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.

With electrodeposition, the goal is to convert all of our analyte from one form to another. Increasing the potential results in a more rapid conversion. Ultimately, all of the analyte is converted.

With polarography, we use a small electrode that limits how fast we can convert our species. This results in only a small portion of our sample being converted.

### Voltammetry
A group of analytical methods in which only a small portion of a material is reduced (or less commonly oxidized) electrolytically.

**Several types of methods based on**
- Electrode type,
- How the potential is applied,
- How the current is measured.

### Polarography

**Summary**
- Subject to high relative errors (≥ ±1%)
- Works best in the $10^{-5} - 10^{-2}$ M range.
- Requires a calibration curve.
- Provides both qualitative and quantitative information.

With polarography, we use a small electrode that limits how fast we can convert our species.

This results in only a small portion of our sample being converted.
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.

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

Two types of information are obtained.

- $i_d$: diffusion current
- $E_{1/2}$: halfwave potential

**Diffusion current**

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

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

- $i_d$: current in $\mu A$
- $n$: # e$^-$/transfer
- $C$: concentration
- $D$: diffusion coefficient
- $m$: mass of drop
- $t$: drop time

**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.
E\textsubscript{1/2} values are listed verses the SCE.

Not the same as E\textsuperscript{0} values

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

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

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

Note how the E\textsubscript{1/2} value can be shifted by changing the supporting electrolyte.

Potential is still varied linearly with time but the current is only sampled for 5-20 msec/drop - near the end.

This results in smoother data.
Normal pulse polarography

Sample like with TAST but you only apply a current when sampling.
Results in even less drop noise and uses less sample.

Differential pulse polarography

The potential is applied as a ramped square wave. The current is sampled just before and near the end of each 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.

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.

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 are used.
- Method looks at oxidation, reduction and if the reaction is reversible.
- The method is used to study the REDOX process - organics and organometallics.
If the process is not reversible, you get a non-symmetrical plot.

A constant, sinusoidal AC potential of a few mV is superimposed on a normal DC potential ramp.

For this method, peak height is proportional to concentration.

One advantage is that a ‘lock-in’ amplifier can be used to reduce noise.

Only a signal of the proper frequency will be detected.
**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.

**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.

---

**Stripping voltammetry**

**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.