

February 11, 2005

➤ **Exam #1:** Wed Feb 16th - See Info page!

➤ **Review Session:**

- Sunday, Feb 13th, 7 pm
- B203 Angell
- Come with questions!

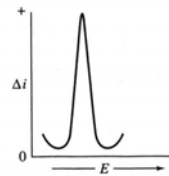
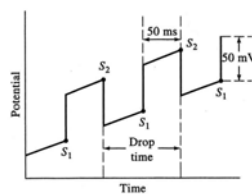
➤ **Office Hours:**

- Modified for today: 3:30 - 4:30 (300 Waterman)

1

Differential Pulse Polarography: Peaks!

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



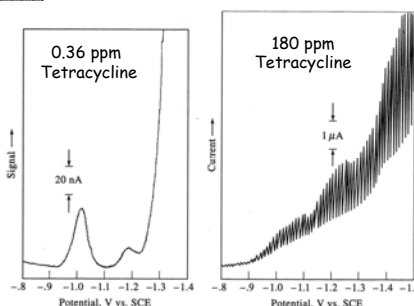
- $\Delta i = S_2 - S_1$
- Plot Δi versus E_{app}

2

Benefits of DPP

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

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



Other EChem Methods

ac Polarography

- superimpose $\pm 5 \text{ mV ac}$ (10 - 50 Hz) potential onto linear sweep
- only measure *ac component* of current
- get a peak for any *reversible* analyte reaction

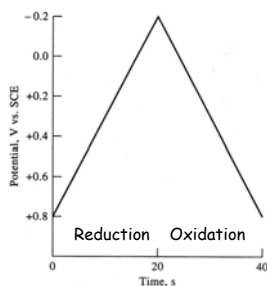
Square-Wave Polarography

- apply an *increasing* square wave potential ramp
- use on a *single Hg drop*
- rapid* sweep (scan 1 volt in <1 second)
- differential current measurement (get a *peak*)

4

Cyclic Voltammetry

- On a single Hg drop (HMDE), apply both an *anodic* and a *cathodic* sweep:



5

A Cyclic Voltammogram

System is *reversible* if:

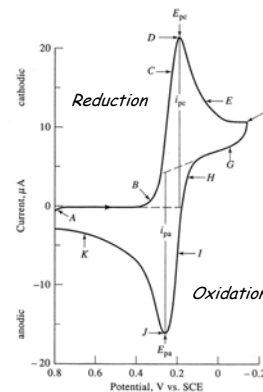
$$\Delta E = 0.0592/n$$

and

$$i_{pc} = i_{pa}$$

Note: $E_{pc} \neq E^{\circ}$

$$E_{pc} = E^{\circ} - 1.1[RT/nF]$$



Stripping Methods: The Ultimate in Detectability

■ Concept:

- *Pre-concentrate* analyte species onto electrode (electrolysis)
- *Strip* reduced species off of electrode and measure current (voltammetry)

■ Requirement:

Reduced analyte must form an *amalgam* with Hg electrode

7

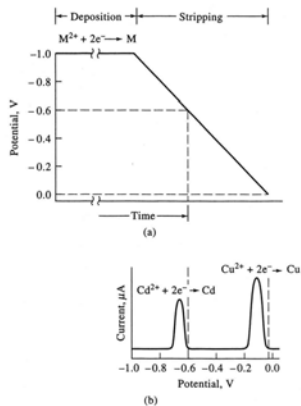
Anodic Stripping Voltammetry (ASV)

- Use a HMDE
- Stir solution and apply potential ~200 mV more negative than E° of analyte
 - Allow reduction to proceed for 5 - 60 minutes
 - Stop electrolysis and stop stirring solution
- ➡ Apply a *slow* ANODIC potential ramp (or DPP)
- ➡ Measure current due to *oxidation of reduced analyte species*

8

ASV: Example

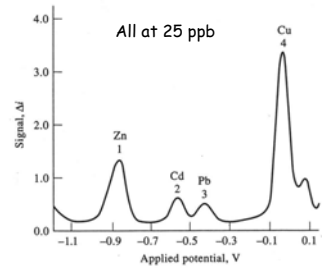
Can you find the mistake?



DPP-ASV: Multi-Component Ultra-Trace Analysis

-all components must be able to form an *amalgam* with Hg
(about 15 - 20 elements can)

-Detection limits can be as low as $10^{-9} M$



..