CHEM 221

Instrumental Analysis

FINAL EXAM

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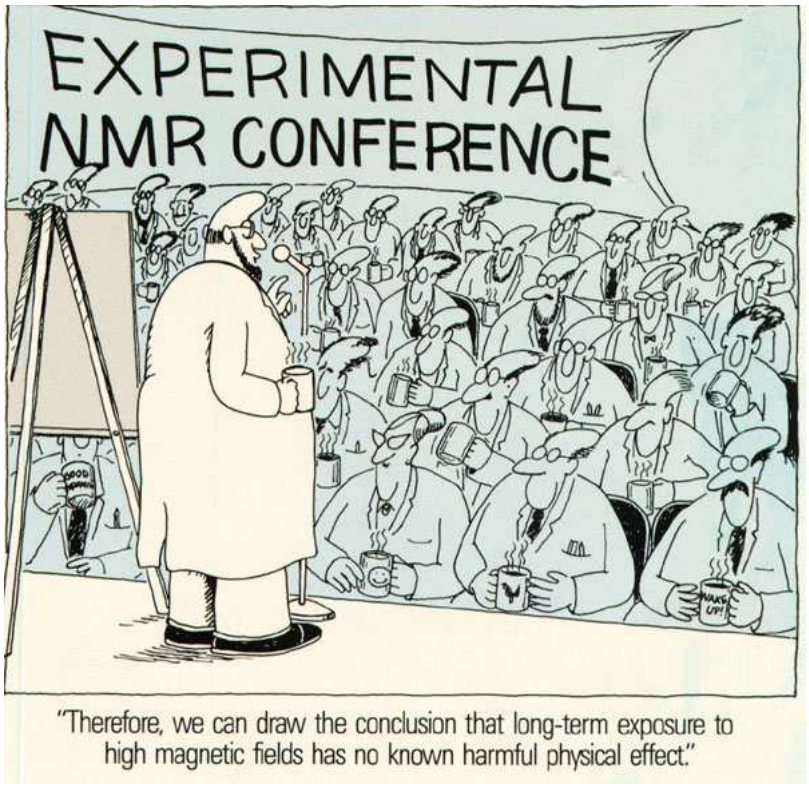
Name: Khee

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. **<u>QUICKIES</u> - Limit response to about 2 sentences, please! - *20 pts each***

a. The parent ion peak in the mass spectrum for Br_2 actually consists of more than one peak. How many parent ion peaks would there be for Br_2 and at what masses would they be found? Explain. (There are two stable isotopes of Br (^{79}Br and ^{81}Br) and they have identical natural abundances.)

The two isotopes of Br can combine to form Br_2 in THREE different combos:

$^{79}Br^{79}Br$ - 158 amu

$^{79}Br^{81}Br$
$^{81}Br^{79}Br$ - 160 amu

$^{81}Br^{81}Br$ - 162 amu

Since there is an equal probability of obtaining each of the four combos, they should have abundance ratios of 1:2:1 at masses 158, 160 and 162.

b. Explain the differences between the chemical ionization mass spectrum for a compound and its corresponding electron impact ionization mass spectrum.

-Decreased fragmentation due to lower energy ionization

-Molecular ion peak will occur at either M+1 or M-1 due to addition or abstraction of proton during ionization process.

c. Explain why increasing the magnetic field strength results in an increased signal in NMR.

-increased magnetic field results in an increase in the *energy* of the transition ($\Delta E \propto B_o$).

According to Bolzmann:

$$N_2/N_1 = e^{-\Delta E/kT}$$

So, increasing ΔE will *decrease* N_2/N_1, allowing <u>*more transitions*</u> to occur between the two states per unit time (and so, an increased signal).

