

CHEM 221
Instrumental Analysis
EXAM #1

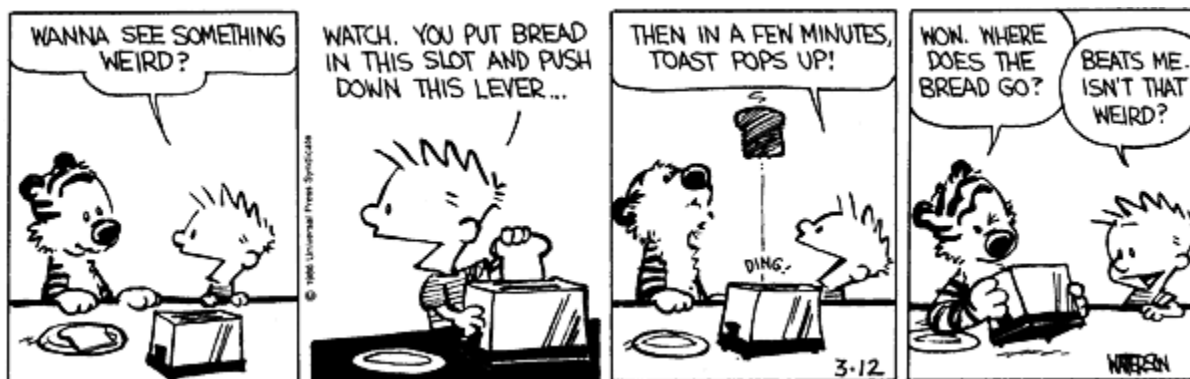
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INSTRUCTIONS: Read through the entire exam before you begin. Answer all of the questions. For questions involving calculations, show **all** of your work -- **HOW** you arrived at a particular answer is **MORE** important than the answer itself!

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. You are working in an environmental analysis lab and focusing on the determination of hexavalent chromium (Cr(VI)) in drinking water samples. Five replicates are run of the first sample and the following are data (averages and standard deviations) obtained for the Cr(VI) signal:

Blank: avg=0.03, std dev=0.01

Sample: avg=0.05, std dev=0.01

- a. [20 pts] Based on the average signal obtained for the sample, you determine from your standard calibration plot that the water sample contains 0.5 ppb of Cr(VI), *five times* the MCL (Maximum Contamination Limit) proposed in California for Cr(VI) in drinking water!. Your supervisor, after looking at the data, says that there is no detectable amount of Cr(VI) 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 Cr(VI) is, indeed, detectable in the sample:

$$\text{Signal} = X_{\text{avg}}(\text{Sample}) - X_{\text{avg}}(\text{blank}) = 0.05 - 0.03 = 0.02$$

$$\text{Noise} = \text{std dev} = 0.01$$

$$\text{So, } S/N = 0.02/0.01 = 2 < 3$$

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

- b. [15 pts] If a 10.0 ppb Cr(VI) standard gave an average signal of 0.43, what would the detection limit (ppb Cr(VI)) be for the determination of Cr(VI) using this instrument?

With one calibration point at 10.0 ppb Cr(VI), 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 10.0 ppb standard to the S/N at the detection limit (S/N = 3).

$$10.0 \text{ ppb } S/N: \frac{\text{Signal}}{\text{Noise}} = \frac{0.43 - 0.03}{0.01} = \frac{0.40}{0.01} = 40.$$

$$\text{Thus: } \frac{10.0 \text{ ppb}}{\text{DL}} = \frac{40}{3.0} \Rightarrow \text{DL} = \frac{0.75 \text{ ppb Cr(VI)}}{1}$$

2. [20 pts] Losing weight was on my list of New Year's resolutions and I received, as a present, a new scale! And just in time as my new diet (errr, I mean "lifestyle change") should result in my losing *exactly* 1.0 pounds/week. My old digital scale had a readout standard deviation of 0.5 pounds, but my new digital scale has a readout standard deviation of just 0.1 pounds. Being obsessed with losing weight, I weigh myself every day and then use a spreadsheet to track my progress. If we assume that I lose weight at a constant rate throughout the week (for a total of 1.0 pounds every 7 days), after how many days of weighings on each of these scales could I conclusively state that I have lost weight? (HINT: what is the smallest change in my weight that is detectable with each scale?)

