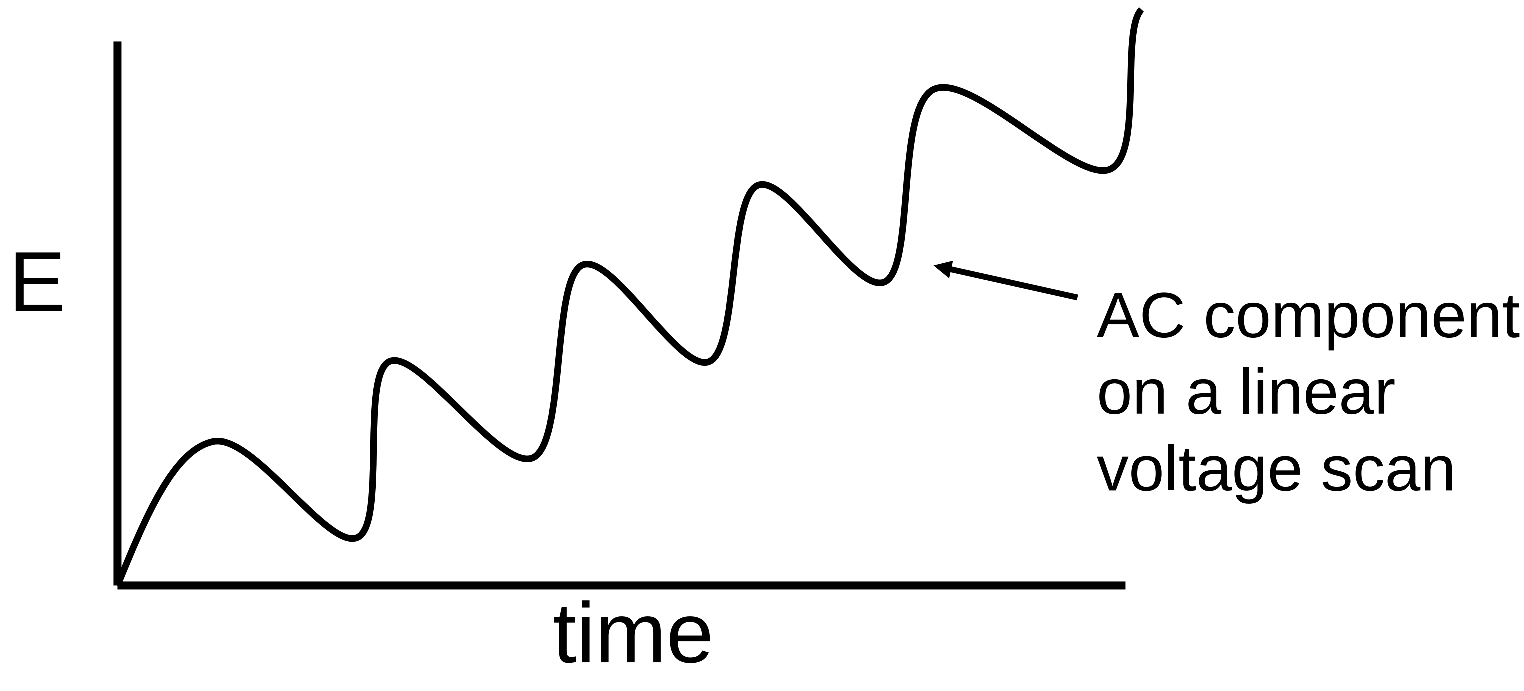
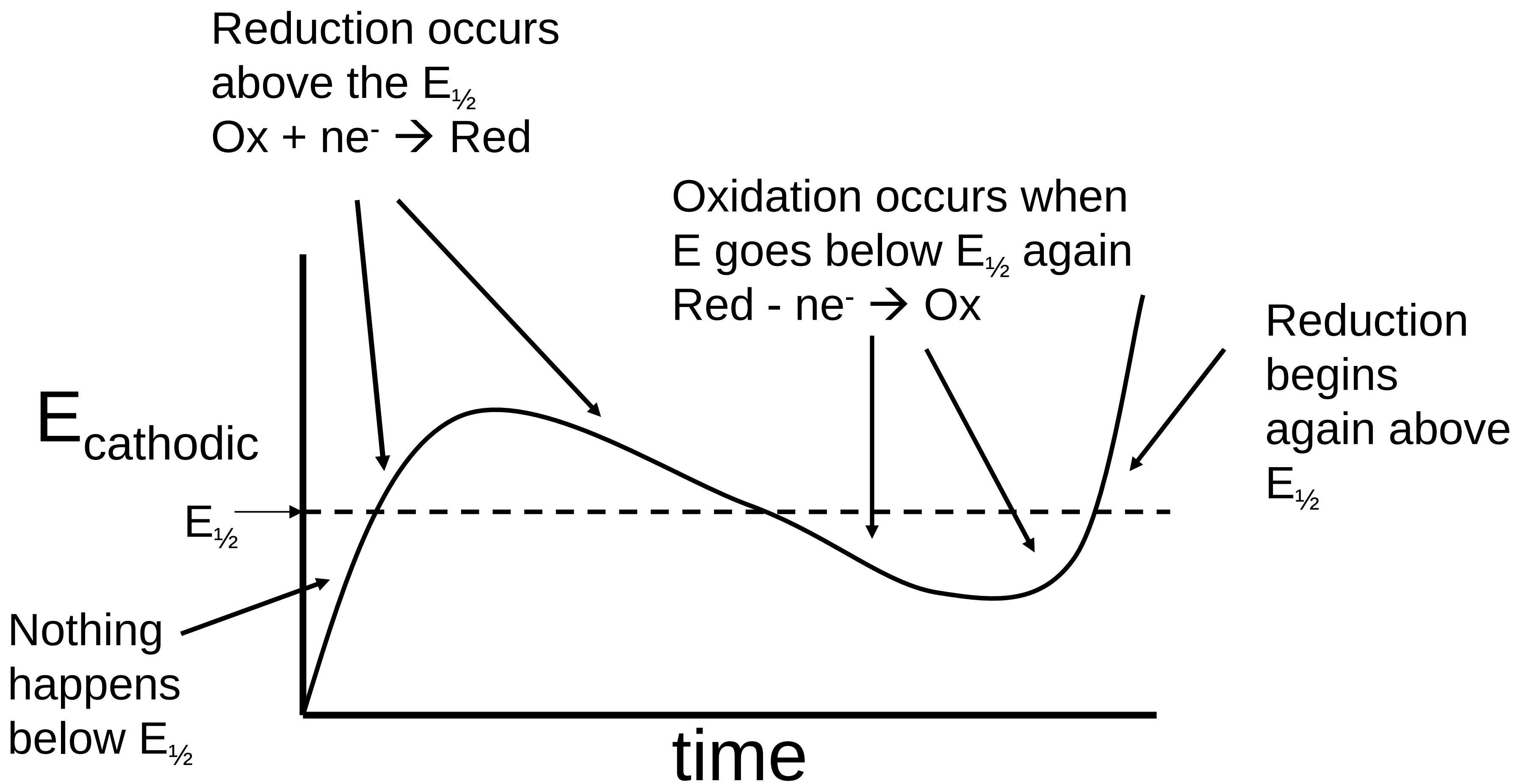
Variations on Polarography

