

CHEM 221
Instrumental Analysis
EXAM #1

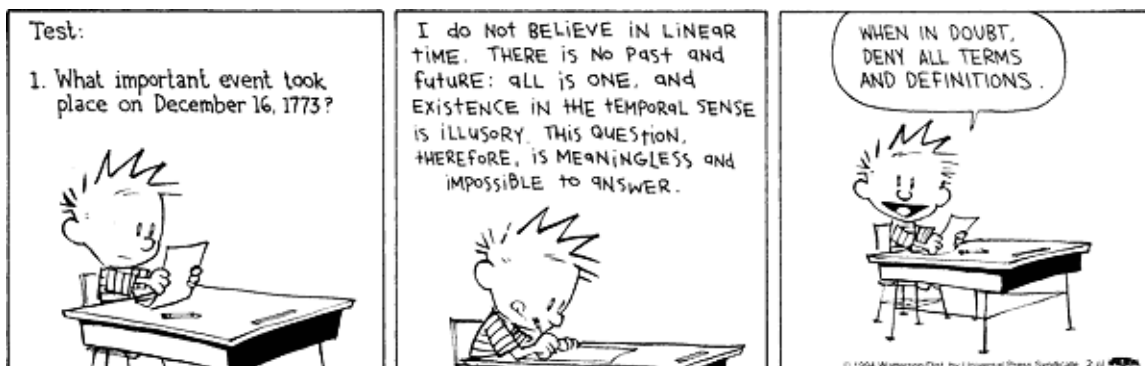
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Name: Saul Lusions

INSTRUCTIONS: Read through the entire exam before you begin. Answer all of the questions. For questions involving calculations, show **all** of your work -- **HOW** you arrived at a particular answer is **MORE** important than the answer itself!

The entire exam is worth a total of 200 points. Attached are a periodic table and a formula sheet jam-packed with useful stuff!

Good Luck!



1. **a. (20 pts)** You've just set up your first GC experiment in the lab and decide to use the fanciest and fastest oscilloscope for recording your first chromatogram. This oscilloscope has a frequency response of 10 MHz and allows you to store the digitized output signal on a computer in the lab. Your chromatogram takes about 1 minute to run, but the signal that you observe on the 'scope is VERY noisy. You save it anyway and show it to one of your more experienced labmates, who suggests that you replace the 'scope with an old strip chart recorder. Skeptical, you reluctantly do so and, to your surprise, find that the resulting chromatogram has a far superior signal to noise ratio (S/N) than the one obtained using the 'scope. **Estimate the magnitude of the S/N improvement and identify the type of noise that was reduced.**

- Digital 'scope has a $\Delta f = 10^7$ Hz; strip chart recorder has $\Delta f \sim 10^0$ Hz
- 60-second chromatogram signal is easily measured by SCR PLUS it will exclude any noise at freq > 1 Hz
- So: Δf is reduced by 10^7
- And: Noise $\propto (\Delta f)^{1/2}$
- THUS: Noise decreases by a factor of $(10^7)^{1/2} = 3.16 \times 10^3$
- Since signal is unchanged: S/N increases by $\boxed{3.16 \times 10^3 \times}$

b. (15 pts) Four years have passed and you are beginning to write up your Ph.D. dissertation. Alas, the first chromatogram that you recorded on that expensive oscilloscope is your only chromatographic record (the original strip chart trace having been lost years ago) demonstrating the presence of a toxic impurity in a commonly used surgical anesthetic (a discovery that has become the focus and subject of your research and has saved countless lives). The peak corresponding to this trace impurity is, unfortunately, buried in the noise of the 'scope record of the chromatogram (see figure on the next page). **Is the peak corresponding to this trace impurity above the limit of detection (i.e., does it have a S/N of at least 3)?** (You must show your work to receive credit for your answer.)

