With potentiometric methods, we simply measured $E_{\text{cell}}$ and used the Nernst equation to quantify a substance.

With electrogravimetry and coulometry, a potential is applied, forcing a reaction to go.
- polarize the cell
- causes unexpected things to happen.
- work is done on the system
- $E_{\text{cell}}$ can change during an analysis

When we apply a voltage, it can be expressed as the following:

$$E_{\text{applied}} = E_{\text{back}} + iR$$

Where

$E_{\text{back}}$ = voltage required to ‘cancel out’ the normal forward or galvanic reaction.

$iR$ = $iR$ drop. The work applied to force the reaction to go. This is a function of cell resistance.

A cell is polarized if its potential is made different than its normal reversible potential - as defined by the Nernst equation.

The amount of polarization is called the overpotential or overvoltage.

$$\eta = E - E_{\text{rev}}$$

If $iR$ drop = 0.1 volts and $E_{\text{forward}} = 1$, you must apply 1.1 to stop.
Apply a value with the goal of reaching the ‘final’ concentration.

Concentration overpotential:
This occurs when there is a difference in concentration at the electrode compared to the bulk of the solution.

This can be observed when the rate of a reaction is fast compared to the diffusion rate for the species to reach the electrode.

For our example, let’s assume that

\[ [\text{Cu}^{2+}]_{\text{bulk}} = 10^{-2} \text{ M} \]
\[ [\text{Cu}^{2+}]_{\text{electrode}} = 10^{-4} \text{ M} \]

then
\[ E_{\text{bulk}} = 0.337 + \frac{0.0592}{2} \log(10^{-2}) = 0.278 \text{ V} \]
\[ E_{\text{electrode}} = 0.337 + \frac{0.0592}{2} \log(10^{-4}) = 0.219 \text{ V} \]
\[ \eta_{\text{conc}} = E_{\text{electrode}} - E_{\text{bulk}} = -0.059 \text{ V} \]

Concentration overpotential can never be eliminated. However, it can be reduced.

Use efficient stirring

Use a low current density
Low current - slower reaction
Large electrode - more area for reaction.
So the E for electrolysis is actually:

\[ E_{\text{app}} = (E_{\text{anode}} + \eta_{\text{lac}} + \eta_{\text{aa}}) - (E_{\text{cathode}} + \eta_{\text{cc}} + \eta_{\text{ca}}) \]

- \( \eta_{\text{lac}} \) = concentration overpotential at anode
- \( \eta_{\text{aa}} \) = activation overpotential at anode
- \( \eta_{\text{cc}} \) = concentration overpotential at cathode
- \( \eta_{\text{ca}} \) = activation overpotential at cathode

This explains why many reactions do not proceed as expected or will not occur at all.

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**Electrolytic cells**

**In electrolytic cells**

The reaction requiring the smallest applied voltage will occur first.

As the reaction proceeds, the applied E increases and other reactions may start.

Let's look at an example to determine if a quantitative separation is possible.

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**Electrolytic example**

Can Pb\(^{2+}\) be quantitatively separated from Cu\(^{2+}\) by electrodeposition?

Assume that our solution starts with 0.1M of each metal ion.

We'll define quantitative as only 1 part in 10,000 cross contamination (99.99%)

- \( \text{Cu}^{2+} + 2e = \text{Cu} \quad E = 0.337V \)
- \( \text{Pb}^{2+} + 2e = \text{Pb} \quad E = -0.126V \)

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**Electrolytic example**

**Copper**

We start with 0.1 M and begin our deposition. We don’t want any lead to deposit until at least 99.99% of the copper has been removed - 10\(^{-5}\)M Cu\(^{2+}\)

\[
E = 0.337 - \frac{0.0592}{2} \log \frac{1}{10^{-5}} \\
E = 0.189 V
\]

---

**Electrolytic example**

**Lead**

It would start depositing at:

\[
E = -0.126 - \frac{0.0592}{2} \log \frac{1}{0.1} \\
E = -0.156 V
\]

The separation is possible but our calculations neglect any overpotential.
Electrogravimetry

A quantitative method based on weight gain. It is also referred to as electrodeposition.

✔ A very old method.

✔ When it works, it works well.

✔ Unfortunately, it only works for a limited number of materials.

The starting potential must initially be high to insure a complete deposition.

Overpotential can cause gas generation.

Our species may not be able to diffuse rapidly enough.

The deposition will slow down as the reaction proceeds.

Steps in the analysis

- The Pt electrode is cleaned, dried and its weight determined.
- The electrode is then placed in the system and a potential is applied.
- The analyte deposits on the electrode.
- The electrode is removed and brought to constant weight.

The method can be conducted either with or without a controlled potential.

No control

Simply set a fixed potential and run.
This is a simple and inexpensive option.

Unfortunately, it causes problems.
As the reaction proceeds, the current decreases, resulting in the deposition becoming much slower.

Only a limited number of species work well with electrodeposition. Only a few metals deposit from an acid solution quantitatively without hydrogen formation. Not many metals form a smooth, well held coating on the cathode - can lose metal.

Only a few metals deposit from an acid solution quantitatively without hydrogen formation.

Not many metals form a smooth, well held coating on the cathode - can lose metal.

Cathode electrodepositions.
- Copper - Commonly done in an acid solution using a Pt cathode.
- Nickel - Conducted in a basic solution
- Zinc - Requires an acidic citrate solution

Some metals can be determined by deposition of metal complexes (cyanides). Ag, Cd, Au.