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

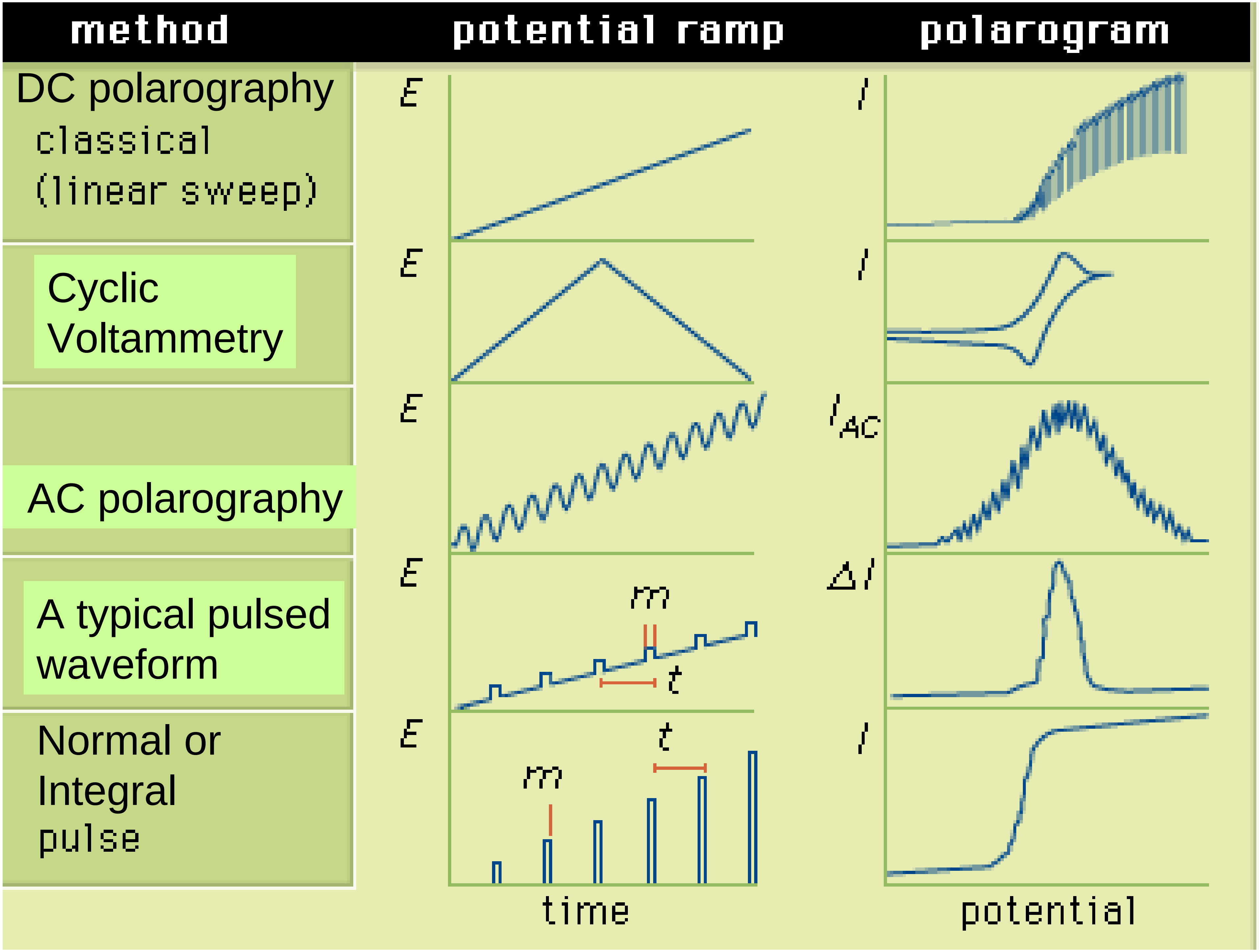
1) Alternating Current (AC) Polarography



- Surface concentrations change in response to AC potential
- Expanded view of 1 cycle in vicinity of $E_{½}$



- 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


method
potential ramp
polarogram
DC polarography
classical
(linear sweep)
Cyclic
Voltammetry
AC polarography
A typical pulsed
waveform
Normal or
Integral
pulse
E
I
I
I
AC
ΔI
m
t
time
potential

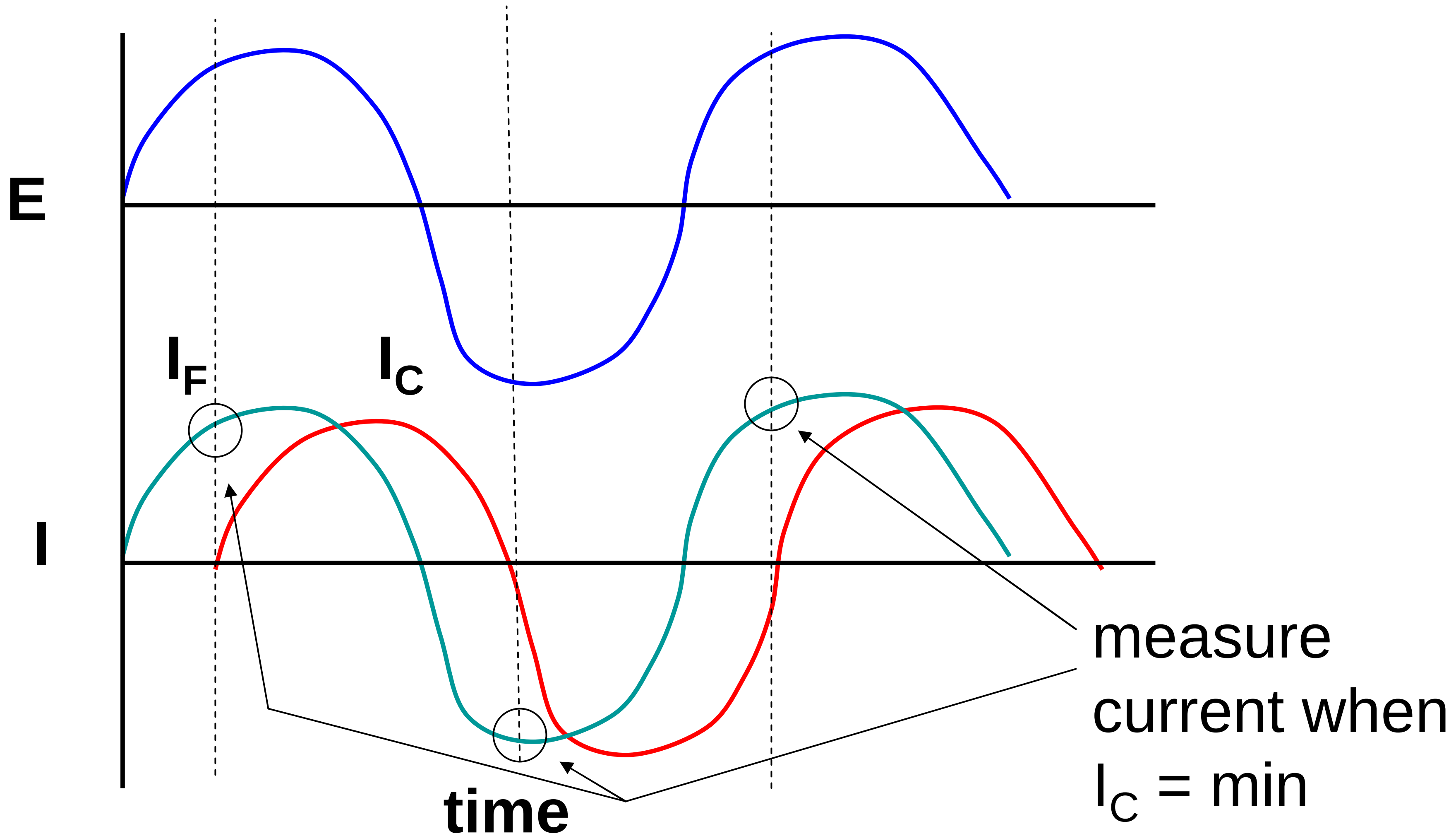
- Frequency of AC voltage component typically 60 – 100 Hz
- The higher the frequency → the faster the electron transfer rate must be to keep up with potential changes and give an appreciable AC current → related to time-scale of the measurement
- Irreversible processes generate no AC wave
- Magnitude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