The measurement std dev for each scale is the noise for each measurement, so the smallest detectable change in signal must be an amount equal to THREE times the noise (for a S/N=3):

$$\text{Old Scale: } 0.5 \times 3 = 1.5 \text{ lbs; New Scale: } 0.1 \times 3 = 0.3 \text{ lbs.}$$

Old Scale: 1.5 lbs x 7 days/lb = 10.5 days - on the 11th Day weight loss would be detected

New Scale: 0.3 lbs x 7 days/pound = 2.1 days - on the 3rd Day weight loss would be detected

3. a. [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 55 spectra, the S/N for this feature is 0.70, calculate the S/N for this spectral feature after signal averaging the spectrum for the entire weekend (48 hours). Assume that it takes 2.0 minutes to scan a single spectrum.

$$\text{S/N after 55 scans} = 0.70$$

$$\text{So: } (S/N)_{n=55} = (55)^{1/2} (S/N)_{n=1} = 0.70$$

$$(S/N)_{n=1} = 0.09439$$

At 2 min/scan, in 48 hours:

$$48 \text{ hours} \times \frac{60 \text{ min}}{1 \text{ hour}} \times \frac{1 \text{ scan}}{2 \text{ min}} = 1.440 \times 10^3 \text{ scans}$$

So, what is S/N after 1.440×10^3 scans?

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

$$(S/N)_n = (1.440 \times 10^3)^{1/2} (0.09439)$$

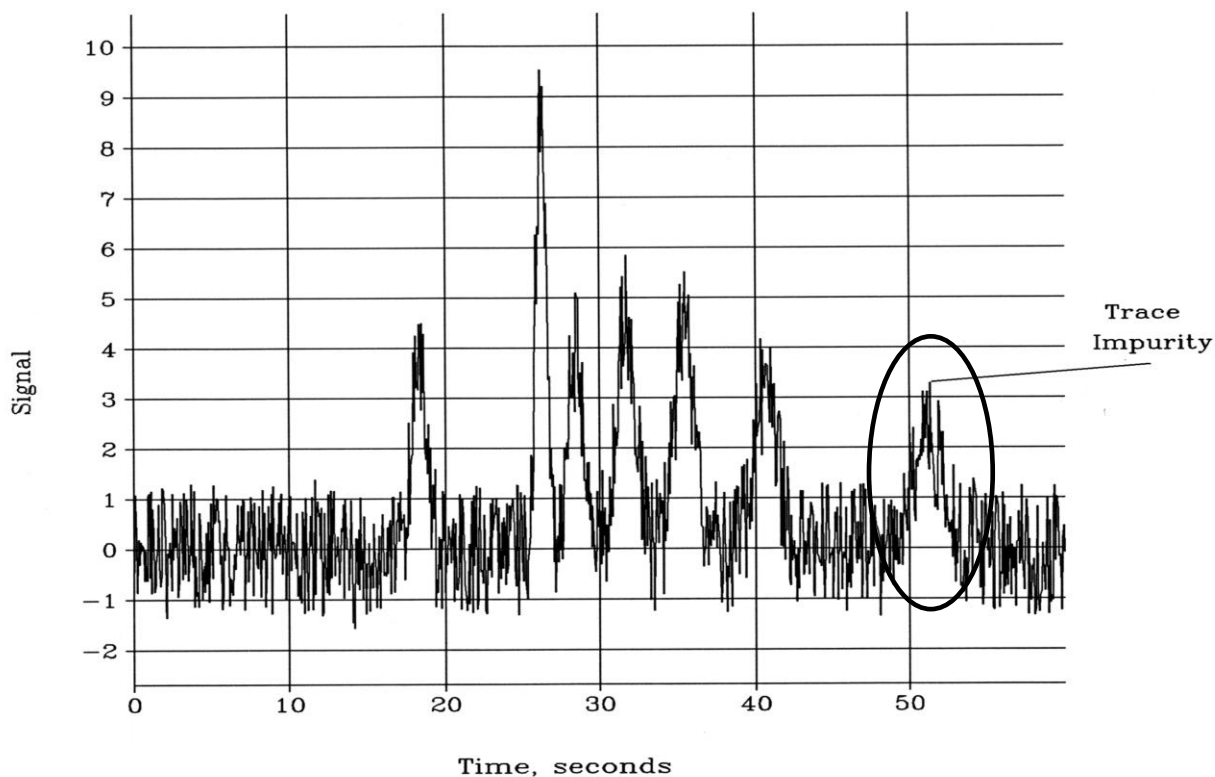
$$(S/N)_n (37.9473)(0.09439)$$

$$(S/N)_n = 3.582 = \boxed{3.6}$$

b. [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. The following chromatogram was the result of your very first experiment performed as part of your Ph.D. research:



- a. [15 pts] Calculate and then report an estimate of the S/N for the peak eluting just after 50 seconds (marked "trace impurity").