Anode electrodepositions
- Some metals can be assayed by deposition on the anode.

This requires that we go to a higher oxidation - deposited as metal oxides.

\[
\begin{align*}
\text{Pb}^{2+} & \rightarrow \text{PbO}_2 \\
\text{Mn}^{2+} & \rightarrow \text{MnO}_2
\end{align*}
\]

A coulomb (coul) is a quantity of electricity. Current is the rate of electrical flow.

96500 coulombs of electricity are required to reduce 1 gram equivalent weight of a metal to a lower oxidation state (1 e\textsuperscript{-} change).

96500 coulombs = 1 Faraday (F)

Current = Amps = \(i = \text{coul/ sec}\)
The number of equivalents deposited can be found by:

\[
\text{# equivalents} = \frac{\text{grams}}{\text{gram equivalent weight}} = \frac{g \times \text{# in transfer}}{\text{formula weight}} = \frac{\text{# coulombs}}{96500} = \frac{it}{96500}
\]

The number of grams deposited then is:

\[
\text{grams}_{\text{deposited}} = \frac{it}{96500} \left( \frac{\text{FW}}{n} \right).
\]

Where
- \( i \) = current in amps
- \( t \) = time in seconds
- \( \text{FW} \) = formula weight
- \( n \) = number of electrons transferred per species

Example

Determine the number of grams of \( \text{Cu}^0 \) that could be deposited if a current of 6 amps is applied for 5 minutes to a solution of \( \text{Cu}^{2+} \).

\[
g = (6 \text{ A}) \left( 5 \text{ min} \times 60 \frac{\text{sec}}{\text{min}} \right) \left( \frac{63.54 \text{ g}}{\text{mol}} \right) \left( \frac{96500}{2 \text{ e}^-} \right)
\]

\[
= 0.0988 \text{ g}
\]

Efficiency

Unfortunately, not all of the electrons are used in the reaction - not 100% efficient.

This must be accounted for in our expression.

\[
\text{grams}_{\text{deposited}} = \frac{eff \cdot it \cdot \text{FW}}{96500 \cdot n}
\]

Another example

How long will it take to remove all copper from one liter of a 1.0 M solution of \( \text{Cu}^{2+} \)?

\( i = 0.1 \text{ amps, 50\% efficiency.} \)

\[
t = \frac{g}{(\text{eff}) (i) (\text{FW})}
\]

\[
t = \frac{(63.54 \text{ g} / \text{mol})(96500)(2 \text{ e}^-)}{(0.1 \text{ A})(63.54 \text{ g/mol})}
\]

\[
t = 3.86 \times 10^6 \text{ sec} = 44.68 \text{ days}
\]

Coulometric methods

Rather than relying on electrode weight gain, an analysis can be conducted based on electrical usage.

Resistance, voltage, current and time can all be measured with great accuracy.

A precipitate is not required so a larger number of reactions can be used.

Smaller quantities can be measured.
Coulometric methods

Direct Coulometry
Methods in which a substance is quantified by either oxidation or reduction directly at an electrode.

Two approaches
- Constant Potential
- Constant Current

Direct coulometry

Constant potential
As the reactants are consumed, the current decreases. When the reaction is complete, the current is negligible.

The area under the curve equals the number of coulombs used.

Direct coulometry

Constant current
The current is held constant by ‘floating’ the potential. The reaction is complete when the potential no longer changes.

Either type of curve is possible based on the reaction involved.

Direct methods are of limited interest.
Approach is hard to control.
Suffers from the same problems with overpotential as electrodeposition.
Unexpected reactions can be a major problem.
Indirect coulometric methods are more useful.

Indirect coulometry or coulometric titrations

Basis
A low concentration of a ‘titrant’ is generated electrochemically at a constant rate from a high concentration of the oxidized or reduced form of the titrant.

As it is generated, it reacts stoichiometrically with the substance being determined.

The method overcomes
Difficulties associate with direct methods because of the high concentration of the titrant source.

Prevents side reactions
Increases reaction efficiency
The titrant need not be stable.
### Determination of Fe(II)

Reaction used: \(\text{Ce}^{4+} + \text{Fe}^{2+} \rightarrow \text{Ce}^{3+} + \text{Fe}^{3+}\)

- Ce\(^{4+}\) solutions are not stable so:
  - Add a large excess of Ce\(^{3+}\) to the sample.
  - Convert Ce\(^{3+}\) to Ce\(^{4+}\) which in turn reacts with our Fe\(^{2+}\)
  - While direct oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) may occur, it results in no error.

The endpoint can easily be determined by monitoring the potential of the system.

During the titration, the Ce\(^{4+}\)/Ce\(^{3+}\) is relative constant as long as Fe\(^{2+}\) is present.

Since the amount of Ce is much larger than Fe, it determines the overall \(E_{\text{cell}}\).

Once all Fe\(^{2+}\) is reacted, Ce\(^{4+}\) begins to build up in the system and there is a large change in the potential of the system.

### Endpoint detection

Easily determined.

The amount of Fe\(^{2+}\) can then be found based on the time and applied current.

### Indirect coulometry

- Constant current source
- Potentiometer
- Generating electrode
- Indicating electrode
- Timer

### Advantages

- Can detect \(\mu\)g amounts because \(i\) and \(t\) can be accurately measured.
- No standards are required if current efficiency is known.
- Can use unstable reagents.
- Can easily be automated.
- Relatively inexpensive method of analysis.