Advantages of AC Polorography

- 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

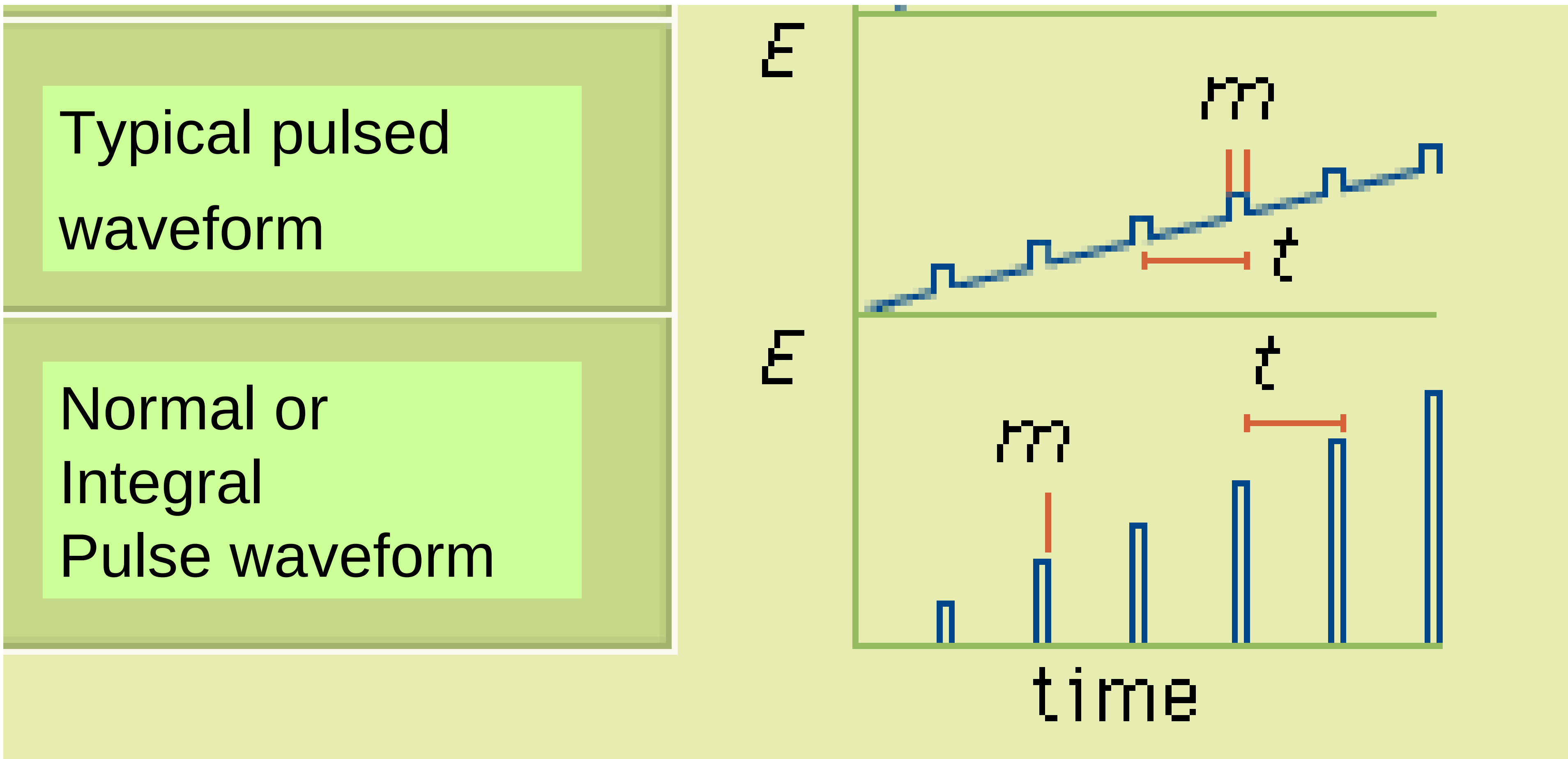
Phase Selective AC Polarography

- Capacitive current lags voltage by 90º
- Faradaic current & applied potential are in-phase

