[ i = \frac{dq}{dt} \]

Coulombs of charge measured

\[ q = \int i \, dt \]

\[ \frac{nF}{nF} \]

Amperometry: Constant potential mode

In amperometric experiments the potential of the indicator electrode(s) is adjusted to a value so that redox processes could occur (stirred solutions).

The current flowing between the indicator electrode and a second electrode in the solution is measured.

There is a minimum potential required to initiate an oxidation or reduction reaction at an electrode.

To effect a net Faradaic process the magnitude of the applied potential must be sufficiently higher in magnitude than the minimum equilibrium potential.

Faradaic current proportional to the concentration of the species undergoing transformation (redox).

A standard curve of current as a function of concentration of a series of standard solutions is prepared, and the concentration of the analyte is determined from the curve.
Amperometry is also used to locate the end point in amperometric titration curves; a plot of current as a function of titrant volume.

The shape of the curve varies depending on the chemical species (titrant, analyte, products) that are electroactive and the reversibility of the redox couple.

The plot consists of linear and nonlinear regions before and after the end point and are extrapolated to intersect at the end point.

Some information from un stirred solutions may be used to design amperometric experiments.

Convention (i – V plots) (polarographic):

- Y- axis: Cathodic currents positive direction (up)
- X- axis: Negative potential increases to the right

+ Stronger oxidant
- Stronger reductant

\[ \text{E}_{\text{app}} \text{ vs } \text{E}_{\text{ref}} \]

For stirred solutions the current is directly related to the concentration.

For unstirred solutions, the current is generally plotted for analytes. Such plots contains the unique redox characteristic (potential) of the redox couple; i = steady current and every point here is from a 'new experiment'.

Amperometric Titrations;

- single polarizable electrode – RE; combination.

\[ \text{T} + \text{X} \rightarrow \text{T}' + \text{X}' \]
Amperometric Titrations; dual polarizable electrodes

\[ T + X \rightarrow T' + X' \]

Reversible electroactive

\[ X^* \cdot X'^* \]

\[ T^* \cdot T'^* \]

Coulometry

Constant current mode.

Amperometric detection.

Coulometric determination with amperometric detection.

\[ q = i \cdot t \]

Br + Br → 2Br

\[ 2Br → Br_2 + 2e \]

Amperometric detection with amperometric detection.

Detector circuit

To power supply

Analyzer solution

Counter electrode

Fritted-glass disk

Magnetic stirring bar

Karl Fisher Titration; water determination

Analysis of water is based on the quantitative reaction

B = base;

\[ 2B + I_2 + B\cdot SO_2 + H_2O \rightarrow 2BH^+ + I^- + BSO_3 \]

BSO_3 + ROH → BH^+ R-OSO_3

I_2 generated electrochemically via (i); 2I^- → I_2 + 2e

1 mol I_2 = 1 mol H_2O = \frac{2F}{i}

moles \( H_2O = \frac{it}{2F} \)

Detector circuit

Constant current amperometric detection mode

Eg. Ascorbic acid + I_2 →

Electrochemically generated or added I_2 in solution.

Monitor voltage required to maintain a constant current. Voltage drops once unreacted I_2 start accumulating in solution.
$B, ROH, SO_2, solvent, KI$

\[
2I^- \rightarrow I_2 + 2e
\]

$I_2 + 2e \rightarrow 2I^-
$

$2I^- \rightarrow I_2 + 2e$

$Bases: imidazole, diethanolamine$

$Alcohols: methanol, diethylene glycol monomethyl ether$

$Organic solvent: chloroform, methanol, carbon tetrachloride, formamide, ..$

$CH_3OH + SO_2 + RN \rightarrow [RNH]^{+}[SO_3CH_3]^{-}$

$2RN + I_2 + [RNH]^{+}[SO_3CH_3]^{-} + H_2O \rightarrow 2[RNH^+] + [RNH][SO_3CH_3]^{-}$

Electrode reactions performed at electrodes in stirred solutions can be driven to completion. The total charge involved in such work is related to the amount of electro-active materials oxidized or reduced. The process requires a considerable time. (coulometry).

