Variations on Polarography

- Can apply different types of electrical signals to electrochemical cells to modify and improve output signal

1) Alternating Current (AC) Polarography

\[ E \text{ vs. time} \]

AC component on a linear voltage scan
- Surface concentrations change in response to AC potential
- Expanded view of 1 cycle in vicinity of $E^{1/2}$

\[ \text{Reduction occurs above the } E^{1/2} \]
\[ \text{Reduction: } \text{Ox} + \text{ne}^- \rightarrow \text{Red} \]

\[ \text{Oxidation occurs when } E \text{ goes below } E^{1/2} \text{ again} \]
\[ \text{Reduction: } \text{Red} - \text{ne}^- \rightarrow \text{Ox} \]

$E_{\text{cathodic}}$

$E^{1/2}$

Nothing happens below $E^{1/2}$
- Measure AC component of current
- Current fluctuates in the vicinity of the $E_{1/2}$ because a positive or reduction current is produced above the $E_{1/2}$ and a negative or oxidation is produced below the $E_{1/2}$
- A peak is generated only near the $E_{1/2}$ because it is only in this region that the current fluctuates (giving an AC component) as the potential goes above and below the $E_{1/2}$ value
- Early in the experiment, no current is generated
- Late in the experiment, at potentials above the $E_{1/2}$, the total current is relatively constant and there is no AC component of the current to be measured so the AC signal flattens out
AC polarography

DC polarography
classical
(linear sweep)

Cyclic Voltammetry

AC polarography

A typical pulsed waveform

Normal or Integral pulse
• Frequency of AC voltage component typically 60 – 100 Hz
• The higher the frequency → the faster the electron transfer rate must be to keep up with potential changes and give an appreciable AC current → related to time-scale of the measurement
• Irreversible processes generate no AC wave
• Magnitude of the applied AC voltage is typically 10 mV peak to peak
Advantages of AC Polarography

- Detection limits slightly better than DC polarography, but still limited by capacitive current
- Capacitive current produces an AC component associated with charging and discharging of the electrode surface
- AC polarography produces peaks which solves problem of small wave on top of big wave
- Multiple components gives multiple peaks
- Can use solid electrodes instead of DME with AC applied potential waveform
Phase Selective AC Polarography

- Capacitive current lags voltage by $90^\circ$
- Faradaic current & applied potential are in-phase

\[ E \]
\[ I \]
\[ I_F \]
\[ I_C \]

measure current when $I_C = \text{min}$
• Instead of measuring total AC current, measure current only at the selected points in the cycle when $I_C = \text{min}$ & $I_F = \text{max}$
• Selectively measuring $I_F$ in the presence of $I_C$ improves detection limits by about 10X
• This represents the case for applied potential in the form of a sine wave in Phase-Selective AC Polarography and Phase-Selective AC Voltammetry
• The same is true for the digitized version of a sine wave or a pulsed waveform
Pulsed Waveforms for Pulsed Polarography and Voltammetry

Typical pulsed waveform

Normal or Integral Pulse waveform
During pulse sequence

Cottrell equation

Exponential decay \( e^{-kt} \)

Measure current when \( I_C = \text{min} \)
Pulsed Polarography

- Only measure current during the later part of the pulse
- Take advantage of the fact that $I_C$ decays more rapidly than $I_F$
- Improves detection limits to $10^{-7}$ M or slightly lower
- Easy to accomplish with modern electronic instrumentation
Normal Pulse Polarography
or Integral Pulse Polarography

A very widely used form of polarography

Typical pulsed waveform

Normal or Integral Pulse waveform
E

IF

exponential decay \( e^{-kt} \)

Cottrell equation

1\text{st} drop

2\text{nd} drop

3\text{rd} drop

pulses synchronized with drops

exponential decay \( e^{-kt} \)
• Synchronize Hg drop with applied pulse by using an electronically actuated drop dislodger or drop knocker

• Input signal is a square voltage pulse approx. 40 – 100 msec long applied late in the DME drop life

• Point of measurement is at the end of applied pulse when I_C has fallen off
- Pulse amplitude increases with time eventually reaching the $E_{\frac{1}{2}}$ value and exceeding it.
- At the end of the pulse the applied signal returns to the baseline level (zero).
- Resulting output signal is a wave.
• Normal Pulse Polarography (NPP)
DC Polarography

NPP showing steps in wave

Potential, V vs. Ag/AgCl

0.25 μA
Differential Pulse Polarography

- Most widely practiced variation on polarography
- Constant amplitude pulses on continuously varying potential
- Measure current at A & B then subtract

![Diagram of Differential Pulse Polarography](Image)
DPP for low concentration sample showing a hint of the steps in the peak
Applied potential waveform for DPP

Linear potential ramp

Pulses on ramp showing pulse duration and sampling times before & at the end of pulse

Current behavior during pulse
Advantages of DPP

- DPP gives a well resolved peak allowing the determination of species that have $E_{1/2}$ values as close as 40 mV to be measured.
- Detection limits to approx. $10^{-8}$ M.
- Relatively fast with modern DME’s and scan rates in the 10 – 50 mV/sec range.
- Instrumentation costs are comparatively low in the $5K$ to $10K$ range.