From the figure:

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

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

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

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

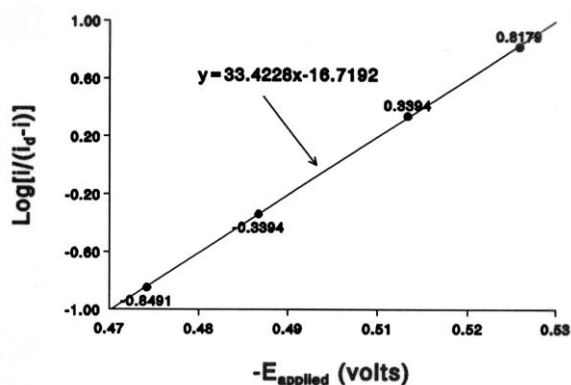
- b. [10 pts] Could signal averaging ("ensemble averaging") be used to improve the S/N of the chromatogram? Briefly explain why or why not.

It *could* be tried, but it is unlikely that it would improve S/N as expected. Why? First: synchronization. The success of ensemble averaging requires that each "ensemble" to be averaged (in this case: a chromatogram), be as perfectly superimposable upon each replicate as possible. There is too much variation from chromatogram to chromatogram in the timing of the compounds eluting - those temporal variations will lead to reductions in both resolution and in any S/N benefits. Second: time. If each chromatogram takes a minute to record, and are not easily replicable, then other variations will be more significant than those that could be addressed by ensemble averaging. It is likely that the injection-to-injection variations will be more significant than the random variations within a chromatogram that ensemble averaging would address.

4. A current-sampled dc polarogram of an unknown solution containing either Cd or Cr was acquired and found to have a limiting current of 5.00 μA . From the rising portion of the polarographic wave, the following data were obtained:

E(applied), volts	Current, μA
-0.475	0.62
-0.490	1.57
-0.510	3.43
-0.525	4.38

Further processing of these data produced the following plot, with the included linear least squares fit to the data:



- a. [15 pts] From the data and plot provided above, determine the value of E° for the reduction – you must show how you determined E° and any assumption implicit in that determination in order to receive credit for your answer.

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° :

$$y = 33.4228x - 16.7192 = 0$$

$$33.4228x = 16.7192$$

$$x = \frac{16.7192}{33.4228} = 0.5002333 = -E_{\text{appl}}$$

So: $E^\circ = -0.500 \text{ volts}$

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

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

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

$$n = \text{slope} \times 0.0592 = 33.4228(0.0592) = 1.98 \approx 2$$

Since $n=1$ for Cr^{3+} to Cr^{2+} and $n=2$ for Cd^{2+} to Cd, the reduction must be due to: Cd

5. **EChem QUICKIES (20 points each)**

a. Explain why differential pulsed polarography (DPP) gives superior detection limits to sampled-dc polarography.

-Pulsing E_{appl} enhances the Faradaic current (i_f) more than it enhances the charging current (i_{cc}), giving improved S/B.

-Differential measurement reduces i_{cc} further by subtracting out background nearly simultaneously with signal measurement (giving even better S/B).

b. Explain how diffusion-controlled mass transport of oxidized species to the electrode surface is ensured in hydrodynamic voltammetry, even though the solution is stirred.

In the bulk solution, flow is turbulent, but as you approach the surface of a planar electrode, the flow becomes highly structured (Laminar Flow). This results in a very narrow region nearest the electrode surface that is stagnant (no flow - as though the solution were not stirred at all). This stagnant region is called the Nernst Diffusion Region and is about 10-100 μm thick. Mass transport from the bulk (stirred) solution, then, occurs by diffusion from the Laminar Flow Region to the electrode surface through the Nernst Diffusion Region (due to the concentration gradient - the concentration of oxidized species is that of the bulk concentration in the Laminar Flow Region, and is near zero at the electrode surface when the applied potential is negative of the standard reduction potential of the analyte).

c. Briefly describe the origin of the residual or background current in a voltammetric 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.*