

February 3, 2012

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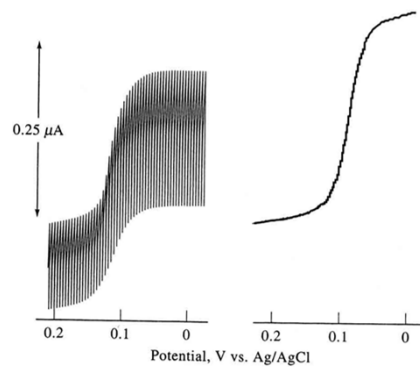
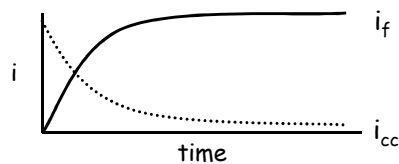
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Current Measurement

- Since current is relatively *constant* late in the drop lifetime, measure current only near the end of the drop lifetime:

• Sampled-dc Polarography:

- Use drop knocker with DME
- Current measured only during final 5 - 10 ms of drop
- Simpler polarogram with *slight* improvement in DL



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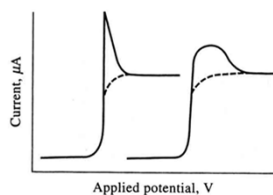
Applications

First, some practical considerations:

■ Purge system of O_2

- O_2 reducible at ~ 0 volts
- Bubble N_2 before analysis to remove O_2
- Keep gentle flow of N_2 over electrode during analysis

■ Add surfactant to solution



e.g., Triton x-100, gelatin
-eliminates current maxima that occur due to surface adsorption effects

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Qualitative Analysis

■ Analyte must be reducible in solution

■ Recall: $E_{\frac{1}{2}} = E^{\circ}$

- IF:
 - system is *electrochemically reversible*
 - no competing reactions (e.g., complex formation)

How do we know if a system is *reversible*?

Electron transfer is *fast* relative to the E_{applied} scan rate

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Confirming Reversibility

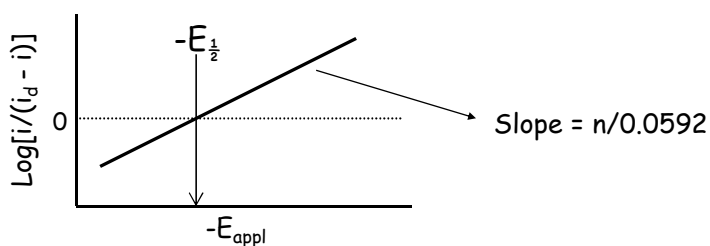
Recall:

$$E_{\text{appl}} = E^{\circ} - (0.0592/n) \text{Log}[i/(i_d - i)]$$

Rearranging:

$$\text{Log}[i/(i_d - i)] = (n/0.0592)(E^{\circ} - E_{\text{appl}})$$

So, a *plot* of $\text{Log}[i/(i_d - i)]$ versus $-E_{\text{appl}}$ should be *linear*:



Quantitative Analysis

■ From Ilkovic equation:

$$i_d = kC$$

usually use method of Standard Additions
(with μL additions, no volume correction needed)

■ Detection Limits: $\sim 10^{-5} - 10^{-6} \text{ M}$ (low ppm)

■ Resolution: $\Delta E_{\frac{1}{2}} \approx 0.2 \text{ v}$ (not very good)

How can DL and resolution be improved?

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Pulse Voltammetry

Recall *initial* shape of current after application of E_{appl} more negative than E° :

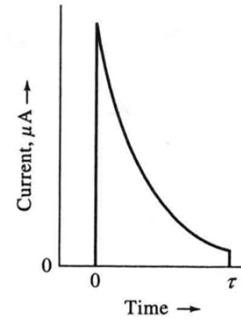
Faradaic Current (i_f) Enhancement

-high concentration of analyte species at electrode surface

Charging Current (i_{cc}) Attenuation

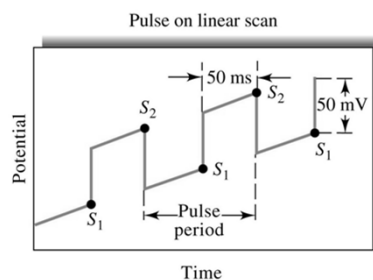
-decays more rapidly than does i_f

So: -Apply short pulse (~50 ms) at E_{appl} near end of drop lifetime
 -Measure current near the end of the pulse
 -*enhanced* i_f and *attenuated* i_{cc} gives S/B enhancement

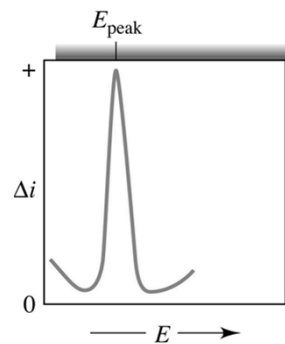


Differential Pulse Voltammetry: Peaks!

- Make a *differential* current measurement to change the shape of the voltammogram:



(a)



$$\bullet \Delta i = S_2 - S_1$$

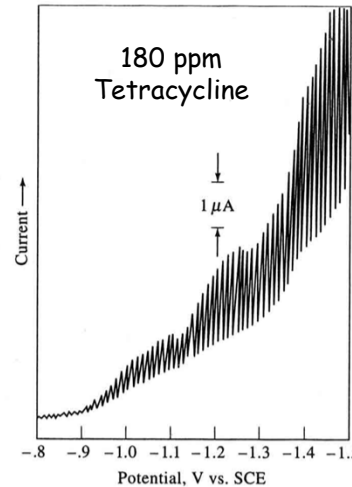
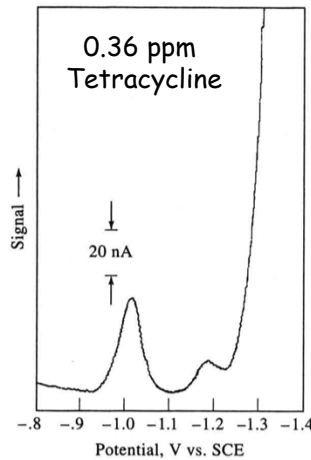
• Plot Δi versus E_{appl}

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Benefits of Differential Pulse Excitation

✓ **Resolution:**
 $\Delta E \approx 50 \text{ mV}$

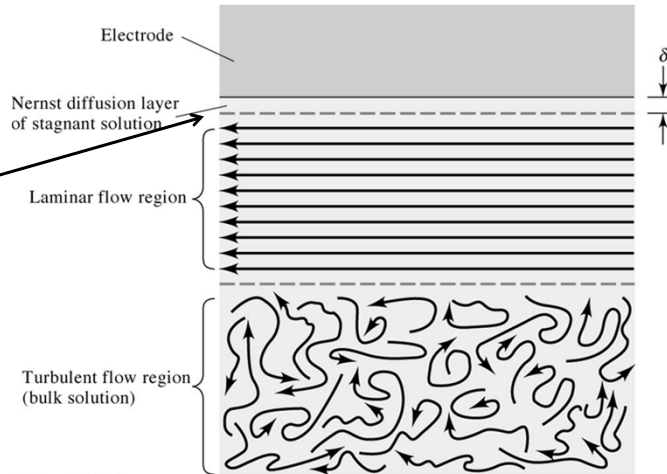
✓ **Det. Limits:**
 $\sim 10^{-8} \text{ M}$



Hydrodynamic Voltammetry

Effects of Stirring:

0.01-0.1 mm



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