

CHEM 221
Instrumental Analysis
EXAM #1

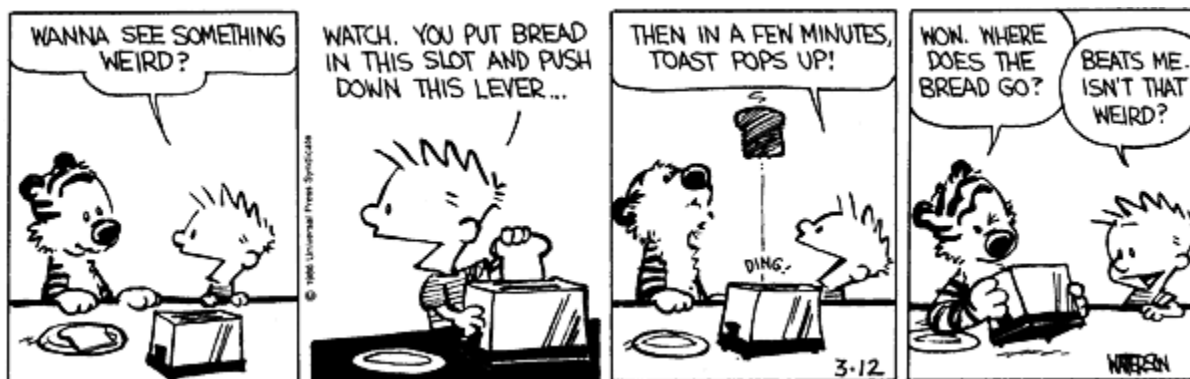
February 16, 2011

Name: _____

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.)

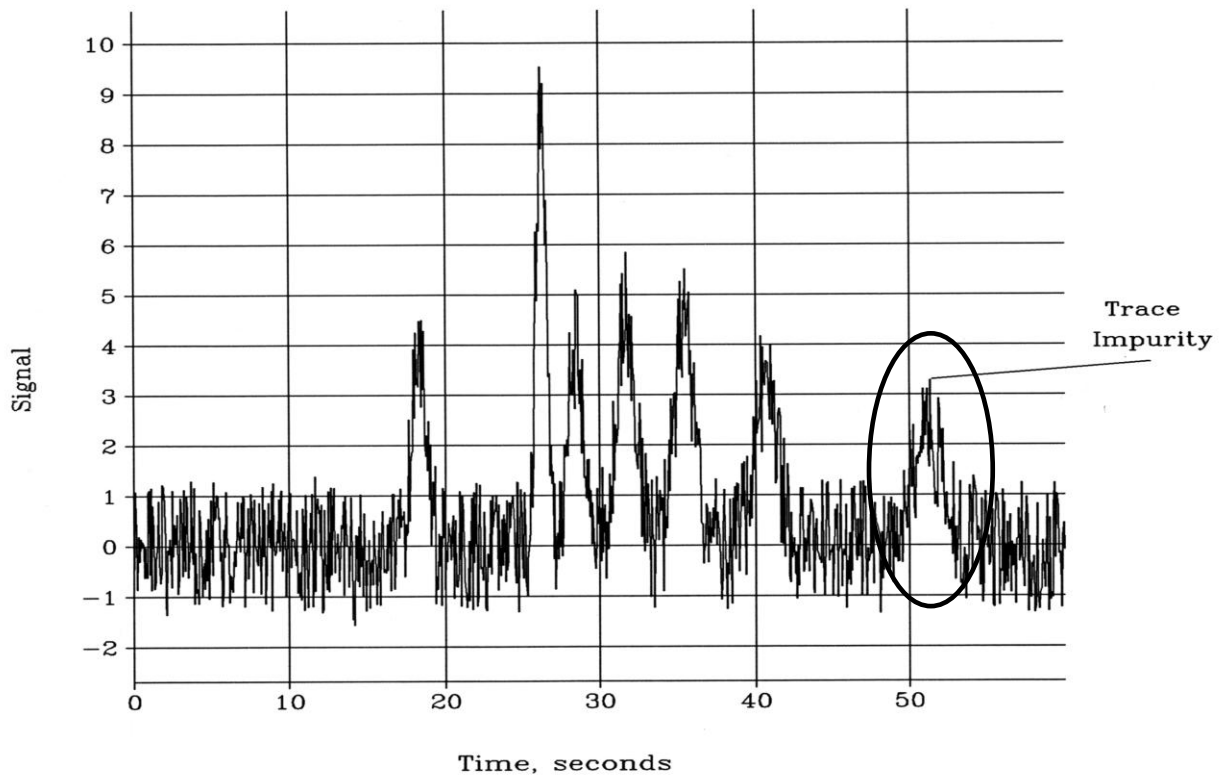
b. **[15 pts]** If a 10.0 ppb Cr(VI) standard gave an average signal of 0.43, what would the detection limit (ppb Cr(VI)) be for the determination of Cr(VI) using this instrument?

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?)

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.

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.

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



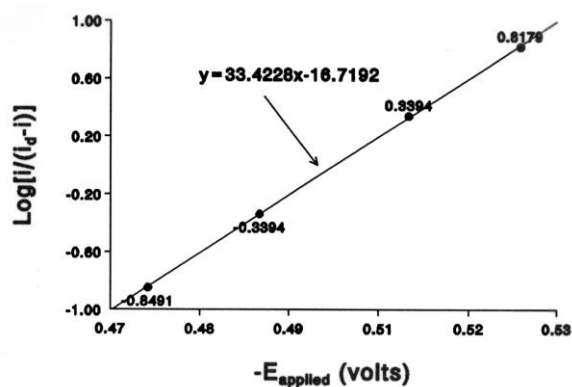
- a. **[15 pts]** Calculate and then report an estimate of the S/N for the peak eluting just after 50 seconds (marked "trace impurity").

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

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.

- 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+} ?

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

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

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.

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