

CHEM 221
Instrumental Analysis
EXAM #3

April 20, 2005

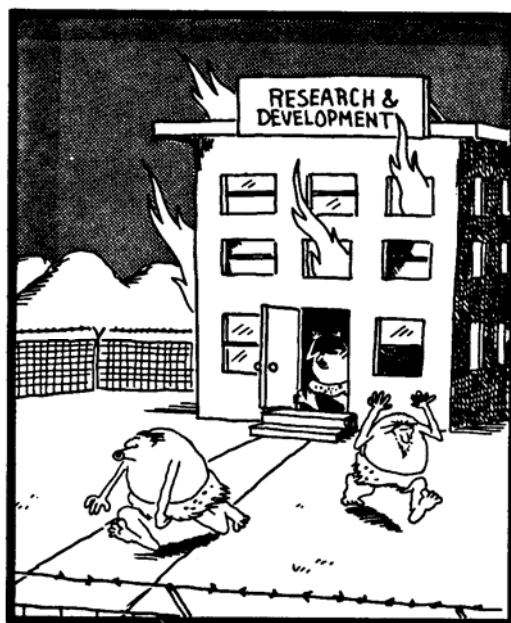
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INSTRUCTIONS: Read through the entire exam before you begin. Answer all of the questions. For questions involving calculations, show **all** of your work -- **HOW** you arrived at a particular answer is **MORE** important than the answer itself!

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!): A.S.K.

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.

AES: Selectivity is determined by $\Delta\lambda_{\text{eff}}$ of dispersive device (slitwidth-limited resolution), so a high resolution monochromator is needed.

AAS: Selectivity is controlled by the linewidths of the hollow cathode lamp source. The monochromator acts only as a filter with a large $\Delta\lambda_{\text{eff}}$.

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?

Sample Consumption: 100% with graphite furnace, 1-5% with flames

Atom Residence Time: 1-5 seconds with graphite furnace, 10-20 ms with flame

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

For absorbance spectrometry, $\Delta\lambda_{\text{eff}}$ should be less than 10% of the peak width. For molecules, this is easily attainable with a monochromator ($\Delta\lambda_{\text{eff}} \sim \text{nm}$), but for atoms ($\Delta\lambda_{\text{eff}} \sim 10^{-3} \text{ \AA}$) it is impossible with conventional monochromators, necessitating the use of narrow line sources, such as hollow cathode lamps.

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

1. **HOT** (8000 - 10,000 K) - results in efficient atomization and excitation of sample.
2. **ANNULAR SHAPE** (cooler on the inside, hotter on the outside) - results in efficient penetration of sample into plasma as well as almost NO self-absorption (giving a LDR of more than 6 decades).

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.

The electrostatic sector limits the spread of kinetic energies of the ions entering the magnetic sector. This improves the resolving power of the instrument to more than 20,000.

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?

The Rayleigh scatter line is at the excitation wavelength:

$$351.1\text{ nm} = 3511\text{ \AA} = 3511 \times 10^{-8}\text{ cm} \rightarrow 28,481.91\text{ cm}^{-1}$$

Anti-Stokes lines will be at greater energy, so:

$$28,481.91\text{ cm}^{-1} + 859\text{ cm}^{-1} = 29,340.91\text{ cm}^{-1}$$

Converting back to nanometers:

$$29,340.91\text{ cm}^{-1} \rightarrow 3408.2 \times 10^{-8}\text{ cm} = 3408\text{ \AA} = \boxed{340.8\text{ nm}}$$

For the Stokes lines, we subtract the Raman shift from the Rayleigh line (lower energy): $27,622.91\text{ cm}^{-1} \rightarrow \boxed{362.0\text{ nm}}$

»The Stokes line at 362.0 nm will be more intense (as scatter originates from the more heavily populated vibrational ground state).

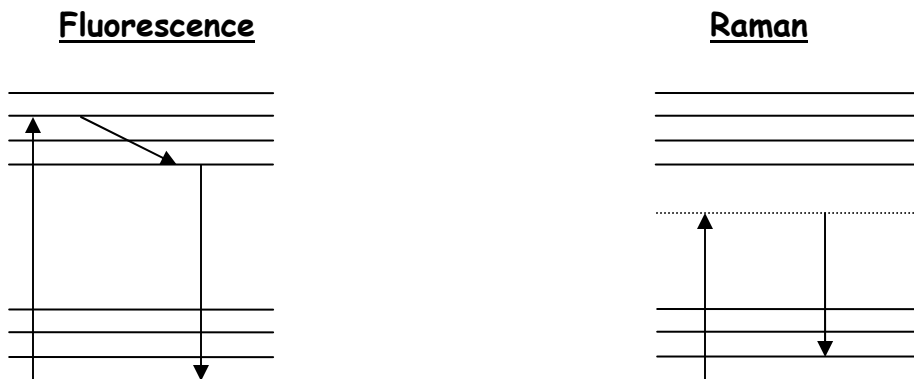
7. Two Raman spectra of CCl₄ were acquired with a Raman spectrometer: spectrum A was excited using the 351.1 nm line from an argon ion laser source and spectrum B was excited using the 1064 nm line from a Nd:YAG laser source. Assuming all instrumental responses and parameters were identical when the two spectra were obtained, identify which spectrum will be more intense and calculate by how much.

