

CHEM 221
Instrumental Analysis
EXAM #1

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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!

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!



"I'm on the verge of a major breakthrough, but I'm also at that point where chemistry leaves off and physics begins, so I'll have to drop the whole thing."

1. You are a supervisor in a laboratory which focuses on the determination of trace and ultra-trace levels of toxic substances in water samples. Usually, for the determination of Pb in water, a Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS) is used but, since it was down for repairs, one of the technicians that you supervise decided to use the operable Flame AAS instrument. After establishing that absorbance varied linearly with the amount of Pb, the following absorbance value data (for 5 replicate measurements) were obtained for a blank and for a sample submitted for analysis:

Blank:	0.001	Sample:	0.003
	0.002		0.002
	0.001		0.004
	0.000		0.002
	<u>0.002</u>		<u>0.003</u>
	<i>average:</i> 0.0012		<i>average:</i> 0.0028
	<i>standard deviation:</i> 0.0008		<i>standard deviation:</i> 0.0008

a. (15 pts) Based on the average absorbance value obtained for the sample, the technician reported that the water sample contained 350 ppb Pb (15 ppb Pb is the maximum Pb level allowed in drinking water!). As the lab supervisor, you are ultimately responsible for the analysis results that are reported. Should this result be reported? EXPLAIN. (NOTE: your response should be based on the above data. HINT: you may wish to calculate the S/N for the sample data . . .)

Let's calculate the S/N for this determination - if $S/N > 3$, then the Pb is, indeed, detectable in the sample:

$$\text{Signal} = X_{\text{avg}} (\text{Sample}) - X_{\text{avg}} (\text{blank}) = 0.0028 - 0.0012 = 0.0016$$

$$\text{Noise} = \text{std dev} = 0.0008$$

$$\text{So, } S/N = 0.0016/0.0008 = 2 < 3$$

Thus, there is no detectable amount of Pb in the sample and the result should NOT be reported.

b. (15 pts) If a 5000 ppb Pb standard gave an average absorbance value of 0.024, what would the detection limit (ppb Pb) be for the determination of Pb using this instrument?

$$5000 \text{ ppb } \text{Signal} = 0.024 - 0.0012 = 0.0228$$

$$\text{Signal at DL} = 3 \times 0.0008 = 0.0024$$

$$\text{Thus: } \frac{5000 \text{ ppb}}{\text{DL}} = \frac{0.0228}{0.0024} \Rightarrow \text{DL} = \underline{500 \text{ ppb Pb}}$$

2. **(20 pts)** The standard deviation for any measurement on the semi-microbalance in my lab is $5 \mu\text{g}$ (even though the digital readout goes out to $1 \mu\text{g}$). Alas, I need to measure masses of some microsamples that I expect will weigh pretty darn close to $3 \mu\text{g}$ and I don't have access to a better (micro) balance. I am not interested in actually *knowing* the masses of these samples, rather I would just like to be able to determine which samples have masses greater than or equal to $3 \mu\text{g}$. Suppose I have a sample that actually weighs $3 \mu\text{g}$ -- how many replicate weighings do I need to average in order to conclusively state that the sample mass is $\geq 3 \mu\text{g}$ (i.e., that a mass of $3 \mu\text{g}$ is detectable)?

$$\sigma = 5 \mu\text{g} = \text{Noise}$$

$$S = 3 \mu\text{g}$$

$$\text{SO: } (S/N)_{n=1} = 3 \mu\text{g}/5 \mu\text{g} = 0.60$$

How many measurements (n) to reach $S/N = 3$?