2. Congratulations! After a semester of instrumental analysis, you have been selected as the senior analytical chemist at a local environmental analysis firm. In spite of the fact that they are very understaffed (hence, your inflated starting position), they are remarkably well-equipped and have most of the analytical instruments that we discussed this semester (surprise, surprise!). The methods available include:

- Flame Atomic Absorption Spectrometry (AAS)
- Graphite Furnace AAS
- Flame Atomic Emission Spectroscopy (AES)
- Inductively Coupled Plasma (ICP) AES
- ICP-Mass Spec
- FT-IR Spectroscopy
- GC-Mass Spec
- Electrospray Ionization (ESI)-Mass Spec
- Mass Spectrometry
- Raman Spectroscopy
- Molecular Fluorescence Spectroscopy
- Nuclear Magnetic Resonance (NMR)
- Hydrodynamic Voltammetry
- Anodic Stripping Voltammetry

a. ***[20 pts]*** Your lab has developed a method for quantifying a particular pesticide commonly found in the soil. This method involves an automated extraction followed by an on-line fluorescence measurement at the emission maximum for the pesticide. One of the samples analyzed in this fashion gave a result that showed an unusually large amount of this pesticide in this soil sample. You suspect that this result is not due to an abnormally large pesticide concentration, but is actually due to a problem with the analytical method. *Choose ONE technique (from the above list) that you would select to investigate this anomalous result.* ***Briefly*** *justify your choice.*

Need a *separation* plus a technique to provide *structural* info:

GC-MS

***GC*:** **Will confirm sample is a *mixture* and will separate into component parts**

MS: Will provide structural info and MW's of the compounds

b. ***[15 pts]*** From the list of techniques above, choose **one** that would benefit from the use of the method of *internal standards* for quantitative measurements. Explain.

Most Obvious:

- ***GC*: corrects for sample introduction variability**
- **MS: corrects for sample intro and ionization variability**
- **AES: corrects for excitation source temperature variability**

c. ***[15 pts]*** The EPA requires that the cooling water effluent from a local manufacturing plant be monitored for various metals as it is discharged into a stream from which drinking water is obtained. Since the plant still uses Cr in its aluminum oxidation processes, you must test for Cr(VI) in the effluent each day. From the list of methods on the previous page, choose the best one for this analysis; ***briefly*** justify your choice.

Need a method that will provide *oxidation state selectivity*:
<u>Hydrodynamic Voltammetry</u> (or other Echem method) is the best choice.

There are other (acceptable) ways:

- **<u>UV/Vis Spec:</u> Form a metal complex that is *specific to Cr(VI)* and quantify by measuring absorption spec.**
- **<u>Any Atomic Spec:</u> Extract just Cr(VI) and then quantify using AES or AAS**

d. ***[20 pts]*** You've been using a GC with an electron-capture detector (ECD) to quantify the components of a mixture which contain chlorine (think of the ECD as a halogen-specific detector). Alas, the old ECD has decided to cease functioning the day that a new batch of samples arrived for analysis. "No problem!" you tell your boss, "I'll just interface the GC with some other instrument, and we'll be back in business." Unfortunately, the only mass spec in the company is tied up with another project and is unavailable. So, with your new job on the line, what "hyphenated" instrument would you construct (GC-**??**) -- justify your answer based solely on functionality (i.e., ability to give the information desired). You may choose from any of the instruments listed on the previous page, EXCEPT those that have a mass spec.

ECD gave a signal that was specific for halogenated compounds – we are specifically interested in Cl-containing compounds