Raman scatter intensities are proportional to $1/\lambda^4$. Changing lasers, results in a factor of $1064/351.1 = 3.0305$ wavelength change.
So:

$$(3.0305)^4 = \underline{84.34}$$

So, the Raman spectrum acquired using the argon-ion laser (at 351.1 nm) will be 84.34 times more intense than the spectrum obtained with the 1064 nm Nd:YAG laser line.

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.



In Fluorescence, a photon is *absorbed* into a quantized electronic energy state - after rapid *vibrational relaxation* to the lowest vibrational energy state, a photon (of lower energy than the absorbed photon) is *emitted* from the system, bringing it to one of the vibrational energy states within the ground electronic manifold.

In Raman, a photon raises the molecule to a *virtual excited state* and then instantly reemits the photon, leaving the molecule in an excited vibrational energy state.

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.

A transition is *saturated* when the rate of absorption is so great that the population of the *excited state* reaches that of the ground state - this results in the greatest possible population of the excited state, so fluorescence intensity is maximized. Under these conditions, the fluorescence intensity becomes *independent of the source intensity*, so that random variations in source intensity (i.e., source noise) is not reflected in the fluorescence intensity. Thus, saturation maximizes the signal while decreasing the noise - improved S/N results in lower detection limits.

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

$\pi \rightarrow \pi^*$ transitions have much larger molar absorptivities than do $n \rightarrow \pi^*$ transitions - thus, their absorption transition probabilities are greater. Absorption transition probabilities are inversely related to the excited state lifetime, so the lifetime of the excited states for $\pi \rightarrow \pi^*$ transitions is shorter than those for $n \rightarrow \pi^*$ transitions. Shorter excited state lifetimes decrease the possibility of *non-radiative* deactivation of the excited state (i.e., greater likelihood of fluorescence decay to ground state).

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

Fluorescence intensity varies linearly with concentration *only* for small concentrations - also, fluorescence intensity varies directly with source intensity so, with an intense source, best analytical quantitation is done for very small amounts of analyte (i.e., "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.

Fluorescence gives an added dimension of selectivity because both the *absorption* wavelength and the *emission* wavelength can be selected, independently. This combination gives one a greater likelihood of being able to differentiate between the emission from two compounds having similar absorption properties. This can be completely mapped by systematically changing the excitation wavelength while recording the emission spectrum - compiled together, this forms an Emission-Excitation Matrix (EEM) which can serve as a *fingerprint* for a compound.

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

A few options here, but two are most significant:

- **Resonance Raman** - when the excitation wavelength resides within a absorption manifold, the Raman bands corresponding to vibrational modes associated with that electronic system can be enhanced by up to 10^6 .
- **Surface-Enhanced Raman** - when adsorbed onto the surface of some metals (e.g., Cu, Ag, Au), the Raman scatter intensity can be enhanced by upwards of 10^6 .

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.

Raman scatter occurs when there is a change in the *net polarizability* during a vibration - the symmetrical stretch of a homonuclear diatomic molecule results in a change in the size of the electron cloud associated with the bond and, so, has a changing ability to be polarized when exposed to EMR. These vibrational modes, then, are Raman-active.

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

Raman scatter intensity is directly proportional to the source intensity - laser sources are the most intense sources that are available.

Raman bands are measured as a *shift* from the exciting source wavelength, so the more monochromatic the source, the smaller the Raman shift can be measured. Laser light is highly monochromatic, so more Raman bands located close to the source wavelength can be detected.

Laser light can be very tightly focused onto a sample, resulting in more efficient coupling of the exciting source radiation to the sample.

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 5.00×10^2 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 2.00×10^3 volts?

First: $R = m/\Delta m = 80/1.998 = \underline{40.0}$ - YES! A TOF could easily resolve these two ions ($R \approx 500$).

Next: Recall that: $\text{velocity} = (2Ve/m)^{\frac{1}{2}}$

So (for ^{79}Br): $\text{Time} = \text{length}/\text{velocity} = L(m/(2Ve))^{\frac{1}{2}}$

$$t = (500. \text{ cm})[(78.9183/6.022 \times 10^{23})/(2(2000. \text{ v})(1.60 \times 10^{-12} \text{ erg/v}))]^{\frac{1}{2}}$$

$$t = 7.1548 \times 10^{-5} \text{ sec} = \underline{71.55 \mu\text{s}}$$

And (for ^{81}Br):

$$t = 7.2448 \times 10^{-5} \text{ sec} = \underline{72.45 \mu\text{s}}$$

So: $\Delta t = \underline{0.90 \mu\text{s}}$