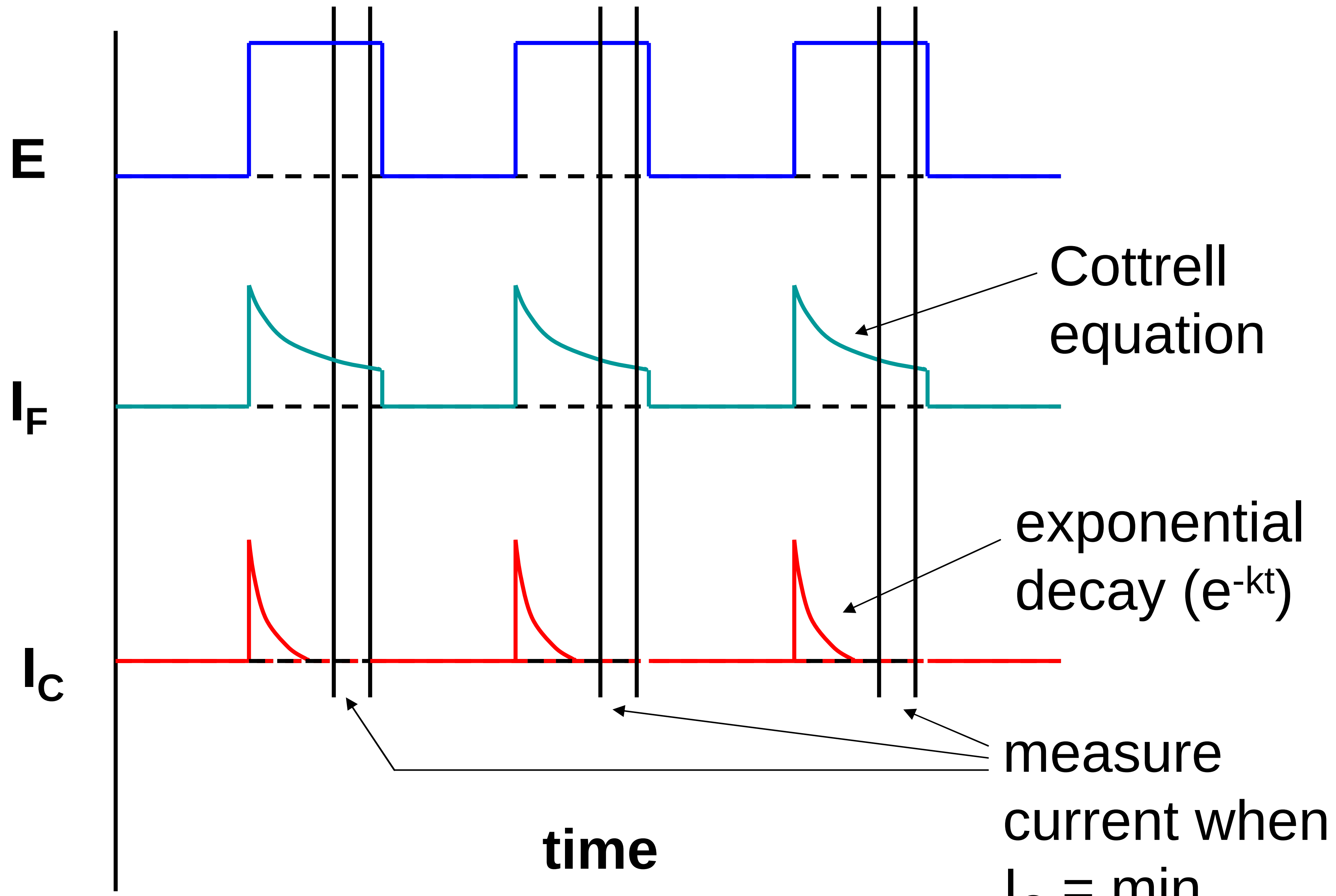


- Instead of measuring total AC current, measure current only at the selected points in the cycle when I_C = min & I_F = max
- Selectively measuring I_F in the presence of I_C improves detection limits by about 10X
- This represents the case for applied potential in the form of a sine wave in Phase-Selective 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



During pulse sequence



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

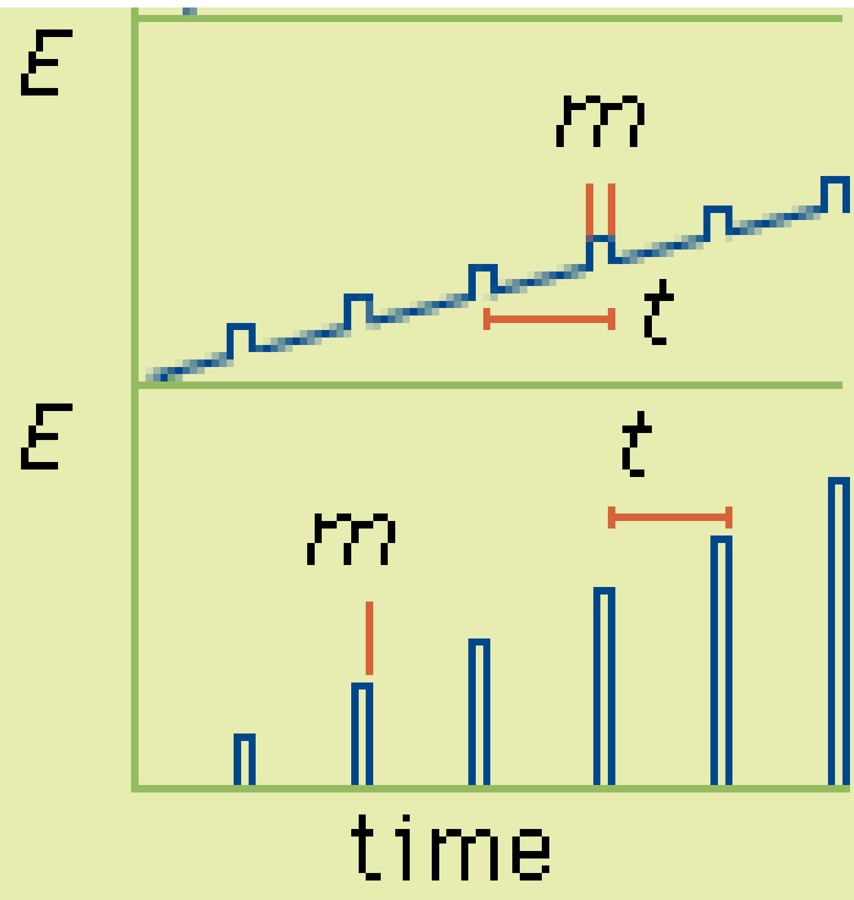
Normal Pulse Polarography or Integral Pulse Polarography