If the current is not maintained for a considerable time and/or the current is very small the change in concentration due to electrode reaction is negligible. At such situations the instantaneous current is proportional to the concentration of the material undergoing the transformation (amperometry).

$Voltammetry$

In voltammetry the current is measured as a function of a varying applied potential at an electrode.

There is a minimum potential required to initiate an oxidation or reduction reaction at an electrode.

Voltammetry is carried out in three electrode systems so that the potential applied to the working electrode can be accurately measured.
Application of a sufficiently negative potential initiates a reduction reaction at the surface.

Oxidized material \([A]\) is removed by the reaction thus its concentration near the surface drops.

Further, a more negative the potential depletion rate is higher further decreasing the concentration at the surface in a shorter time.

Concentration gradients are created and at a certain of the applied potential and beyond the concentration at the surface will be almost zero – steady state.
Concentration profile (in solution)

Electron transfer reaction rate at surface $\alpha_{i}$ measured.

Reaction rate at the interface is directly related to the faradaic current, $i$.

$A^\ast (surface) + e \rightarrow A$  \hspace{1cm} Faradaic current***

The overall electrode reaction rate at steady state;

$A^\ast (bulk) \rightarrow A^\ast (surface) \rightarrow A$

$i \sim$ rate determining slow step (diffusion rate)

In general $i$ increases with the magnitude of the applied potential, maximum $i$ is a limiting value !!

Slow step (mass transfer step):

1. *Migration
   Movement of ions in an electric field. Contribution to migration by analyte of interest, minimized by adding a supporting electrolyte to the test solution.

2. *Convection
   Movement of bulk solution to the surface due to thermal motion and stirring; is eliminated by using quiescent conditions (no stirring during measurement and constant temperature)

3. Diffusion
   Movement of analyte due to the concentration gradient in the solution.
   * Not uniform – can be made to disappear functionally.

$i = i_d = nFAD_i \left( \frac{\partial C_4}{\partial x} \right) = nFAD_i \left( \frac{C_4 - C_4^0}{\delta} \right)$

Highest at the limiting current (diffusion current, $i_d$).

Any further increase of potential (negatively) does not increase diffusion current.

Convention: Cathodic currents positive

Voltammogram

The diffusion current is found by the difference between the current plateau (average) and a linear extension of the low potential response.

Linear sweep voltammetry
Diffusion Current, $i_d$

\[ i_d = nFAD_a \left( \frac{C_A - C_A^0}{\delta} \right) = k_A (C_A - C_A^0) = k_A C_A \]

at steady state because $C_A^0 = 0$ at the diffusion limit.

Heyrovsky-Illkovic Equation

\[ E_{\text{app}} = E_{1/2} + \frac{RT}{\alpha n F} \ln \left( \frac{i_d}{i} \right) \]

Sigmoid!

$0 < \alpha < 1$ and $\alpha = 1$, for reversible redox system

Upon rearrangement:

\[ \ln \left( \frac{i_d}{i} \right) = \frac{\alpha n F}{RT} E_{\text{app}} - \frac{\alpha n F}{RT} E_{1/2} \]

\[ E_{1/2} = \frac{-\text{intercept}}{\text{slope}} \]

allows determination of $n$ experimentally for reversible systems!!!

Electrochemical reaction at the surfaces is an interfacial phenomenon. It's highly dependent of the surface characteristics of the surfaces involved.

Any changes at the surface changes the $i$ vs $V$ curves.

The surface needs refreshing frequently.

It is achieved by employing the dropping Hg electrode.

A new Hg drop is created periodically and the reaction done on a fresh surface (Polarography). and high over-potential of Hg allows use of larger negative limit of applied potential.
Complications:
Spiky nature of the signal ~ noise.
Restructuring of charged species and molecules at the interface, each time a new surface is created.