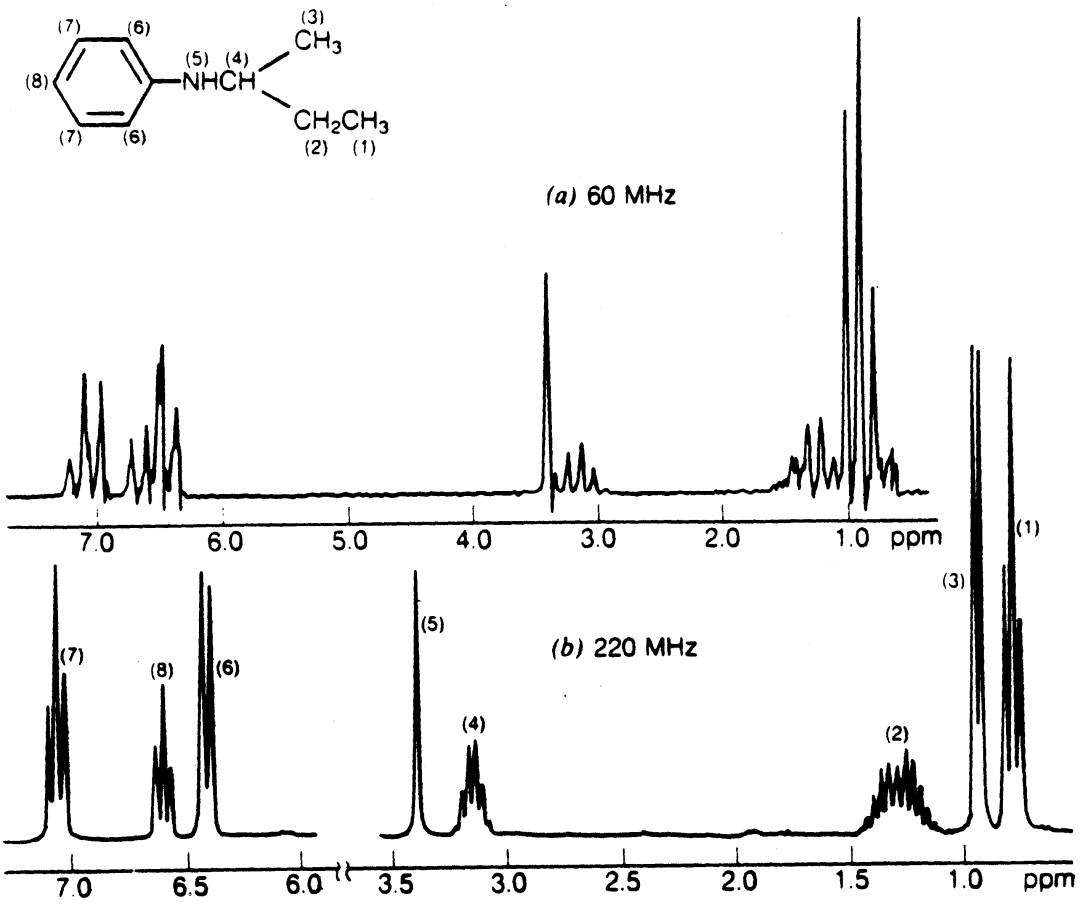
So, use an *element-specific method* that can be selective for Cl:

<u>Atomic Spec</u>

<u>ICP-AES</u> would work:

- **Measure Cl-emission as chromatogram is run**
- **Obtain a chromatogram with ONLY peaks for Cl-containing compounds**
- **Even MORE SELECTIVE than the ECD!**

3. 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 <u>1</u> 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: ↑↑ or ↑↓ ↓↑ or ↓↓. 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. ***[15 points]*** Explain why the resonances for the phenyl protons are observed at the greatest chemical shift values for this compound.

The phenyl protons (*6, 7, and 8*) are influenced by the magnetic field generated by the ring current arising from the delocalized electrons circulating the phenyl ring. This magnetic field *enhances* the applied magnetic field, so these protons on the phenyl ring experience a *greater* magnetic field than they would if there were no ring current. This results in a shift to a greater frequency (similar to what would be observed for deshielded protons). This effect is referred to as *magnetic anisotropy*.

d. ***[10 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_o). Since all resonance frequencies will be shifted *proportionately*, the relative shift (ppm) is unaffected.**

4. **<u>QUICKIES</u> - Limit response to about 2 sentences, please! -** ***20 pts each***

a. If the C-H stretch for an alkane occurs at 2900 cm^{-1}, to what wavenumber would the absorption band shift for the *deuterated* analog?