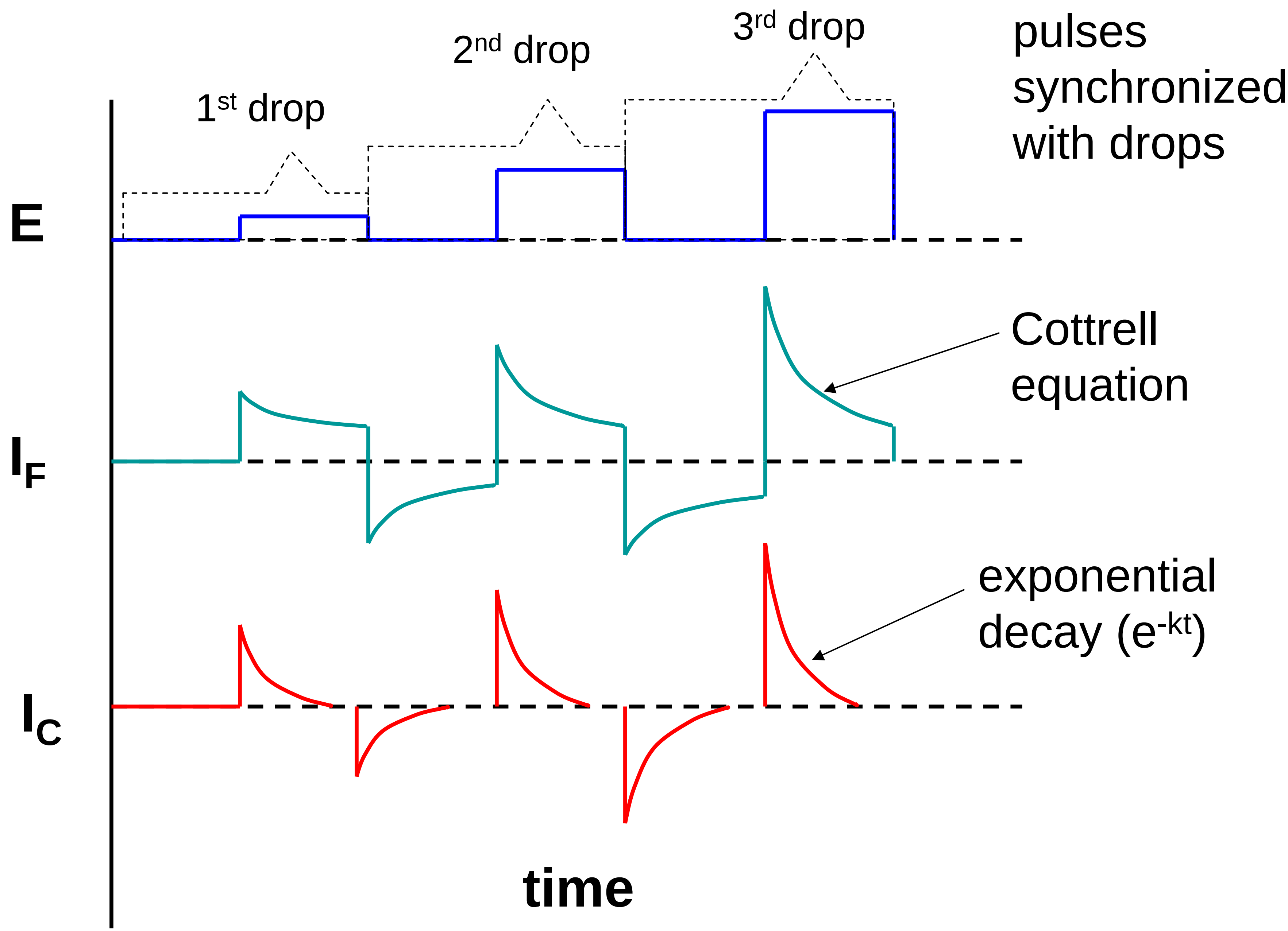
A very widely used form of polarography

Typical

pulsed waveform

Normal or Integral Pulse waveform

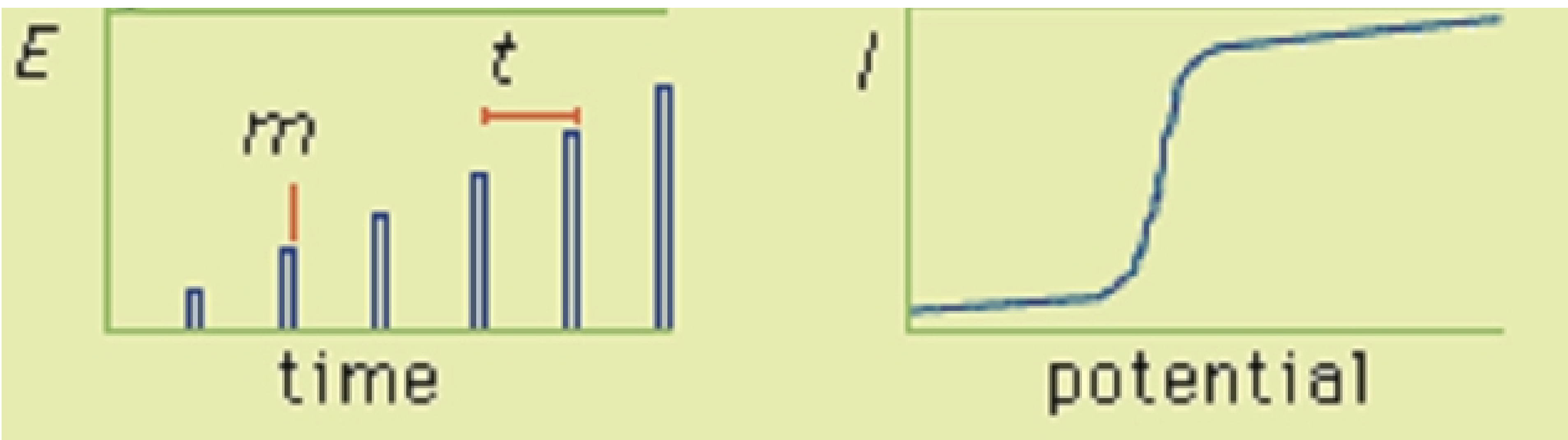




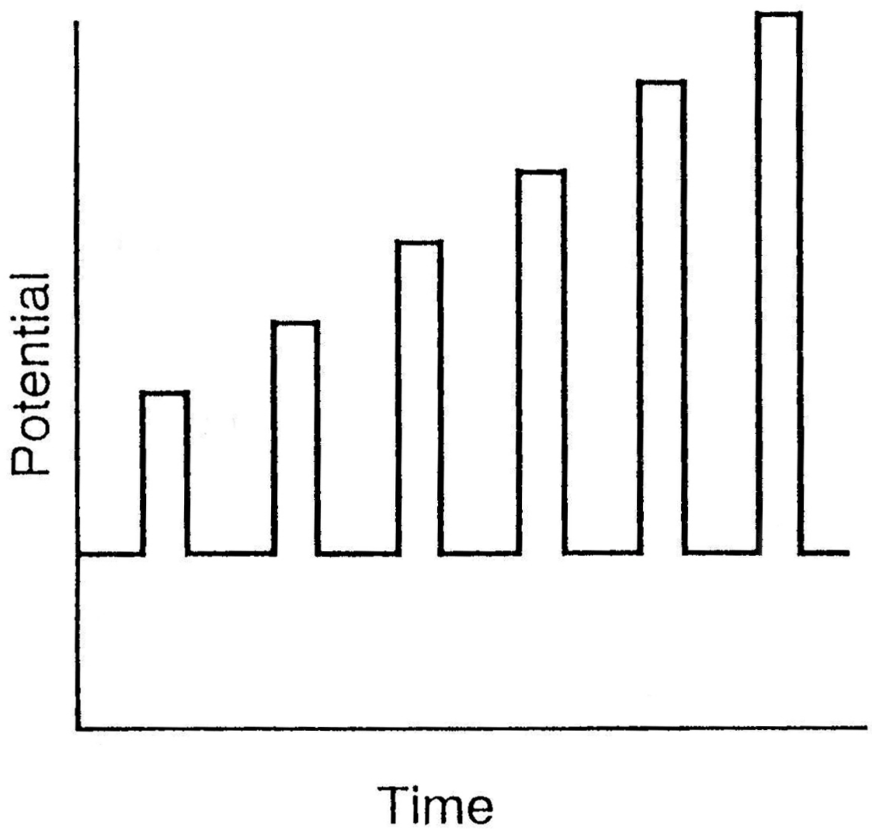
1st drop
2nd drop
3rd drop
pulses synchronized with drops
E
Cottrell equation
I F
exponential decay (e-kt)
I C
time