From the figure:

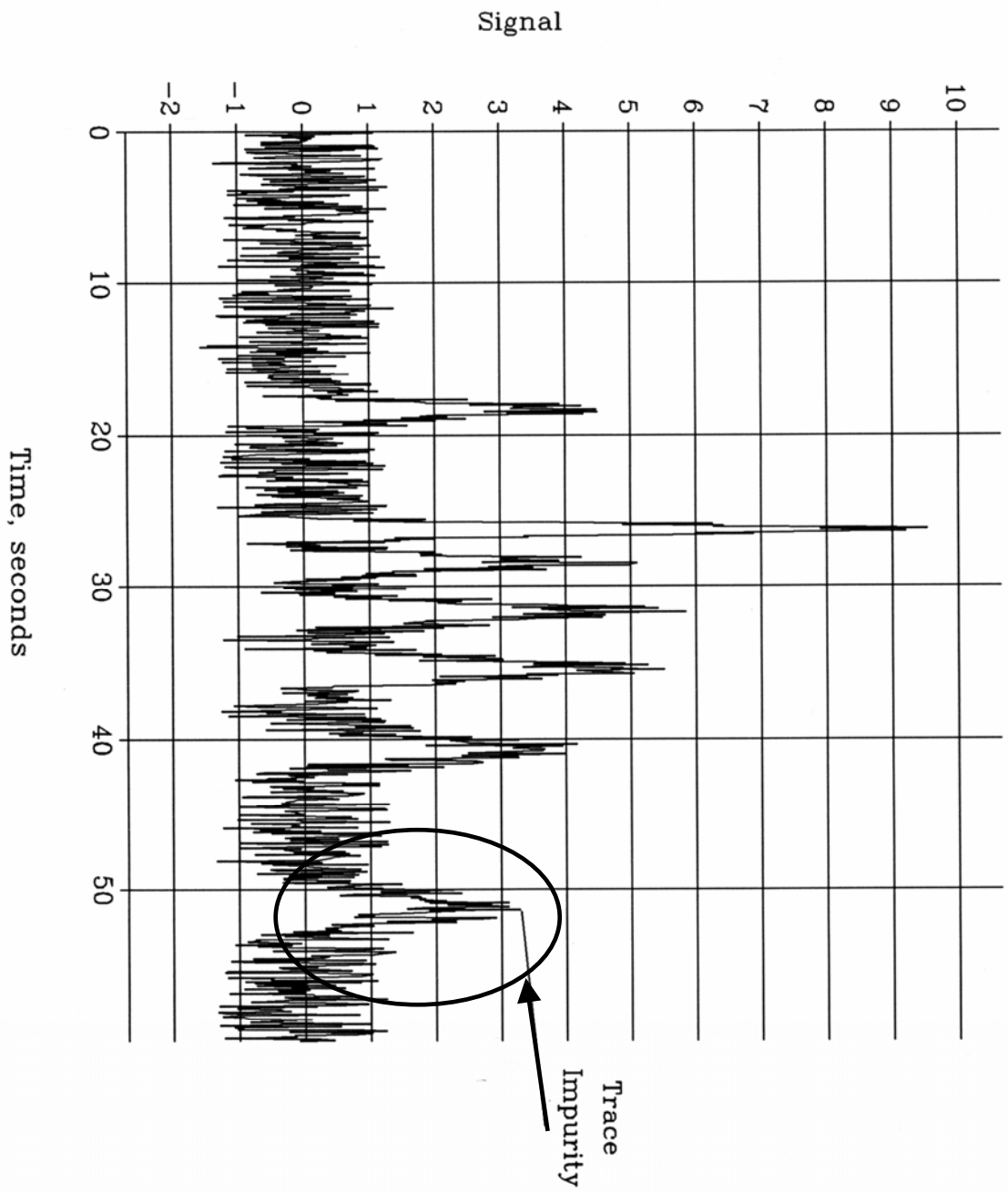
$$S_{\text{avg}} = 2.0$$

$$\Delta S = 2.6 = 5\sigma = 5N$$

$$\text{So: } N = 2.6/5 = 0.52$$

$$\text{Thus: } S/N = 2.0/0.52 = 3.85 \approx \underline{4}$$

(>3 , so yes it is above the detection limit)



2. You are working in an environmental analysis lab and focusing on the determination of dioxin (2,3,7,8-TCDD) in contaminated water samples. Five replicates are run of the first sample and the following are data (averages and standard deviations) obtained for the 2,3,7,8-TCDD peak:

Blank: avg=0.002, std dev=0.001

Sample: avg=0.003, std dev=0.001

a. [20 pts] Based on the average signal obtained for the sample, you determine from your standard calibration plot that the water sample contains 2.0 ppb of 2,3,7,8-TCDD. Your supervisor, after looking at the data, says that there is no detectable amount of 2,3,7,8-TCDD in the sample. Who is right and why? (NOTE: your response should be based on the above data. HINT: you may wish to calculate the S/N for the sample data.)