$\mu_1 = [12(1)/(12+1)] = 12/13$
$\mu_2 = [12(2)/(12+2)] = 24/14$

$\frac{\mu_2}{\mu_1} = \frac{24/14}{12/13} = \frac{13}{7} = 1.8571$

$\bar{\nu} = (5.3 \times 10^{-12})(k/\mu)^{\frac{1}{2}}$

Assuming k is constant: $\bar{\nu}_1/\bar{\nu}_2 = (\mu_2/\mu_1)^{\frac{1}{2}}$

$2900\ cm^{-1}/\bar{\nu}_2 = (1.8571)^{\frac{1}{2}}$

$\bar{\nu}_2 = 2128\ cm^{-1} =$ ***<u>2100 cm^{-1}</u>***

b. Briefly explain why spectrofluorometric (emission) measurements are potentially more sensitive than spectrophotometric (absorption) measurements.

In spectrofluorometry, detection is ultimately limited by the ability to distinguish between two very small signals (the blank and the emission from a very low concentration sample). In spectrophotometry (absorption), detection is limited by the ability to distinguish between two very LARGE signals (I_o and the transmitted signal through a very weakly absorbing sample). Since shot noise is related to the magnitude of the signal, the ability to differentiate between two LARGE signals is considerably less than the ability to differentiate between two SMALL signals. Thus, spectrofluorometric detection limits are lower than corresponding spectrophotometric detection limits.

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

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

5. **<u>QUICKIES</u> - Limit response to about 2 sentences, please! -** ***20 pts each***

a. When recording the spectrum of a new compound you have just synthesized, you find that a critical spectral feature is buried in the background noise of the spectrum. If, after signal averaging 105 spectra, the S/N for this feature is 0.50, ***calculate the S/N*** for this spectral feature after signal averaging the spectrum for an entire weekend (48 hours). Assume that it takes 0.50 minutes to scan a single spectrum.

S/N after 105 scans = 0.50
So: $(S/N)_{n=105} = (105)^{1/2}\,(S/N)_{n=1} = 0.50$
$(S/N)_{n=1} = 0.048795$

At 1.0 min/scan, in 48 hours:
$$48 \text{ hours} \times \frac{60 \text{ min}}{1 \text{ hour}} \times \frac{1 \text{ scan}}{0.50 \text{ min}} = 5.760 \times 10^3 \text{ scans}$$

So, S/N after 5.760×10^3 scans:
$$(S/N)_n = n^{1/2}(S/N)_{n=1} = (5.760 \times 10^3)^{1/2}(0.048795)$$
$$(S/N)_n = (75.895)(0.048795) = 3.703 = \boxed{3.7}$$

b. Calculate the frequency of electromagnetic radiation (EMR) in the IR spectral region at a wavelength (in a vacuum) of 7.291 μm. Compare this with the frequency of EMR commonly encountered in NMR spectroscopy and explain why an interferometer is only needed for FT-IR but not FT-NMR.

$$\nu = c/\lambda = \frac{2.9979 \times 10^8 \text{ m/sec}}{7.291 \times 10^{-6} \text{ m}} = 4.1117816 \times 10^{13} \text{ sec}^{-1} = \underline{4.112 \times 10^{13} \text{ sec}^{-1}} = \nu$$

In NMR, the frequencies are in the <u>10^8 Hz</u> range, which is 100,000 times lower frequency than EMR in the IR. At these lower frequencies (MHz), the oscillations of the EMR can be measured *directly*, which is not possible at the frequencies encountered in the IR (which then requires an interferometer to modulate the intensity of the EMR at frequencies proportional to the frequencies of the IR EMR).

c. Anodic Stripping Voltammetry (ASV) has the best detection limits of any voltammetric methods available today. Briefly outline the steps involved in an ASV analysis and indicate why it has detection limits superior to the other Echem methods we covered.

