

CHEM 221

Instrumental Analysis

EXAM #3

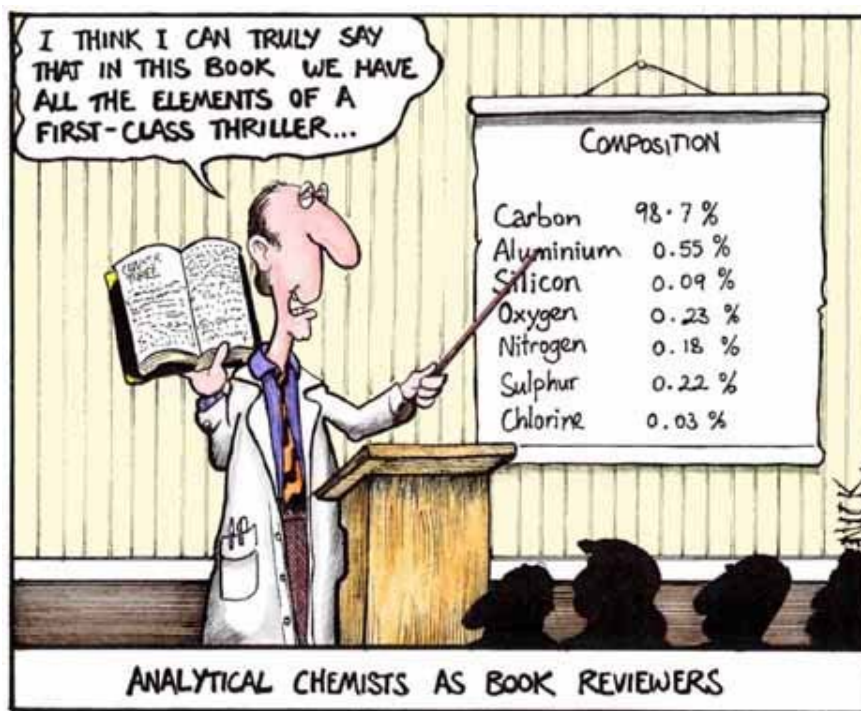
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INSTRUCTIONS: Read through the entire exam before you begin. Answer all of the questions. For questions involving calculations, show **all** of your work -- **HOW** you arrived at a particular answer is **MORE** important than the answer itself! Similarly,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

The emission signal depends on the excited state population while the absorption signal is proportional to the ground state population. At typical flame temperatures, the ground state population is nearly temperature independent (> 99.9% of species being in the ground state). The excited state population, however, varies significantly with temperature, resulting in comensurately large variations in emission intensity.

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.

Photoemissive detectors are based on the *photoelectric effect* in which photons impinging on a metal surface can release electrons in direct proportion to the number of photons striking the surface. The photons must be above a minimum energy, however, and photons in the IR are just not energetic enough - so, IR photons cannot be detected in this manner.

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.

Increasing Frequency →

C-C < C=O < C=C < C≡C < C-H

-Heavy Atoms	-Heavy Atoms	-like C=O, but	-Heavy Atoms	-lightest
-Weak bond	-Stronger bond	with < mass	-Strongest bond	-weak bond

From equation given: $\nu \propto (k)^{\frac{1}{2}}$ - bond strength
 $\nu \propto (1/\mu)^{\frac{1}{2}}$ - mass

C-H is at higher freq than C≡C as k will increase only 3-fold as bond strength increases, while H is less than 10% of the mass of C, so C-H freq is about 3.5x higher than C-C and C≡C freq is only 1.7x higher than C-C.

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?

$$R = m/\Delta m = 260/0.1582 = 1,643 = \boxed{1,600}$$

e. For a drift length of 2.00×10^2 cm in a time-of-flight (TOF) mass spectrometer, what is the arrival time (μs) for the molecular ion of tridecylbenzene (MW=260.2504) if the accelerating voltage is 5.00×10^3 volts?

$$\begin{aligned} \text{Velocity} &= (2Ve/m)^{\frac{1}{2}} \\ &= [2(5000 \text{ volts})(1.6022 \times 10^{-12} \text{ erg/volt})/(260.2504/6.022137 \times 10^{23})]^{\frac{1}{2}} \\ &= [1.6022 \times 10^{-8} \text{ erg}/4.32156226 \times 10^{-22} \text{ g}]^{\frac{1}{2}} \\ &= (3.70746 \times 10^{13} \text{ cm}^2/\text{s}^2)^{\frac{1}{2}} \\ &= 6.08889 \times 10^6 \text{ cm/s} \end{aligned}$$

Time to travel 200. cm at 6.08889×10^6 cm/s:

$$\begin{aligned} \text{Time} = L/V &= 2.00 \times 10^2 \text{ cm}/6.08889 \times 10^6 \text{ cm/s} \\ &= 3.2847 \times 10^{-5} \text{ s} \times \frac{10^6 \mu\text{s}}{\text{s}} = \boxed{32.8 \mu\text{s}} \end{aligned}$$

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

Resolution is limited by the spread of kinetic energies of ions entering the magnetic sector. For an electrostatic sector, only ions having a specific kinetic energy will have the correct radius of curvature of the sector and, so, only ions having a narrow range of kinetic energies will reach the magnetic sector. Thus, the electrostatic sector acts as a kinetic energy filter that limits the range of ion kinetic energies reaching the magnetic sector, thereby increasing the resolving power of the mass analyzer.

