

**CHEM 221**  
Instrumental Analysis  
**EXAM #1**

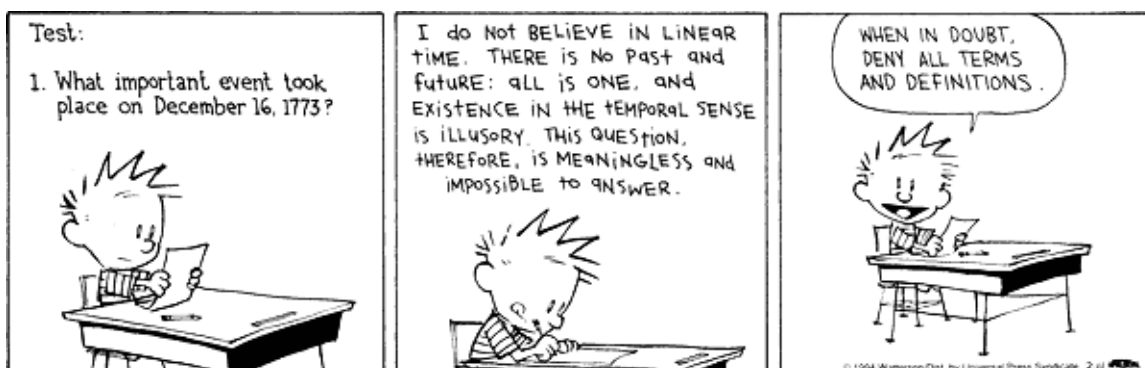
February 16, 2005

**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!

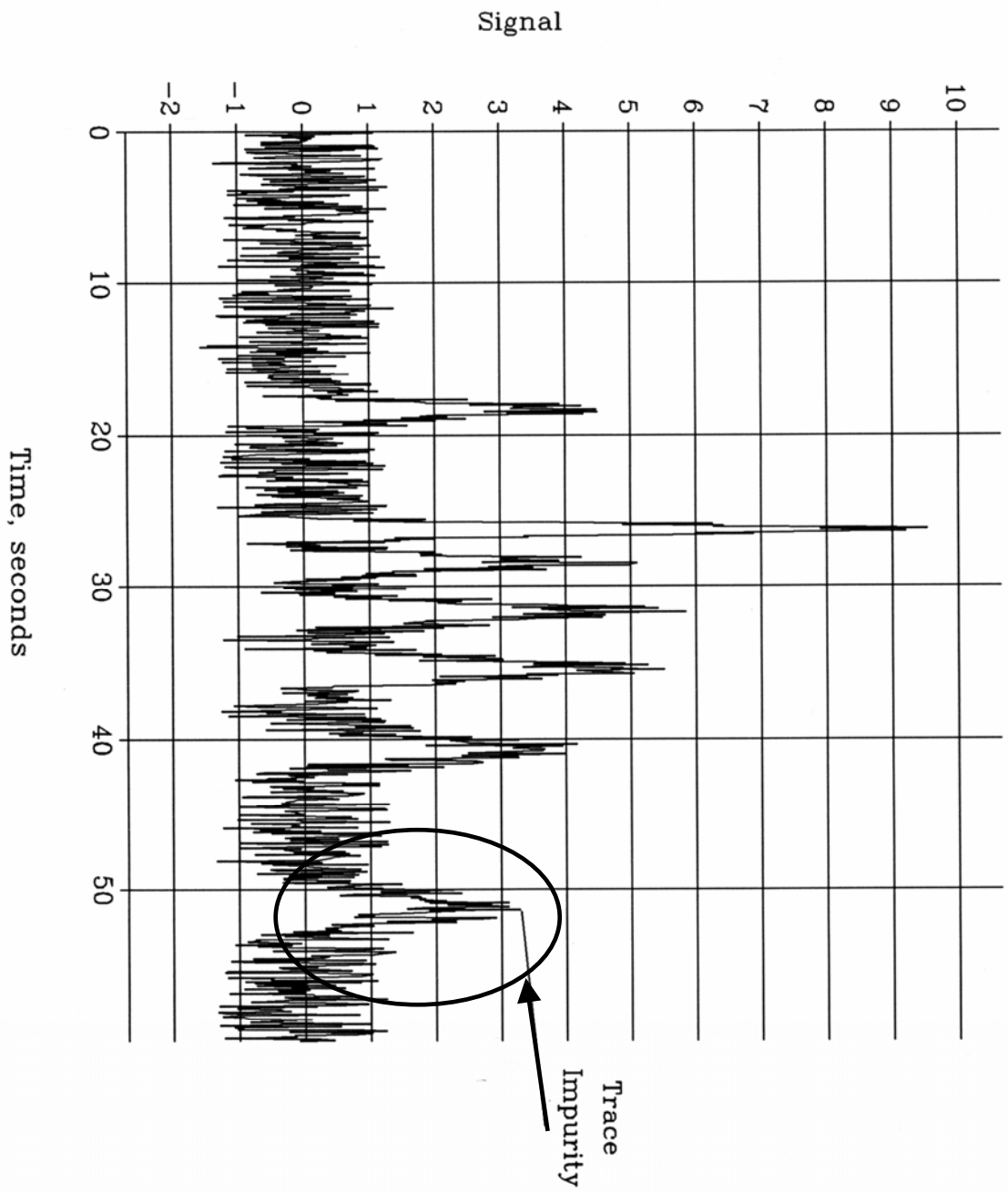
The entire exam is worth a total of 200 points. Attached are a periodic table and a formula sheet jam-packed with useful stuff!