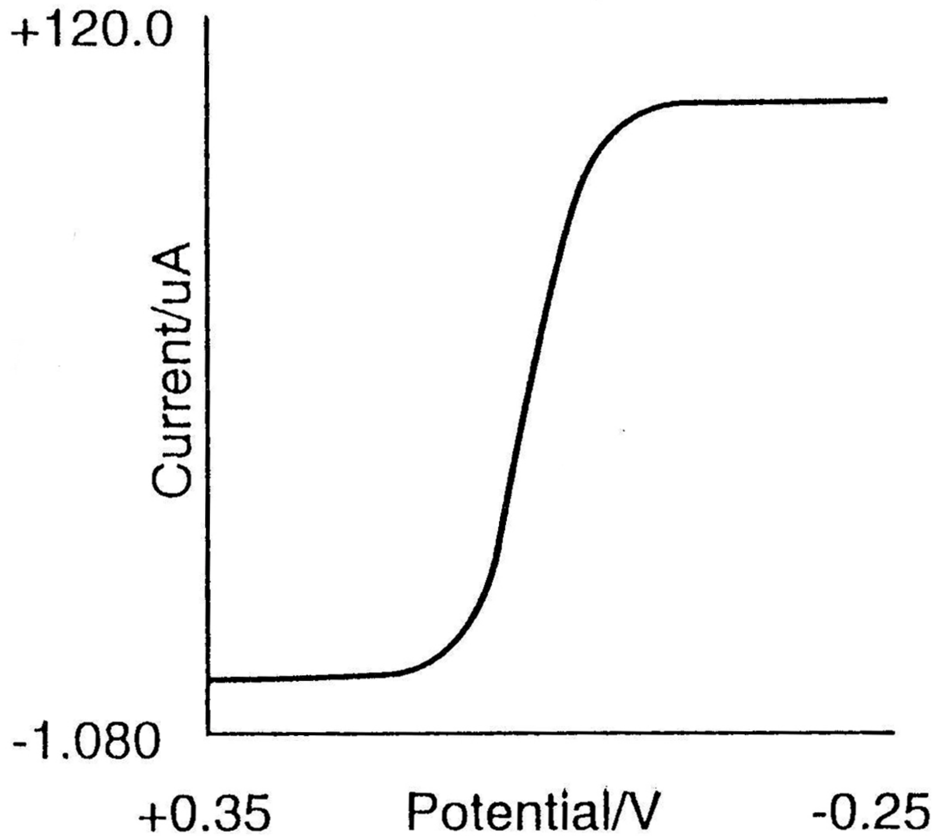
- Synchronize Hg drop with applied pulse by using an electronically actuated drop dislodger or drop knocker
- Input signal is a square voltage pulse approx. 40 – 100 msec long applied late in the DME drop life
- Point of measurement is at the end of applied pulse when I_C has fallen off

- Pulse amplitude increases with time eventually reaching the $E_{1/2}$ 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

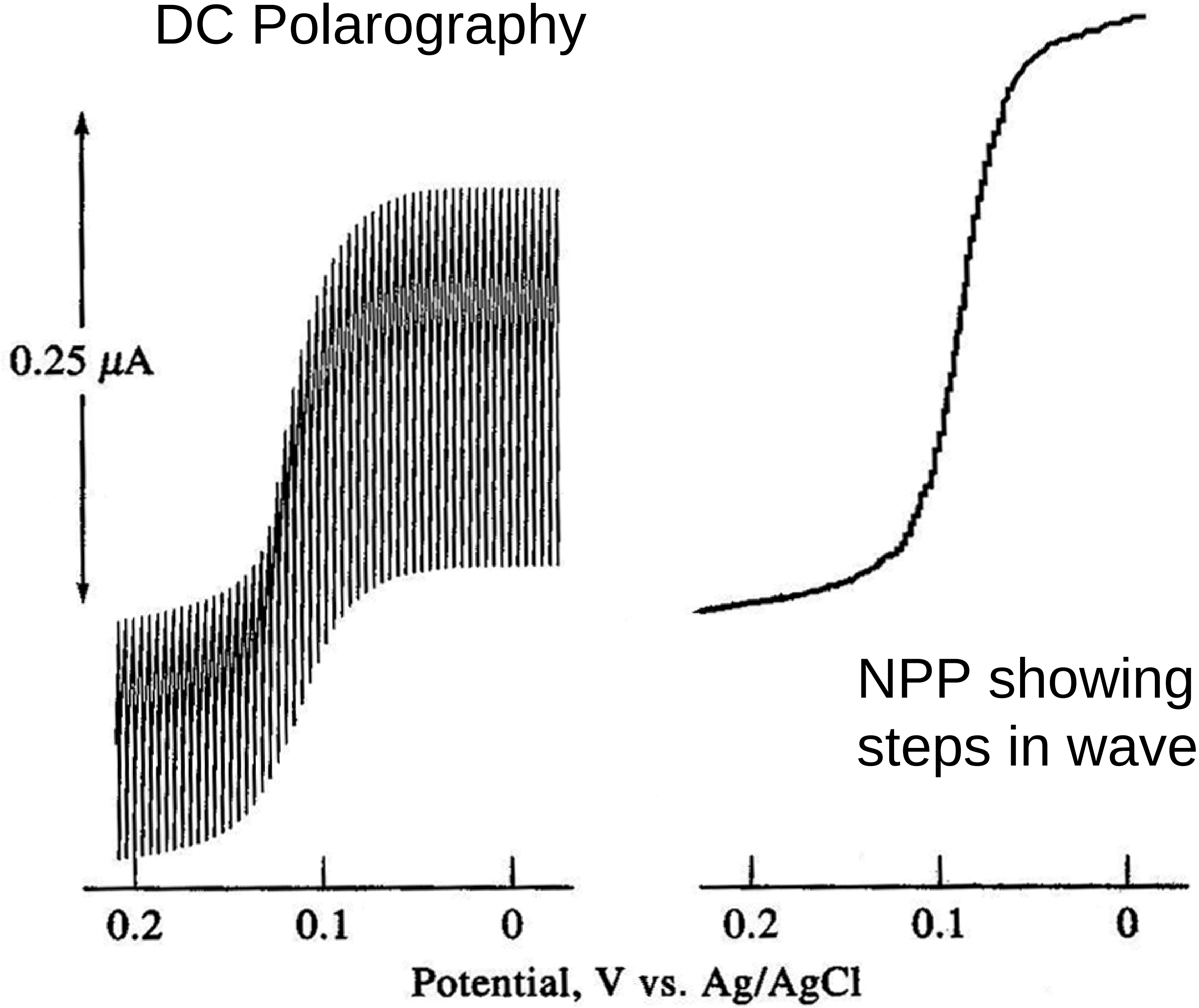


- Normal Pulse Polarography (NPP)





