CHEM 221

Instrumental Analysis

FINAL EXAM

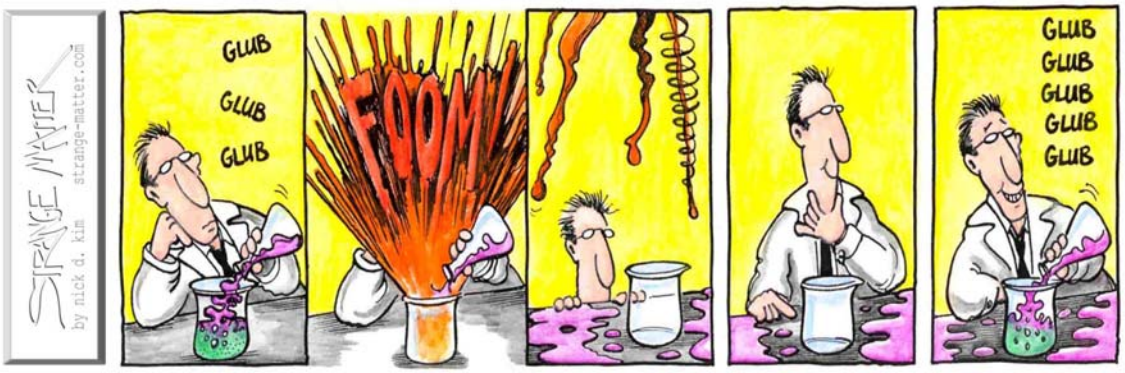
May 10, 2005

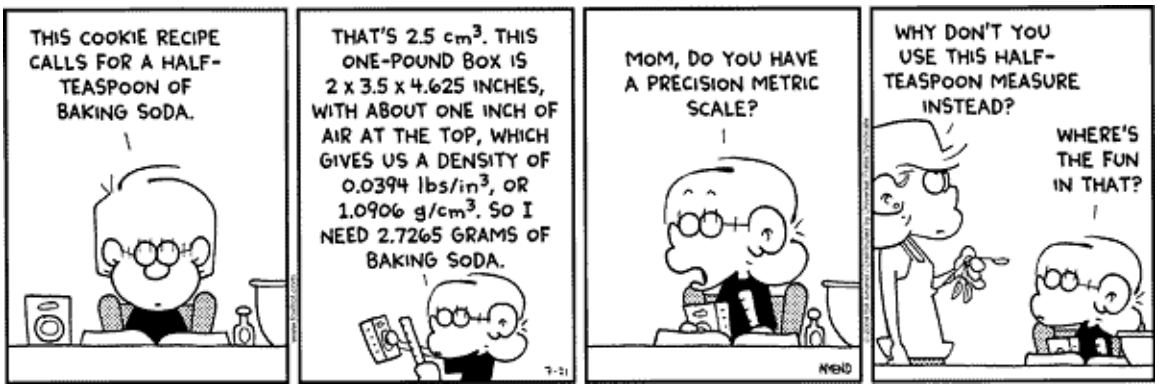
Name:_____

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 400 points. Provided are a periodic table and a formula sheet jam-packed with useful stuff!

Good Luck!





1. **<u>QUICKIES</u>** - **Limit response to about 2 sentences, please!** - ***20 pts each***

   a. Suppose you want to determine the molecular weight of a compound, but the suspected parent or molecular ion peak in its EI mass spectrum (70 eV) is not very intense. Briefly describe two experiments that would help confirm your assignment of the molecular ion peak.

   b. Why are NMR linewidths very broad for solid samples?

   c. If the Larmor frequency of the protons in tetramethyl silane (TMS) is 60.0000 MHz in a 14,092.0 Gauss magnetic field, at what frequency would the protons in TMS precess in a 160,000.0 Gauss magnetic field?

2. Someone from a synthetic lab drops off a sample for you to analyze - it seems that they *may* have come up with a new synthetic route to an interesting new drug. Alas, the lab notebook from the synthetic lab leaves open the possibility that what was actually synthesized is NOT the desired compound. Here's the problem: the two possible compounds have very similar structures and almost exactly the same MW (206.2915 amu versus 206.3008 amu).

a. ***[20 pts]*** What is your first choice of Mass Spectrometer (double-focusing magnetic sector, time-of-flight, or quadrupole) to use for this determination? Briefly explain your choice.

b. ***[30 pts]*** Alas, the *only* mass spectrometer that is operable is the one with limited resolution (R = 500) on the GC-Mass Spec, and it is set to give a mass spectrum of only the molecular ion. Using the GC only as a means of sample introduction (i.e., no separation is done) and armed with the knowledge that one of the compounds contains only C, H, and one Br while the other has only C, H, and one Cl, you conclusively determine which of the two compounds was synthesized. How did you do it? (NOTE: ^{37}Cl natural abundance is 33% of ^{35}Cl; ^{81}Br and ^{79}Br have the same natural abundances).