Let's calculate the S/N for this determination - if $S/N > 3$, then the TCDD is, indeed, detectable in the sample:

$$\text{Signal} = X_{\text{avg}} (\text{Sample}) - X_{\text{avg}} (\text{blank}) = 0.003 - 0.002 = 0.001$$

$$\text{Noise} = \text{std dev} = 0.001$$

$$\text{So, } S/N = 0.001/0.001 = 1 < 3$$

Thus, there is no detectable amount of TCDD in the sample (supervisor is correct!).

b. [15 pts] If a 20.0 ppb 2,3,7,8-TCDD standard gave an average signal of 0.022, what would the detection limit (ppb 2,3,7,8-TCDD) be for the determination of 2,3,7,8-TCDD using this instrument?

With one calibration point at 20.0 ppb TCDD, we can assume that there is a linear relationship between signal and concentration between this point and the detection limit. The easiest way to calculate the DL is to ratio the S/N for the 20.0 ppb standard to the S/N at the detection limit ($S/N = 3$).

$$20.0 \text{ ppb } S/N: \frac{\text{Signal}}{\text{Noise}} = \frac{0.022 - 0.002}{0.001} = \frac{0.020}{0.001} = 20.$$

$$\text{Thus: } \frac{20.0 \text{ ppb}}{\text{DL}} = \frac{20.}{3.0} \Rightarrow \text{DL} = \boxed{3.0 \text{ ppb TCDD}}$$

c. [15 pts] After 3 years of hard work in the lab, you finally have an entire weekend (48 hours) to obtain a spectrum of the reaction mixture that can definitively determine whether the reaction mechanism you've proposed in your dissertation research is correct. You watch the first spectrum pop up on the display and find that the critical spectral feature is buried in the background noise of the spectrum. If, after signal averaging 100 spectra, the S/N for this feature is 0.5, calculate the S/N for this spectral feature after signal averaging the spectrum for the entire weekend (48 hours). Assume that it takes 1 minute to scan a single spectrum.

$$\text{S/N after 100 scans} = 0.5$$

$$\text{So: } (S/N)_{n=100} = (100)^{1/2} (S/N)_{n=1} = 0.5$$

$$(S/N)_{n=1} = 0.05$$

At 1 scans/min, in 48 hours:

$$48 \text{ hours} \times \frac{60 \text{ min}}{1 \text{ hour}} \times \frac{1 \text{ scan}}{\text{min}} = 2.880 \times 10^3 \text{ scans}$$

So, what is S/N after 2.880×10^3 scans?

$$(S/N)_n = n^{1/2}(S/N)_{n=1}$$

$$(S/N)_n = (2.880 \times 10^3)^{1/2}(0.05)$$

$$(S/N)_n = (53.6656)(0.05)$$

$$(S/N)_n = 2.68328 \approx \boxed{2.7}$$

d. [15 pts] Alas, you find that the *actual* S/N of the feature after signal averaging for the weekend is LESS than you predicted, above. Explain and identify the likely noise source that would account for this discrepancy.

Signal averaging over a 2-day period of time introduces the possibility of *drift* or other low-frequency sources of noise - if the S/N was less than predicted, it may very likely be due to the $1/f$ (flicker) noise, which is most significant at low frequencies.

3. **QUICKIES (10 points each) - No more than 2 sentences!**

a. List the two most critical experimental conditions which ensure that diffusion is the only mass transport mechanism operative in a voltammetric experiment – specify the mass transport processes that these two conditions eliminate.

1) **Do not stir the solution** – this ensures that physical mass transport of fresh oxidized species to the electrode surface does not occur.

