

# CHEM 221

## Instrumental Analysis

### EXAM #3

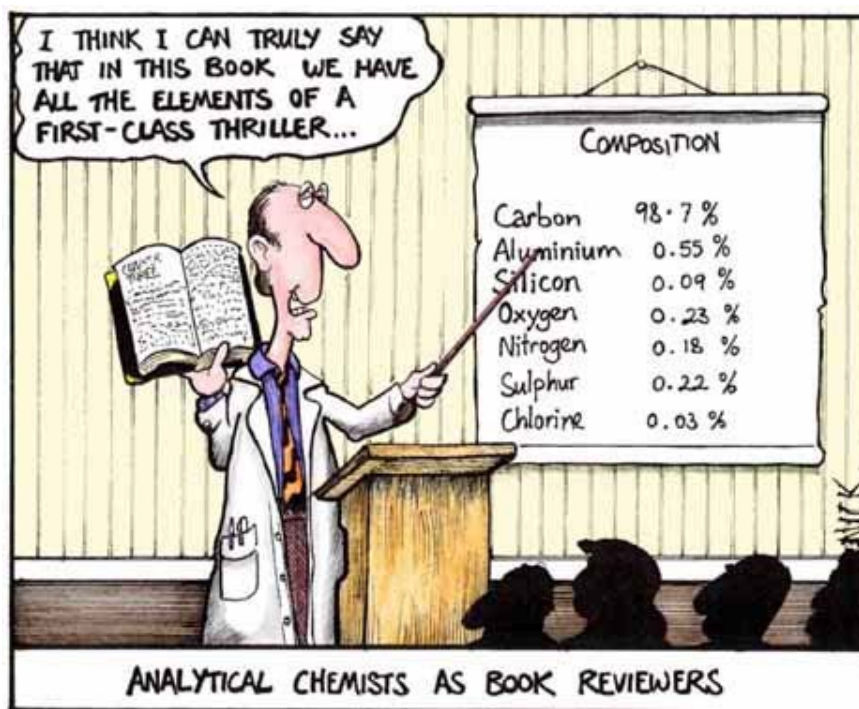
April 23, 2003

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! Similarly, you must explain how you arrived at an answer to a question if you are to receive full credit for your answer. On the back of the last page of the exam, write "I read the instructions for this exam." – this is worth 5 points.

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. QUICKIES (15 points each) – No more than 2 sentences!**

**a.** Explain why the signal in flame atomic *emission* spectrometry is very sensitive to the flame temperature, while the absorbance signal in flame atomic *absorption* spectrometry is relatively insensitive to flame temperature.

**b.** The most common detector used in FT-IR is the so-called TGS (Triglycine Sulfate) detector which is a *thermal* detector and has poor sensitivity. Explain why a photoemissive detector (like the photomultiplier tube commonly used in UV/Vis spectrometry) cannot be used in FT-IR.

**c.** Arrange the following stretches in order of *increasing* vibration frequency: C-H, C-C, C≡C, C=O, C=C. Briefly justify/explain your answer.

**d.** The parent peak spectrum of tridecylbenzene (MW=260.2504) and 2,2-naphthylbenzothiophene (MW=260.0922) would require what resolution for quantitative analysis based on the parent peak?

**e.** For a drift length of  $2.00 \times 10^2$  cm in a time-of-flight (TOF) mass spectrometer, what is the arrival time ( $\mu\text{s}$ ) for the molecular ion of tridecylbenzene (MW=260.2504) if the accelerating voltage is  $5.00 \times 10^3$  volts?

**f.** What is the function of the electrostatic sector in a double-focusing mass analyzer? Explain.

2. (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.

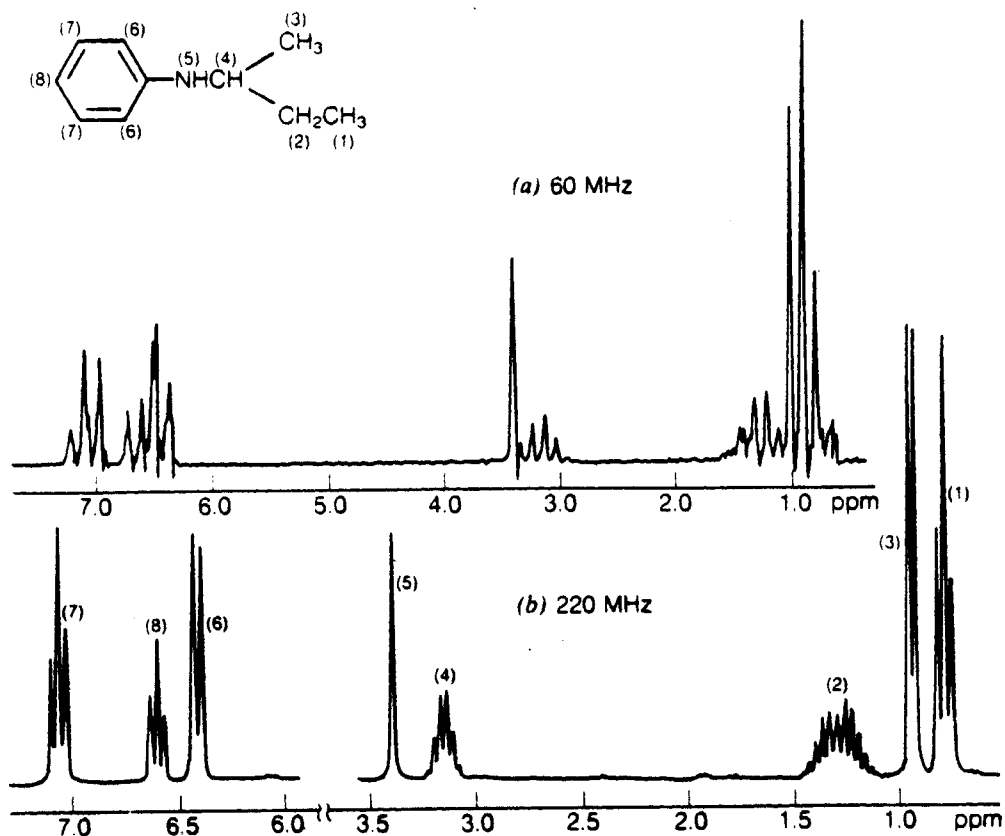
3. **Still more QUICKIES! – No more than 2 sentences!**

a. (10 pts) Is Flame-AAS or ICP-AES better suited for performing qualitative elemental analyses on a sample? Explain.

b. (15 pts) How many fundamental vibrational modes are predicted for water (H<sub>2</sub>O)? Diagram *one* vibrational mode that you would expect to be IR active.

c. (10 pts) Why are NMR linewidths very broad for solid samples?

4. Below are proton NMR spectra of N-sec-butaniline obtained on 60 MHz and 220 MHz instruments:



- a. (10 points) Based on the chemical shifts shown, which protons are most heavily shielded? Explain.

**b.** (15 points) Why are the resonances for the 6 and 7 protons split into 2 and 3 peaks, respectively? Give the expected relative peak areas under the split peaks. Explain.

**c.** (20 points) If these two NMR spectra were plotted as a function of *frequency* instead of chemical shift ( $\delta$ , ppm), explain how the values of the spin-spin coupling constants (J) and how the chemical shift values (remember, in Hz) would be affected by the magnetic field strength of the instrument.