<u>Two steps:</u>

1. **<u>Electrolysis:</u> apply potential about 200 mV more negative than the E^0 of the analyte, stir to ensure high rate of reduction; reduced analyte forms an amalgam with Hg, preconcentrating the analyte within the HMDE – this is what is responsible for the superior detection limits with ASV.**
2. **<u>Anodic Linear Sweep Voltammetry.</u> Slow anodic sweep to oxidize analyte in HMDE; measure anodic current (proportional to concentration of analyte)**

In the measurement process, current is proportional to the concentration of the analyte in the HMDE, which is *far greater* than the concentration in the much greater volume of the original bulk solution.

6. <u>TRUE or FALSE.</u> - *20 pts each*

Indicate whether the following statements are ***TRUE*** or ***FALSE*** and briefly explain ***WHY***.

a. In a magnetic sector mass analyzer, resolution is limited by the rate at which the magnetic field can be swept.

<u>FALSE!</u>

Resolution is limited by the *spread of kinetic energies* of the ions entering the mass analyzer (separation assumes that all ions are accellerated to *exactly* the same potential). This uncertainty in K.E. translates to an uncertainty in the mass that will pass through the mag sector.

b. The flame atomic emission signal from sodium atoms at 589 nm in a sample containing only sodium will *increase* as an easily ionizable element (such as potassium) is added to the sample.

<u>TRUE!</u>

$Na \leftrightarrows Na^+ + e^-$

Adding K results in: $K \leftrightarrows K^+ + e^-$

This increases the concentration of electrons, shifting the Na ionization equilibrium to the *left*, *increasing the population of Na atoms*. So, Na atom emission increases.

c. Lock-in amplification is an effective method of improving the S/N of a measurement plagued by environmental noise occurring at a known specific frequency.

<u>TRUE!</u>

It *can* be used this way, if the signal can be modulated to a frequency *different from that of the noise*, then it can be amplified at the modulation frequency (with a specific phase relationship). In this way, in addition to reducing both flicker and white noise, the environmental noise (at the specific frequency) will be reduced in magnitude relative to the signal.

<u>FALSE!</u>

The sure-fire way to get rid of the environmental noise would be to employ a Fourier Filter, in which the signal is transformed into the frequency domain (via Fourier Transform), where the environmental noise can be isolated and all signal at that frequency eliminated, before performing an *inverse Fourier Transform*, bringing the signal (without the environmental noise) back to the time domain.

7. Still more **TRUE or FALSE.** - ***20 points each, unless stated otherwise***.
Indicate whether the following statements are ***TRUE*** or ***FALSE*** and briefly explain ***WHY***.

a. Spectral interferences are not experienced with ICP-AES methods; rather, spectral interferences are more of a problem with AAS methods.

FALSE!

In ICP-AES methods, resolution is determined by the dispersive device (typically a spectrometer), which limits resolution to about 0.1-0.01 Å. In atomic absorption methods, the hollow cathode lamp provides the selectivity, with linewidths that are typically about 0.01-0.001 Å. So, spectral overlap problems in atomic absorption are very unlikely, whereas they can be problematic (for complex materials) in atomic emission methods.

b. The ICP is an excellent elemental ionization source for mass spectrometry, even though most elements are only about 0.01% ionized in the ICP.

FALSE!

While it is true that the ICP is an excellent ionization source for mass spectrometry, most elements are >90% ionized due to the very high temperatures to which atomized samples are exposed to in the ICP. The fraction of elements *excited* in an ICP is, however, quite low (typically 0.01% or less), but it is a very efficient *ionization* source.

c. ***[5 pts]*** Instrumental analysis is my life . . .

TRUE! **(always and forever . . . at least for this semester ☺)**

Have a great summer!