$$(S/N)_n = n^{\frac{1}{2}}(S/N)_{n=1}$$

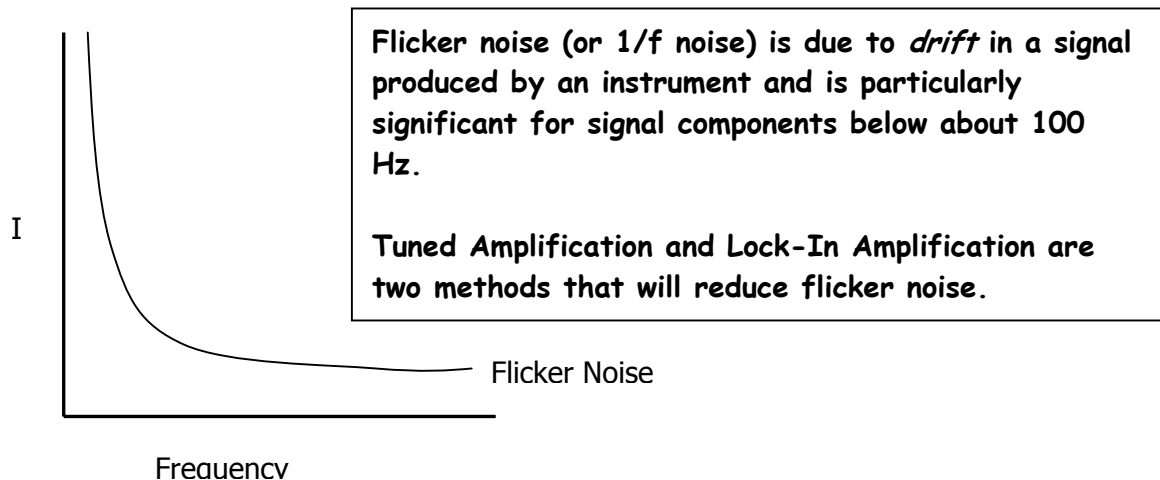
$$3 = n^{\frac{1}{2}}(0.60)$$

$$n^{\frac{1}{2}} = 5.0$$

$$n = (5.0)^2 = 25$$

Thus, need to make 25 measurements

3. **(15 pts)** Sketch the noise power spectrum for flicker noise, briefly explain what flicker noise is (an example would help here!), and give an example of a S/N enhancement method that specifically addresses the reduction of flicker noise.



4. Having just accepted a position with a major chemical company, Ms. (soon to be Dr.) Ima Notakroam Atograffer is interested in fine-tuning her lab skills prior to starting work. Since she will be working in an analytical separations group, she has been busy slaving over a hot GC, trying to resolve some straight-chain alcohols (as well as some of her remaining questions about separation science!). Since you are the resident chromatographer, you have offered to provide guidance on some of the issues raised by soon-to-be Dr. Atograffer over the course of her laboratory investigations.

The following data were obtained for Methanol and Ethanol using a 50.-cm long column at 200 °C:

Methanol:	$t_R=1.73$ minutes	$W=0.22$ minutes
Ethanol:	$t_R=1.90$ minutes	$W=0.24$ minutes

An injection of air gave a peak at 0.30 minutes.

a. (10 pts) Calculate the height of a theoretical plate (H) for Ethanol on this column under these conditions.

$$N = 16(t_R/W)^2 = 16(1.90/0.24)^2 = 1002.778 \text{ plates on the column}$$

For a 50.-cm long column:

$$H=L/N = 50. \text{ cm}/1002.8 \text{ plates} = 0.04986 \text{ cm/plate} = \boxed{5.0 \times 10^{-2} \text{ cm/plate}}$$

b. (10 pts) Calculate the adjusted retention time (t'_R) for a compound having a Kovats Retention Index of 184 on this column under these conditions.

You may recall that the Kovats retention index is *defined* as: $I = 100n$, where $n = \#$ carbons in a homologous series. This compound, then, has *retention behavior* which is *between* that of $n=2$ (ethanol) and $n=1$ (methanol) if $I=184$.

Recall also that a plot of $\text{Log}(t'_R)$ versus n for a homologous series will be *linear*. So, if we determine the equation of the straight line which results from the ethanol and methanol data, we can then solve for the t'_R for the compound (for $n=1.84$):

$$\text{First, calculate: } m = \Delta \text{Log}t'_R / \Delta n = (0.20412 - 0.155336) / 1 = 0.0487839$$

$$\text{Now, calculate: } b = Y - mx = \text{log}t'_R - (m \times n) = 0.155336 - (0.0487839 \times 1)$$

$$b = 0.1065521$$

$$\text{So, for } n = 1.84: Y = (0.0487839)(1.84) + 0.1065521 = 0.19631455 = \text{Log}t'_R$$

$$\text{Finally: } t'_R = 10^{0.19631455} = 1.57150 \text{ min} = \boxed{1.57 \text{ min}}$$

c. (5 pts) Calculate the carrier gas flow velocity (cm/min) used to acquire the above data.

$$u = L/t_M = 50. \text{ cm}/0.30 \text{ min} = 1.667 \times 10^2 \text{ cm/min} = \boxed{1.7 \times 10^2 \text{ cm/min}}$$

d. (10 pts) What effect would reducing the particle size of the packing have on the plate height of a column?