3. After working as an analytical chemist for several months, your boss decides that you are ready to "graduate" and designates you as the GC-Mass Spec specialist. All goes well until the day that the Mass Spec becomes inoperable and you find that it will be at least a week before it can be repaired. Most of the samples can wait, but there is a critical project that MUST be completed before the Mass Spec can be repaired.

You decide to couple the GC with some of the other instruments in the lab in a desperate attempt to get the information you need. After some work, you take the GC and hook it up so that the compounds separated on the GC flow first to an FT-IR and then to an ICP-AES; *you've created the very first GC-IR-ICP!*

a. ***[20 pts]*** Briefly explain why it was important to have the output of the GC go **first** to the IR **and then** to the ICP (i.e., why would it NOT work to have the ICP before the IR?).

b. ***[30 pts]*** Describe what information each of the two "detector" instruments (i.e., the IR and the ICP) provide on the compounds eluting from the GC and compare that with the information that typically would have been provided by the Mass Spec.

4. a. ***[30 pts]*** The utility of NMR for chemical analysis is based heavily on the fact that the resonance for a particular nucleus depends upon its chemical environment – this is quantified by the chemical shift. Briefly describe the origin of the chemical shift (i.e., explain why these shifts are observed).

b. ***[20 pts]*** Spin-spin splitting provides additional information relating to molecular structure. Explain why the resonance for the three methyl protons in ethanol (CH_3CH_2OH) is split into three peaks with relative areas of 1:2:1.

5. ***[30 pts]*** A sodium solution is analyzed by flame emission spectrometry using the 589-nm doublet line (the so-called sodium D-lines). In developing a procedure for the analysis, the analyst notes that a 1-ppm solution of sodium gives a less intense emission signal than a solution containing the same amount of sodium as well as 10 ppm of potassium. In view of the fact that the 10 ppm potassium gives no measurable emission at 589 nm, explain why the potassium enhances the sodium emission. Suggest a method to correct for this easily ionizable element interference and explain how it would eliminate the problem.

6. ***[25 pts]*** In optical (UV/Vis, IR) spectroscopy, the energies associated with transitions resulting in the absorption of photons are very much larger than the energies commonly encountered in NMR spectroscopy. If we limit consideration to simple two-state systems (i.e., those having just a ground and a single excited state), discuss the relative likelihood that saturation will occur in NMR, UV/Vis and IR spectroscopies. Justify your answer with a brief calculation or two using the Boltzmann equation and arrange the three spectroscopic methods (NMR, UV/Vis, IR) in order of *increasing* likelihood of saturation.

7. [25 pts] Lasers are used as sources in many of the spectroscopic instruments we've studied this semester – identify *ONE* such method and indicate what analytical advantage the use of a laser contributed to the method.

8. <u>What's Wrong With THAT?</u>

For each of the statements given below, indicate what part of the procedure described is *not* correct and describe what WOULD be the correct procedure. - ***20 pts each***

a. The method of standard additions was used to quantify the GC-MS analysis because it is an effective way to improve the analysis *precision.*

b. Electrospray ionization (ESI) mass spectrometry was used with the solution sample for elemental analysis at the ultra-trace concentration level.

c. With a blank measurement of 0.001 $\pm$ 0.0005 (average $\pm$ standard deviation) and a sample measurement of 0.002 $\pm$ 0.0005, it was determined from the calibration curve that Pb was present in the drinking water sample at a level of 500 ppb.

9. <u>TRUE or FALSE.</u>

Indicate whether the following statements are ***TRUE*** or ***FALSE*** and briefly explain ***WHY***. ***20 points each, unless stated otherwise***.

a. Signal averaging improves detectability because the signal increases linearly with each measurement while the noise remains unchanged.

b. The dropping Mercury electrode (DME) is the electrode of choice for voltammetry because it is easily recycled.

c. ***[10 pts]*** Instrumental analysis is my life . . .

Have a great summer!