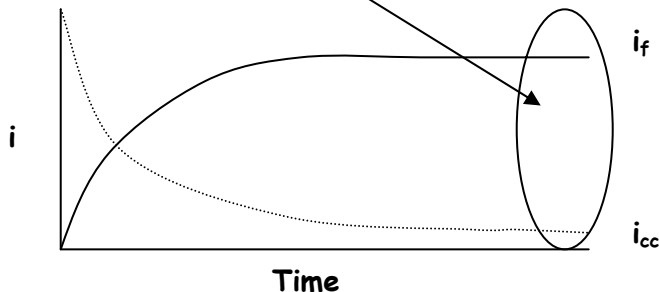
2) **Add bulk electrolyte (e.g., 0.1 M KCl) to the solution** – by flooding the solution with ions, the electrostatic attraction between the electrode and the analyte ions in solution is buffered throughout the ions introduced into solution by the electrolyte. Thus, mass transport due to electrostatic attraction of the oxidized species to the electrode is eliminated.

b. Briefly describe the origin of the residual or background current in a polarographic experiment.

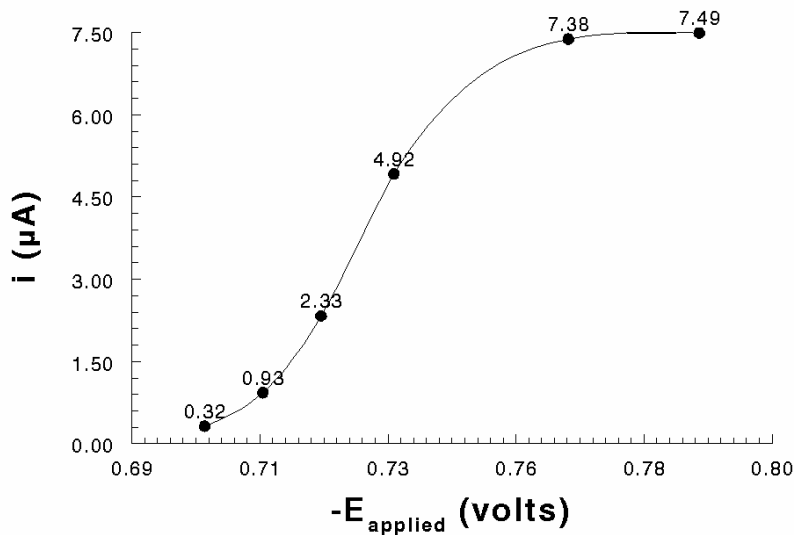
The residual current is the current that flows when there is no species in solution that can undergo an electron-transfer reaction, like reduction. The origin of the residual current flow can be explained by considering the solution ion structure near the surface of the electrode. If the electrode has a positive charge on it, then the negatively charged ions will be the primary layer closest to the electrode, followed by a more diffuse layer of positively charged ions, etc. *The charge separation near the electrode surface acts like a small capacitor and a small current flows to charge that capacitor – this small charging current is the residual or background current that is recorded.*

c. In sampled-DC polarography, why is the current measured only during the final 10 ms of the Hg drop "lifetime"? (HINT: A plot showing current as a function of time over the lifetime of the Hg drop could be helpful here!)

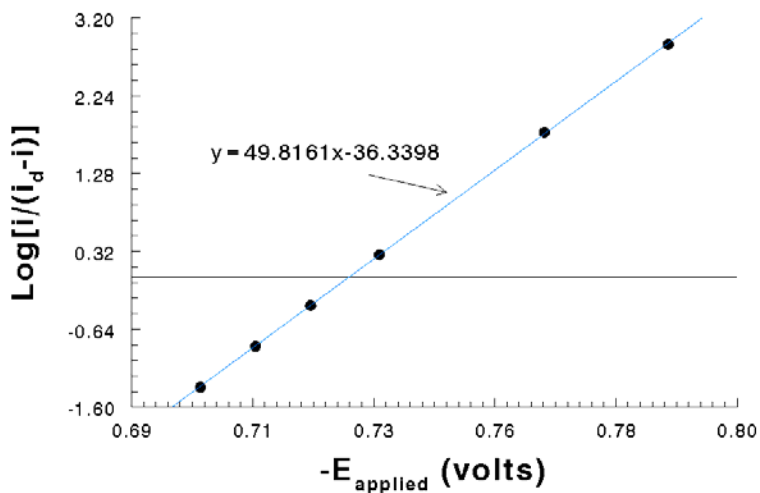
By waiting until the final 10 ms of the drop, i_f (signal) is maximized, while i_{cc} (background) is minimized: gives best S/B



4. A current-sampled DC polarogram of an unknown substance containing either Zn or Cr was acquired and found to have a limiting current of $7.50 \mu\text{A}$. From the rising portion of the polarographic wave, the following data were plotted (current values are indicated on the plot):



Further processing of these data produced the following plot (the equation given is from a linear least squares analysis of the data):



- a. **[20 pts]** From the data provided, determine E° for the reduction (indicate how you determined E° and any assumptions implicit in that determination).