*Good Luck!*



1. **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.**

**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.)



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.)

**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?

**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.

**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.

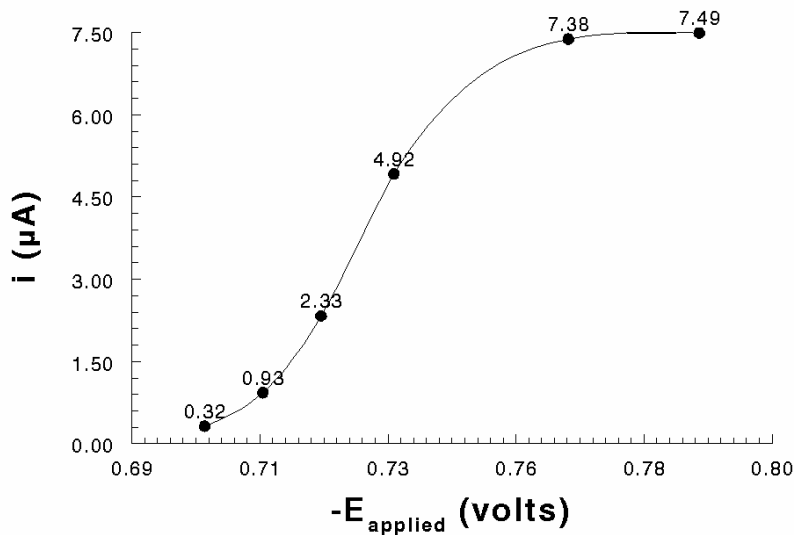
3. **QUICKIES (10 points each) - No more than 2 sentences!**

**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.

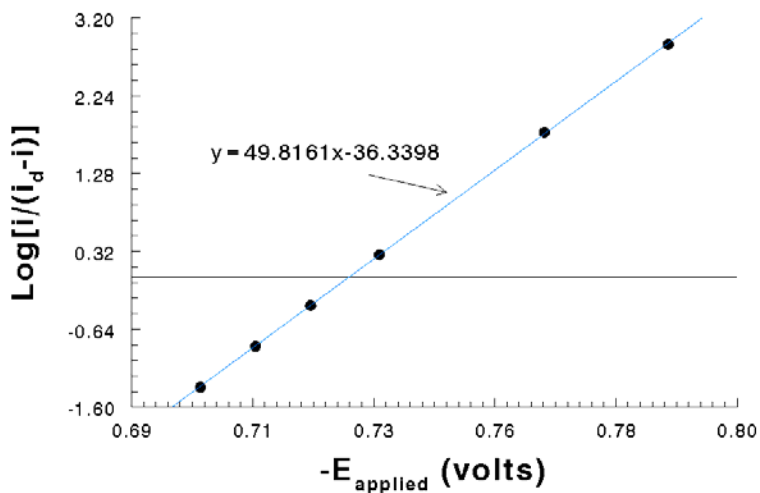
**b.** Briefly describe the origin of the residual or background current in a polarographic experiment.

**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!)

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  $E^\circ$  for the reduction (indicate how you determined  $E^\circ$  and any assumptions implicit in that determination).

b. **[15 pts]** Both the reduction of  $Zn^{2+}$  to Zn as well as the reduction of  $Cr^{3+}$  to Cr have the same  $E^\circ$  (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  $Cr^{3+}$ ?

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).

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.