

# CHEM 221

## Instrumental Analysis

### FINAL EXAM

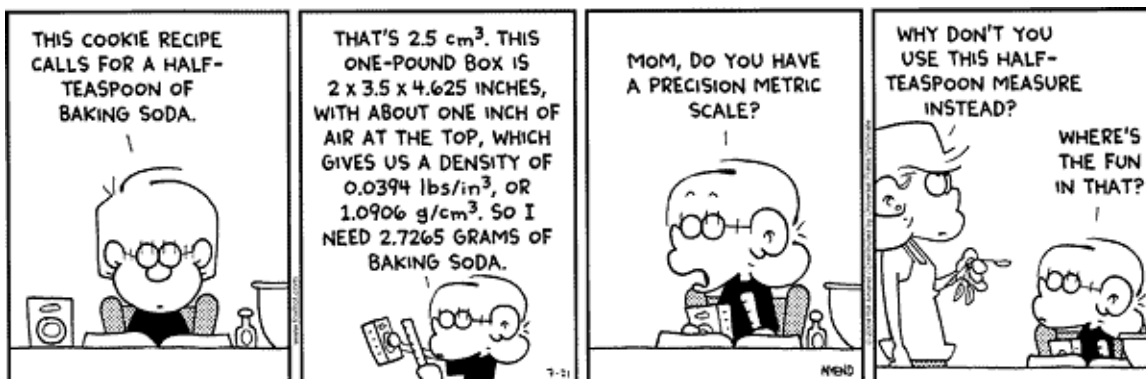
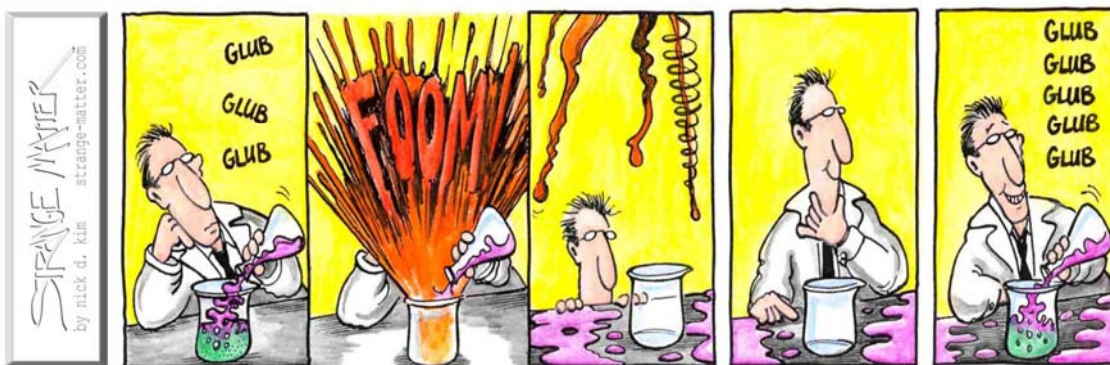
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**INSTRUCTIONS:** Read through the entire exam before you begin. Answer all of the questions. For questions involving calculations, show **all** of your work -- **HOW** you arrived at a particular answer is **MORE** important than the answer itself!

The entire exam is worth a total of 400 points. Provided are a periodic table and a formula sheet jam-packed with useful stuff!

*Good Luck!*



**1. QUICKIES - 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.

**1. Reduce the energy (eV) of the electron beam.**

- Molecular ion peak will *increase*
- Fragment ion peaks will *decrease*

**2. Use a milder ionization source, e.g., Chemical Ionization.**

- Get mostly molecular ion peak at  $MW \pm 1$

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

**Spin-Spin coupling is very efficient in solids due to the close proximity of nuclei - thus,  $T_2$  is small. This gives a short excited state lifetime and, due to the uncertainty principle, a large uncertainty in the excited state energy. Since this large energy uncertainty translates to a large uncertainty in the resulting frequency of the transition, absorption and emission occur over a broad frequency range.**

- 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?

**Since  $\nu \propto H$ :  $\nu_1/H_1 = \nu_2/H_2$**

$$\frac{60.0000 \text{ MHz}}{14,092.0 \text{ G}} = \frac{\nu_2}{160,000.0 \text{ G}}$$

$$\nu_2 = 681.2375816 \text{ MHz} = \boxed{681.238 \text{ MHz}}$$

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.

$$R = m/\Delta m = 206.3/0.0093 = \underline{22,200}$$

**Only a double-focusing magnetic sector could resolve these two molecules.**

- 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:  $^{37}\text{Cl}$  natural abundance is 33% of  $^{35}\text{Cl}$ ;  $^{81}\text{Br}$  and  $^{79}\text{Br}$  have the same natural abundances).

**Both compounds will have *two* molecular ion peaks (separated by 2 amu): one for compounds with each isotope. But, their *relative intensities* will be different (they will follow the natural abundances of the Cl and Br isotopes):**

**Br:** Both peak will be *equal* in intensity

**Cl:** The higher mass peak will have an intensity that is 33% of the lower mass peak

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?).

The compounds eluting from the GC must go first to the “detector” that is non-destructive; the ICP will destroy the compounds (10,000 K plasma, you know!) but the IR will not affect the compounds, so the IR must be the first instrument in the sequence. After the IR spectrum is obtained, the ICP can atomize the compound and its emission spectrum can be recorded. If the compound went first to the ICP, there would be no compound remaining to send to the FT-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.