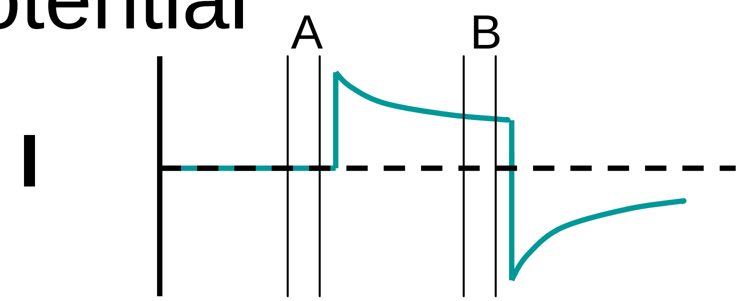
DC Polarography



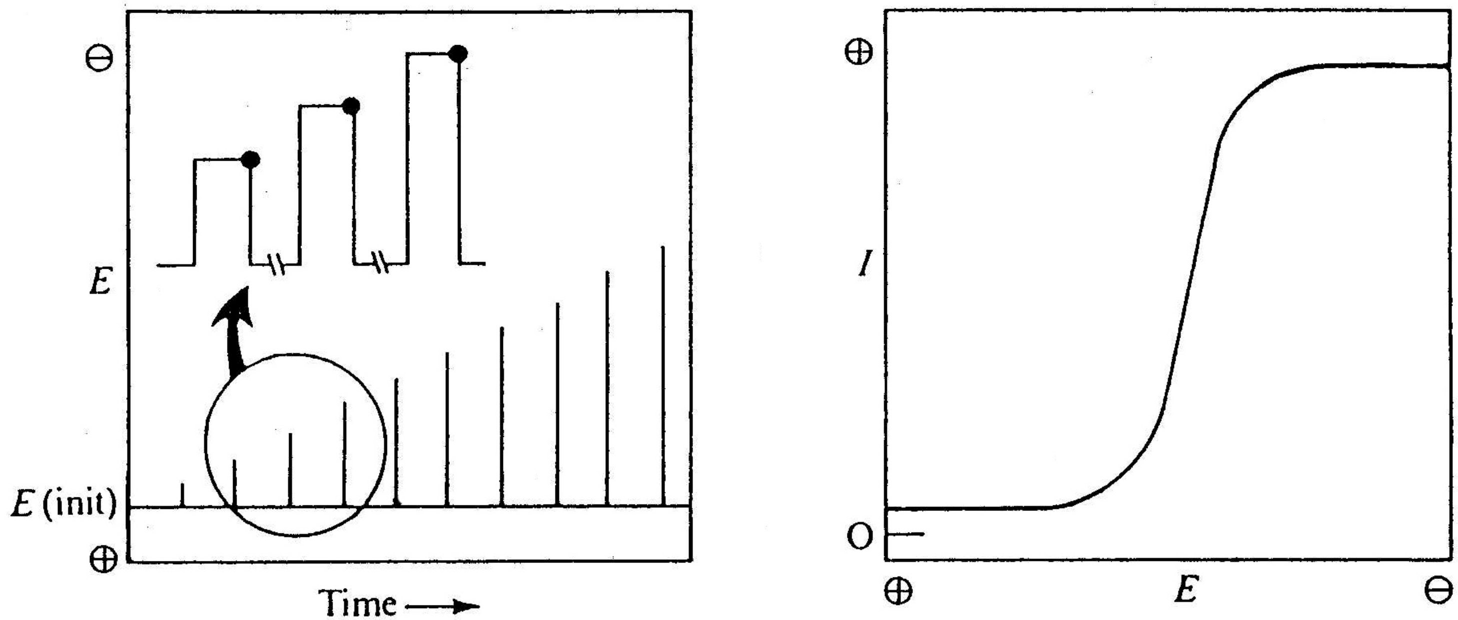
Differential Pulse Polarography

- Most widely practiced variation on polarography
- Constant amplitude pulses on continuously varying potential
- Measure current at