Ilkovic Equation

$$i_d = 706nD_A^{1/2}m^{2/3}t^{1/6}CA$$

- \(n\) = number of electrons
- \(D_A\) = Diffusion coefficient cm²/s
- \(m\) = flow rate of mercury mg/s
- \(C_A\) = conc. mM
- \(t\) = time

A single voltammogram can quantify many species if sufficient separation between waves.
Polarographic experiments on a given surface can be done only within a potential range.

At positive limit, oxidation of water
\[ 2H_2O \rightarrow 4H^+ + O_2(g) + 4e^- \]

At negative limit, reduction of water
\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]

Problems with dissolved O₂ - must purge solutions of dissolved O₂.

Useful media/voltage ranges

Advantages of DME
(as opposed to stationary electrodes):

a. clean surface generated
b. rapid constant current achievement at drop growth
c. remixing of solution when drop falls
d. high Hg overvoltage means even metals with high -ve E⁰ systems can be studied without H₂ formation
e. amalgam formation more favorable vs. metal (s)

http://www.youtube.com/watch?v=CSBMf76FvJg
Disadvantages of DME

a. Hg easily oxidized, limited use as an anode
   \[ E = 0.25V \text{ vs SCE} \]
   \[ 2\text{Hg} + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_4^{2-} + 2\text{e}^- \]

b. non-faradaic residual currents limit detection >10^{-5} M
c. cumbersome to use (toxic mercury)
d. sometimes produce a current maxima for unclear reasons (use maxima suppressor)

Sampled current polarography:

1. Unstirred solutions
2. Create a drop \( r = \text{constant} \Rightarrow \text{const. elect. area} \)
3. Apply a 'new' potential \( E \) \( i = i_{\text{faradaic}} + i_{\text{charging}} \)
4. Delay for a time
5. Measure current \( i = i_{\text{faradaic}} \)
6. Release the drop
7. Repeat 2-6.

Current vs time

Faradaic Current vs. time
Cottrell Equation
\[ |i| = \frac{nFAD}{\sqrt{\pi t}} C_{\text{bulk}} \]
\( C_{\text{bulk}} = \text{Concentration of ion in solution} \)
\( A = \text{electrode area (not time varying)} \)

Note the absence of noisy character of the signal.
Pulsed Voltammetric Techniques:

Pulsed techniques take advantage of the difference in the rate of the decay of the charging and the Faradaic currents following a potential step (pulse).

The charging current decays exponentially, whereas the Faradaic current (for a diffusion-controlled current) decays as a function of $1/\sqrt{t}$.

The charging current is negligible with 5 times the time constant of decay. The measured current is predominantly Faradaic current.

Normal Pulse Voltammetry:

The potential waveform; a series of pulses of increasing amplitude, potential returning to the initial value after each pulse (unstirred).

Re-doxx processes with $E_{1/2}$ difference of ~0.2V resolvable.

Differential Pulse Voltammetry:
Differential Pulse Voltammetry:

The potential waveform; small pulses (constant amplitude) superimposed upon a staircase wave. Current is sampled twice in each pulse period; before the pulse, and at the end of the pulse. The difference between these two current values is recorded and displayed.

Detection Limit: $10^{-7} - 10^{-8}$ M.

Square-Wave Voltammetry:

$\mathbf{i}_p \propto C$
Square-Wave Voltammetry:
The potential wave form; a square wave of constant amplitude superimposed on a staircase wave form.

The current is measured at the end of each half-cycle. The current measured on the reverse half-cycle ($i_r$) and subtracted from the current measured on the forward half-cycle ($i_f$).

This difference current ($i_f - i_r$) is displayed as a function of the applied potential. Same drop.

For a reduction process, with potential well positive of the redox potential, both the forward and reverse currents are zero, so the difference current is also zero.