FT-IR: Provides information on the vibrational modes of the compounds, enabling elucidation of its *molecular structure*.

ICP-AES: Provides information on the elemental composition of the compound - this should enable one to determine the *empirical formula* for the compound and to quantify the amount of each compound in the sample mixture.

GC-MS: Provides both quantitative and qualitative information, specifically *molecular structure* (based on the fragmentation patterns) and the *molecular weight* (which can then be used to determine the *molecular formula*).

Overall: while the Mass Spec would be best, the FT-IR plus ICP-AES combo provides similar information and would be a reasonable alternative until the MS is fixed.

**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).

- **Electronic environment near the nucleus will *shield* it from the full applied magnetic field**
- **As the electron density about the nucleus *increases*, resonance shifts to *lower frequencies* (lower energy) due to *increased shielding***

**b. [20 pts]** Spin-spin splitting provides additional information relating to molecular structure. Explain why the resonance for the three methyl protons in ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) is split into three peaks with relative areas of 1:2:1.

The protons on the carbon *adjacent* to the methyl group will also affect the magnetic field that they experience. There are *two protons* on the carbon adjacent to the methyl group and their spins can either be aligned with or against the applied magfield. There are **FOUR** different combos of these spin states:

↑↑	↑↓ ↓↑	↓↓
1	2	1

In one case, the magfield is *increased*, in one other configuration, the magfield is *decreased*, and in the remaining two cases, the spins cancel, resulting in *no effect*. So, the methyl protons' resonance is split into three peaks with peak 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.

**We need to look at the equilibrium between the atoms and ions in the flame. For sodium:**



**The position of this equilibrium will vary with the electron density.**

**For potassium:**

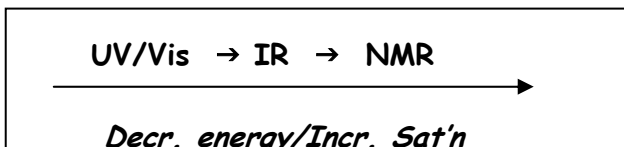


**Since potassium is an *easily ionizable element*, its presence in a sample will increase the electron density of the flame, shifting the ionization equilibrium of the analyte (sodium) to the left (atoms). Since we are monitoring the emission from sodium *atoms*, the increased concentration of sodium atoms results in an increase in emission measured at the sodium atom emission line.**

**The real problem here is the *variability* of the electron density due to variable (and unknown) amounts of easily ionizable elements in the sample(s) to be analyzed. The solution is to *flood the system* with an easily ionizable element (e.g., Li) so that a constant, sample matrix independent electron density is obtained in the flame. Add this *ionization suppressor* to each solution measured, and the fractional ionization of the analyte should remain constant for all measurements. Problem solved!**

**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.

**Saturation should have *increased probability* as the transition energy decreases:**



We predict, then, that at the same temperature, there would be **FEWER** species in the excited state for UV/Vis transitions than for NMR (RF) transitions. Let's calculate some ratios using Boltzmann:

UV/Vis: at 5000 Å,  $E = hc/\lambda = 3.97 \times 10^{-19}$  J

At 298 K:  $N_2/N_1 = e^{-\Delta E/kT} \approx 10^{-42}$

So, virtually **ALL** species are in the ground state (VERY difficult to saturate a transition - need a laser)

NMR (RF): at 500 MHz,  $E = h\nu = 3.31 \times 10^{-25}$  J

Again, at 298 K:

$N_2/N_1 = 0.99992$

So, the populations of the two states are almost identical, making saturation easy to reach.

**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.

Laser-Excited Fluorescence - since fluorescence intensity is proportional to the source intensity, the very high-intensity output from a laser provides the *maximum possible* fluorescence signal (and, in the extreme, allows the transition to be saturated). Also: small beam diameter allows spatial localization on the micron scale and pulsed operation allows a very high degree of temporal resolution.

Laser Raman Spectroscopy - same benefits as given for fluorescence: increased scatter intensity with high spatial and temporal resolution possible. Highly monochromatic source gives broader spectral range.

### 8. What's Wrong With THAT?

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*.

**Ouch! The method of standard additions is used to compensate for changes in signal due to the sample *matrix* - it will improve analysis *accuracy*.**

**To improve analysis *precision*, the method of internal standards is commonly used with GC-MS analyses.**

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

**Another Ouch! ESI-MS is commonly used for the analysis of very high molecular weight biopolymers (e.g., proteins) because of electrospray's tendency to produce ions with multiple (sometimes 50 or more!) charges/ion.**

**For elemental analysis at ultra-trace levels, the ICP makes a very nice ion source for mass spectral detection.**

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.

**Minimum detectable signal ( $S/N = 3$ ) would be:**

Blank	0.001
+3x Noise	<u>3(0.0005)</u>
	0.0025 > 0.002 (sample)

**Thus, sample measurement is below the detection limit and indistinguishable from the blank.**

**9. TRUE or FALSE.**

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.

**FALSE.**

Signal is proportional to  $n$   
Noise is proportional to  $n^{1/2}$

So, S/N increases with  $n^{1/2}$

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

**FALSE!**

DME provides:

- Fresh electrode surface with each drop
- Increasing surface area (with time) to counteract the naturally *decreasing current* (with time)

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

***But, of course!*** ☺

Have a great summer!