CHEM 221

Instrumental Analysis

EXAM #3

April 20, 2005

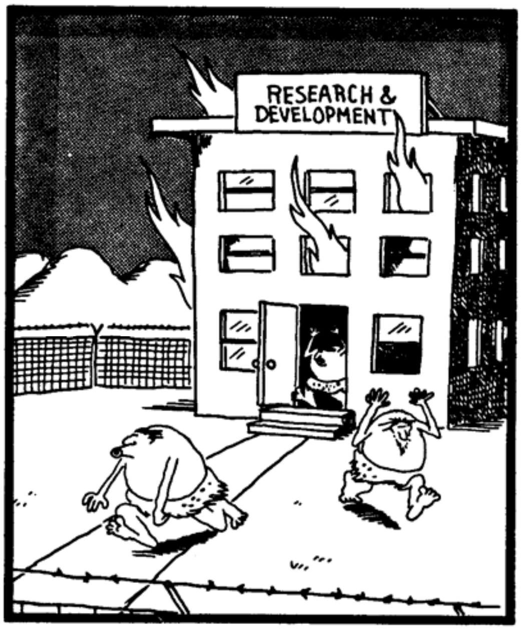
Name:__________________________

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!

All questions are worth 15 pts each – answer **any 13** of the 16 questions (for a total of 200 points). You can receive extra credit by answering additional questions (up to 5 extra credit points per question) – if you do so, you must CLEARLY identify those questions which are to be graded as extra credit by writing "EC" next to the question number. If no questions are marked "EC" and more than 13 questions are answered, then I will grade the first 13 answers at full credit value (15 points each) and any remaining questions at extra credit value (5 points). Attached are a periodic table and a formula sheet jam-packed with useful stuff!

Initial here to indicate you have read these instructions (worth 5 pts!): _______

Good Luck!



Atomic Spectroscopy is invented.

1. Explain why a high-resolution monochromator is needed for atomic emission spectroscopy while atomic absorption spectroscopy requires a monochromator having only low-to-moderate resolving power.

2. Graphite furnace atomizers are renowned in Atomic Absorption Spectrometry for their exceptionally low detection limits (10^{-12} g and lower for many elements). Why are detectabilities so much better with graphite furnaces than with flame atom cells in AAS?

3. Continuum light sources work just fine for molecular absorption spectrophotometry, yet narrow line sources must be used for *atomic* absorption spectrophotometry – Explain.

4. What properties of the Inductively Coupled Plasma (ICP) make it an almost *ideal* source for atomic emission spectroscopy (AES)?

5. What is the function of the electrostatic sector in a double-focusing mass analyzer? Explain its role in improving the resolution obtained with a magnetic sector mass analyzer.

6. A molecule has a Raman shift of 859 cm^{-1} when excited by an argon ion laser at 351.1 nm. What are the wavelengths (nm) of the Stokes and anti-Stokes Raman lines? Which of these is more intense?

7. Two Raman spectra of CCl_4 were acquired with a Raman spectrometer: spectrum A was excited using the 351.1 nm line from an argon ion laser source and spectrum B was excited using the 1064 nm line from a Nd:YAG laser source. Assuming all instrumental responses and parameters were identical when the two spectra were obtained, identify which spectrum will be more intense and calculate by how much.

8. To the neophyte spectroscopist, the differences between molecular fluorescence and Raman spectroscopies can often seem subtle and confusing. Draw two simple energy-level diagrams for a molecular system which illustrate the differences between these two similar, yet profoundly different, techniques.

9. The ability of laser sources to saturate (or nearly saturate) an electronic transition has resulted in significant improvements in molecular fluorescence methods. Briefly describe the phenomenon of saturation, how it affects fluorescence intensity, and how it improves fluorescence methods.

10. Briefly explain why fluorescence excitation involving $\pi \rightarrow \pi^*$ transitions typically results in more intense fluorescence than excitation involving $n \rightarrow \pi^*$ transitions.

11. Briefly explain why fluorescence is said to be best suited for “trace analysis”.

12. Fluorescence spectra of solids and liquids are characterized by the same broad spectral bands typically observed in UV/Vis molecular absorption spectra. Yet, fluorescence measurements *can* result in greater **selectivity** than can be obtained by absorption measurements. Explain.

13. Briefly describe one modification of the Raman method which results in a significant enhancement in Raman scatter intensity.

14. In order for IR absorption to occur, there must be a change in the *dipole moment* of a molecule during a vibration, so homonuclear diatomic molecules, like N_2, are "IR inactive". Explain why these very same molecules, however, DO produce Raman spectra with Raman shifts associated with their "IR inactive" vibrational modes.

15. Briefly describe the properties of laser sources that make them ideally suited for exciting Raman spectra.

16. Calculate the mass spectrometer resolving power needed to just resolve the two isotopes of Bromine (Atomic Masses: 78.9183 and 80.9163). Would a time-of-flight (TOF) mass spectrometer be able to resolve these two isotopes? For a drift length of 5.00 x 10^2 cm in a time-of-flight (TOF) mass spectrometer, what is the difference in arrival times (μs) for the singly-charged ions of these two isotopes of Bromine if the accelerating voltage is 2.00 x 10^3 volts?