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.

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!

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.

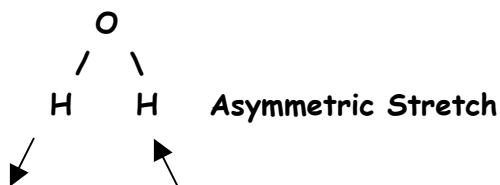
ICP-AES is best. With AAS, a separate hollow cathode lamp is needed for each element, so it is not possible to obtain an absorbance spectrum (needed for qualitative analysis). The ICP will excite all elements, enabling acquisition of an emission spectrum suitable for qualitative analysis.

b. (15 pts) How many fundamental vibrational modes are predicted for water (H₂O)? Diagram *one* vibrational mode that you would expect to be IR active.

There will be $3N-6$ vibrational modes for a non-linear molecule, so:

$$3N-6 = 3(3) - 6 = \boxed{\text{Three Vibrational Modes}}$$

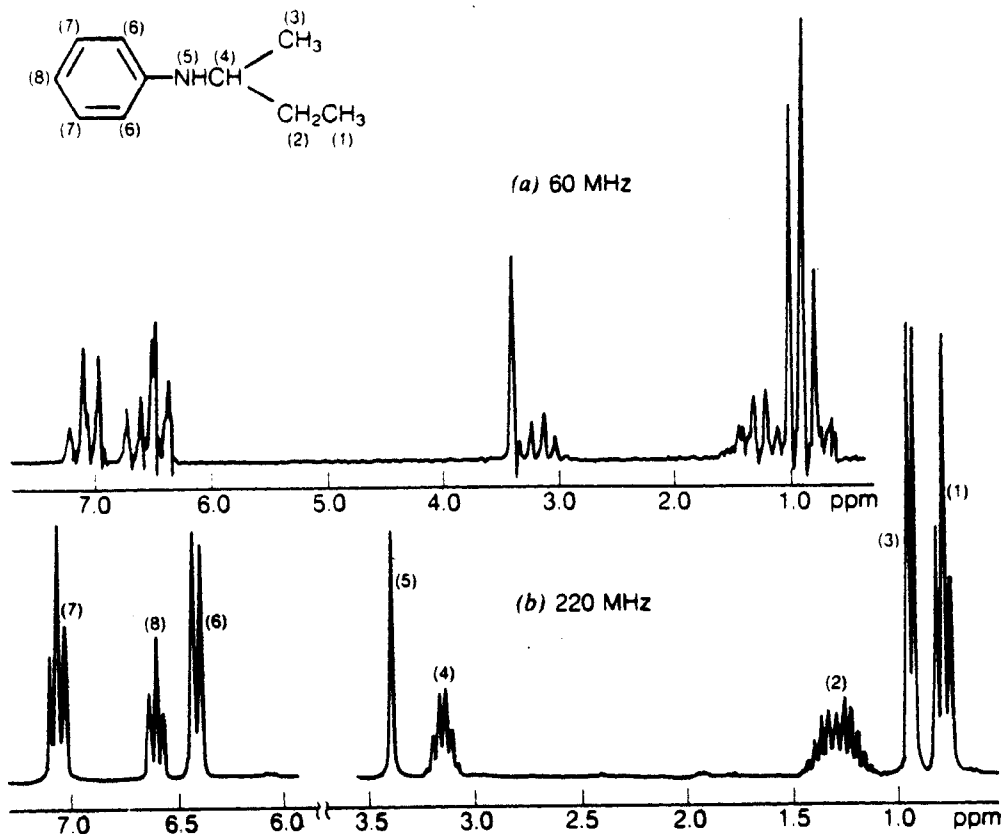
In order to be IR active, the dipole moment must change during the vibration:



c. (10 pts) 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.

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



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

The 1 protons are most heavily shielded, as they have the smallest chemical shift (0 ppm is defined by TMS, which has very heavily shielded protons). These methyl protons are farthest away from any electron withdrawing groups, so there is very little opportunity for deshielding.

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.

The 7 protons have 2 protons on adjacent carbons which can result in spin-spin splitting, resulting in the following spin alignments: $\uparrow\uparrow$ or $\uparrow\downarrow$ $\downarrow\uparrow$ or $\downarrow\downarrow$. This gives three possible configurations and will split the 7 peak into three peaks with relative areas of 1:2:1.

The 6 protons have only one proton on an adjacent carbon which will result in two different spin orientations, splitting the 6 peak into two peaks having identical areas.

c. (20 points) If these two NMR spectra were plotted as a function of *frequency* instead of chemical shift (δ , 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.

Increasing the magnetic field will:

1. Have no effect on J-values, as they depend only on the nuclear spin environment near the proton - J values (in Hz) remain unaffected by a change in applied field.
2. Increase absolute chemical shift values (Hz), as the field increase will increase the resonance frequency for each peak (ν and B_0). Since all resonance frequencies will be shifted *proportionately*, the relative shift (ppm) is unaffected.