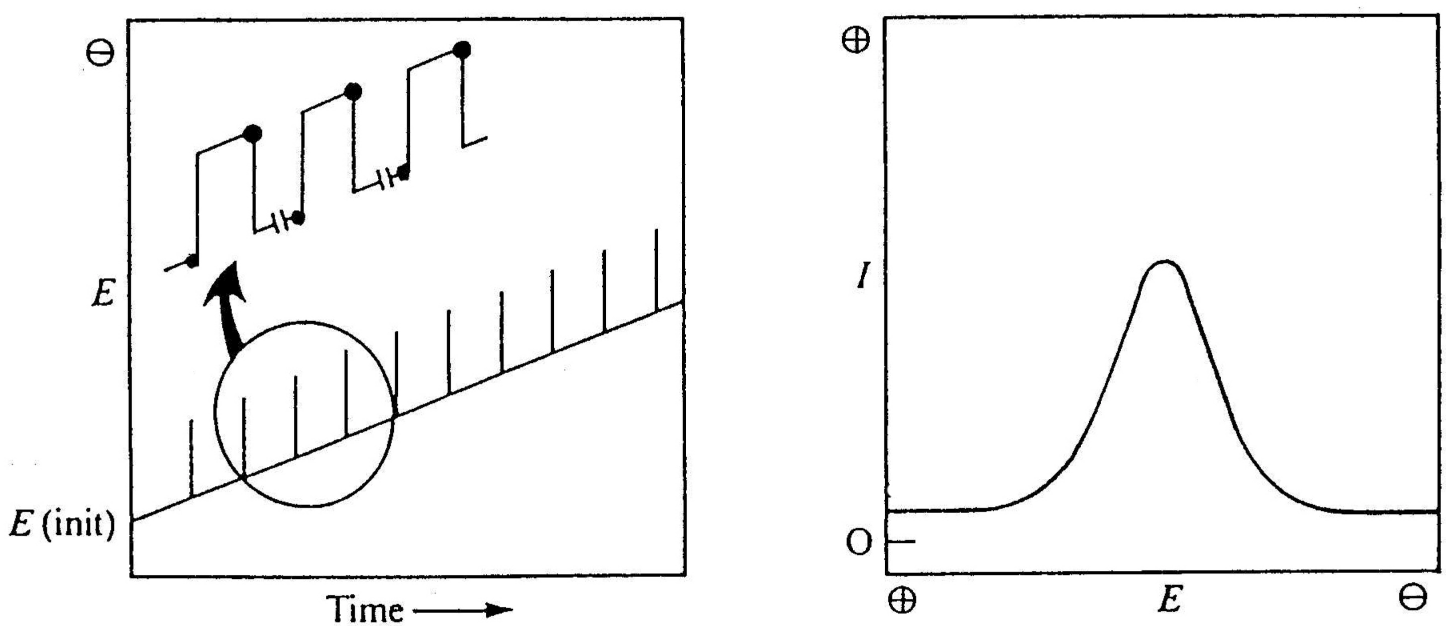
  A & B then subtract

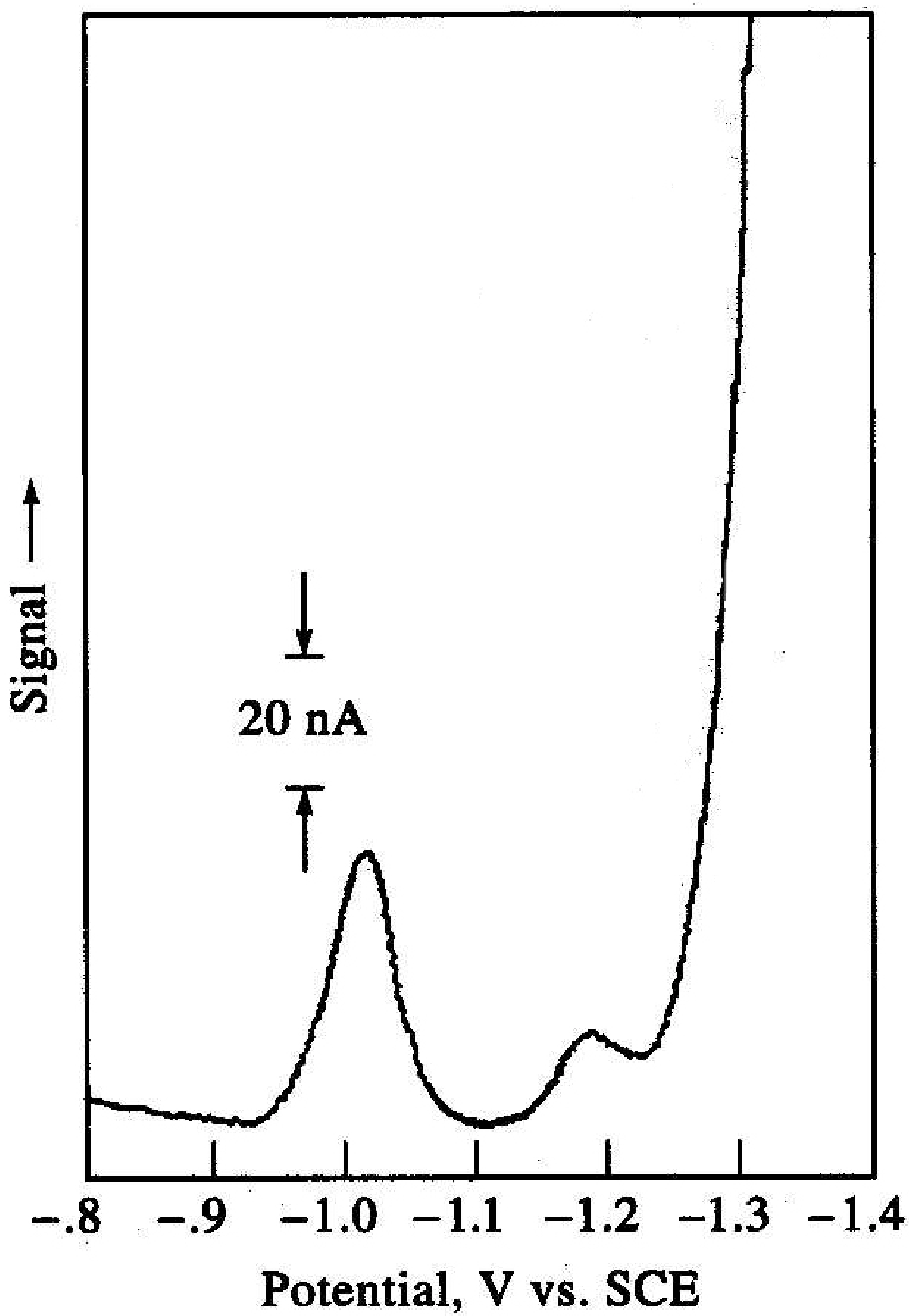


NPP



DPP





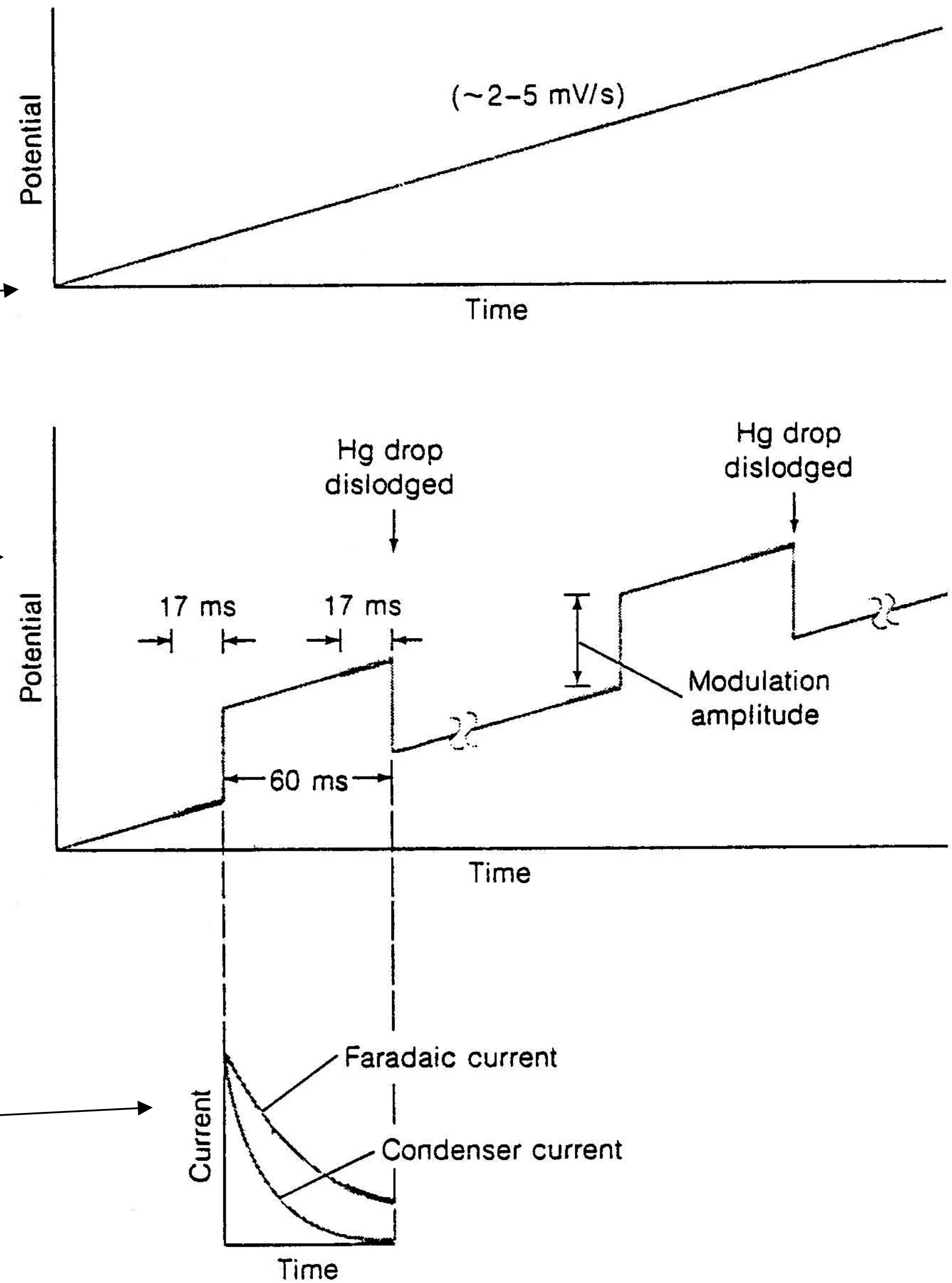
DPP for low concentration sample showing a hint of the steps in the peak

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 $E_{½}$ 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