Since the plot of $\text{Log}[i/i_d - i]$ versus $-E_{\text{appl}}$ is linear, the system is *reversible*.

For a reversible system, $E^\circ = E_{1/2}$ which occurs when $i = i_d/2$

If we set $i = i_d/2$, then $\text{Log}[i/i_d - i] = 0$, so we can solve the linear least squares equation for x when $y=0$ to get the value of E° :

$$\begin{aligned} y &= 49.8161x - 36.3398 = 0 \\ 49.8161x &= 36.3398 \\ x &= \frac{36.3398}{49.8161} = 0.7294790 = -E_{\text{appl}} \end{aligned}$$

So: $E^\circ = -0.729 \text{ volts}$

- b. **[15 pts]** Both the reduction of Zn^{2+} to Zn as well as the reduction of Cr^{3+} to Cr have the same E° (and it's equal to the value that you determined in *part a*, above). Based on the data provided, is the reduction wave due to Zn^{2+} or Cr^{3+} ?

We need to determine the number of electrons transferred per mole (n) which we can get from the *slope* of the plot:

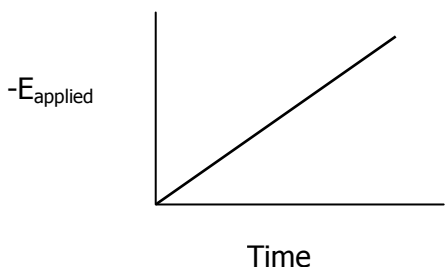
$$\text{slope} = n/0.0592$$

$$n = \text{slope} \times 0.0592 = 49.8161(0.0592) = 2.95 \approx 3$$

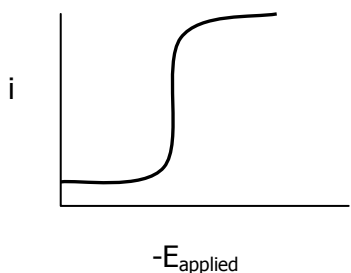
Since $n=2$ for Zn^{2+} to Zn and $n=3$ for Cr^{3+} to Cr, the reduction must be due to: Cr

- c. **[25 pts]** Describe how a differential pulsed polarographic experiment (DPP) differs from the sampled-DC polarographic measurements described above (i.e., show how the applied potential versus time curves differ; show how the resultant polarograms differ).

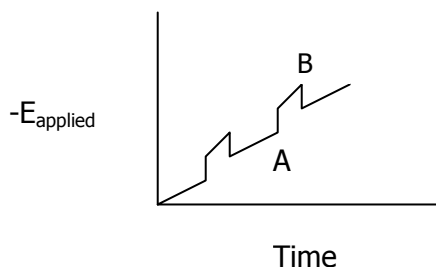
Sampled-dc



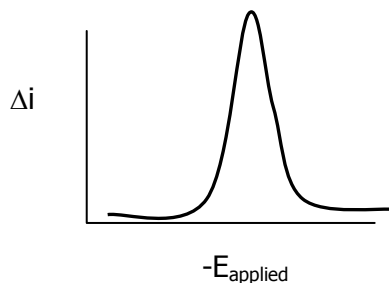
Measure current only during last 10 ms of drop lifetime.



DPP



Measure current at pts B and A; plot the difference



- d. **[10 pts]** Based on your response to *part c* (above), briefly explain why *selectivity* (i.e., *resolution*) using DPP is much better than selectivity obtained using sampled-DC polarography.

By making a *differential* measurement, the shape of the reduction wave on a DPP polarogram is a *peak* rather than an *inflection point*. This improves the *resolution* possible, thus improving the *selectivity* of the method.