At potentials well negative of the redox potential, the current is diffusion-controlled, and the potential pulse has no effect; hence, the forward and reverse currents are equal, and the difference current is again zero.

The largest difference between the forward and reverse currents (and hence the largest current response) is at the redox potential.

Advantages to measuring the difference current.

1. Increase of the discrimination of the charging current, since any residual charging current is subtracted out.
2. The output of the current response is a symmetric peak, rather than the sigmoidal curve typically found for normal pulse voltammetry.
3. Easy resolution of peaks; $E_{1/2}$ difference of ~0.05V resolvable.

Anodic Stripping Voltammetry

In ASV, a mercury electrode is held at a sufficiently negative potential to reduce metal ions in solution and form an amalgam with the electrode.

The solution is stirred during deposition of the analyte (metal) referred to as pre-concentration step. The reduced metals form amalgam with mercury.

After reducing and accumulating the analyte for some period of time, $t_d$, allow a quiescence time and change the potential on the electrode (increase) to re-oxidize the analyte and generate a current signal; in NPV, DPV or SWV ramps.

$C_A = \frac{i_f t_d}{n F V_{Hg}}$

$C_A$ = concentration of analyte on ‘deposit’

$i_f$ = limiting current at deposition

$t_d$ = time of deposition

$n$ = number of electrons for reduction

$F$ = Faraday constant

$V_{Hg}$ = volume of mercury (in the electrode)

The re-oxidizing (stripping) current $\propto C_A \propto C_{A,solution}$

Primary advantage of ASV is the pre-concentration step of the analyte which allows to enhance output signal (Detection limit $10^{-10}$ M).
Cyclic Voltammetry:

A triangular waveform applied to the WE.

Linear wave forms used are increased and decreased in either anodic or cathodic fashion.

Table 17-3: Detection limits for stripping analysis

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Stripping mode</th>
<th>Detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>Anodic</td>
<td>2 x 10⁻⁹ M⁺</td>
</tr>
<tr>
<td>Trichloroethane</td>
<td>Anodic</td>
<td>2 x 10⁻¹⁰ M⁺</td>
</tr>
<tr>
<td>I⁻</td>
<td>Cathodic</td>
<td>1 x 10⁻¹⁰ M⁻</td>
</tr>
<tr>
<td>DNA or RNA</td>
<td>Cathodic</td>
<td>2-5 pg/ml</td>
</tr>
</tbody>
</table>

Excitation Potential Current – Potential Response

\[ i = nFACD \frac{D}{V} \text{; Cottrell Equation} \]

Cyclic Voltammogram of a reversible redox system.

\[ A + ne = B \]

\[ E_{1/2} = \frac{E_{pa} + E_{pc}}{2} \]

\[ E_{pa} - E_{pc} = \frac{RT}{nF} \frac{59.0mV}{n} \]

\[ i_{pc} = \frac{1}{i_{pa}} \]
Electrochemical detectors

The mobile phase is flowing past the electrodes, the solvent will be continuously replaced as the peak passes through the detector.

The electrochemical detector responds to substances that are either oxidizable or reducible. The detector normally has three electrodes, the working electrode (oxidation/reduction occur), the auxiliary electrode and the reference electrode. The electrical output results from an electron flow caused by the chemical reaction that takes place at the surface of the electrodes.

There are two modes of operation in electrochemical detection; coulometric detection and amperometric detection.

Coulometric detection: If the reaction at the electrode surface exhausts all the reactant and the current becomes zero, the total charge that passes will be proportional to the mass of solute detected.

Amperometric detection: While there is solute present between the electrodes, a current will be maintained (albeit varying in magnitude).
Derivatizing of samples has become vitally important in making the analytes conducive for detection.

Derivatization of reactive analytes with redox functional groups for HPLC shows following advantages:

- increases analyte stability
- higher selectivity and sensitivity

Additionally the altered polarity from the functional group may lead to better chromatographic separation.