Two effects:

- 1) Decreased Eddy Diffusion (A term decreases)
- 2) Increased particle surface area, resulting in decreased stationary phase thickness and increased mass transfer in/out of the stationary phase (C term decreases)

BOTH of these will result in a decreased plate height.

e. (10 pts) Based on these data, will a mixture of Methanol and Ethanol be baseline resolved on this system? (Yes, you must do a calculation in order to get credit for your answer!)

$$R_S = \frac{2(\Delta Z)}{W_A + W_B} = \frac{2(1.90 - 1.73)}{(0.22 + 0.24)} = \frac{0.34}{0.46} = 0.739 < 1.5 \text{ - not baseline resolved}$$

f. (5 pts). Using the data given, calculate the capacity factor (k') for Ethanol.

$$k' = t'_R/t_m = \frac{(1.90 - 0.30) \text{ min}}{0.30 \text{ min}} = \frac{1.60}{0.30} = 5.33333 = \boxed{5.3}$$

g. (10 pts) Suppose the column length was doubled to 100. cm; what effect would this have on the capacity factor (k') for Ethanol?

The capacity factor (k') is a *thermodynamic quantity* and will vary only with the temperature of a system. This is shown clearly in the following equation:

$$k' = K(V_s/V_M) \text{ where: } \begin{array}{l} K = \text{Partition Coefficient} \\ V_s = \text{Volume of the stationary phase} \\ V_M = \text{Volume of the mobile phase} \end{array}$$

None of these terms should vary with the carrier gas flow velocity, so k' should be invariant with changes in carrier gas flow velocity: **NO CHANGE**

h. (10 pts) Calculate the retention time (t_R) for Ethanol on the 100.-cm column.

Doubling column length: 1) will double t_M (=0.60 min)
2) will have no effect on capacity factor (k')

So:

$$k' = (t_R - t_M)/t_M$$

$$5.33333 = (t_R - 0.60)/0.60$$

$$t_R = (5.3333 \times 0.60) + 0.60 = \boxed{3.80 \text{ min}}$$

i. (10 pts) Would Methanol and Ethanol be baseline resolved on the 100.-cm long column? (Yes, you need to do a calculation!)

Given that: $R_s = (N^{1/2}/4) [(\alpha - 1)/\alpha] [k_B'/(1 + k_B')]$

But we also know that α and k_B' are constant and that doubling the column length should double the number of plates, so we can write:

$$\frac{R_s(50 \text{ cm})}{R_s(100 \text{ cm})} = \frac{(N_{50 \text{ cm}})^{1/2}}{(N_{100 \text{ cm}})^{1/2}} \Rightarrow \frac{0.739}{R_s(100 \text{ cm})} = \frac{(1003)^{1/2}}{(2006)^{1/2}} = 0.707107$$

$$R_s = 0.739/0.707107 = \boxed{1.05 < 1.5 \text{ so still not resolved!}}$$

j. (15 pts) After compiling retention data on straight-chain alcohols from Methanol to Decanol, Ms. Atograffer attempts to separate a mixture containing ALL TEN of the alcohols. In her first attempt, she operates the column at 200 °C and finds that it takes too long for the last alcohol to elute (more than 5 minutes). However when she increases the temperature to 350 °C to speed up the separation, the first eluting alcohols are not resolved anymore. Describe the phenomenon she is observing - base your description on capacity factors (k') and suggest a way in which Ms. Atograffer can successfully separate all ten of the alcohols in a single chromatogram.

This is the *General Elution Problem*: conditions which give good α -values (k' ratios) for *some compounds* give near unity α -values for others (i.e., there is no single temperature at which all ten alcohols will elute with k' -values less than 10 and give satisfactory α -values).

The solution: vary the temperature over the time of the chromatogram (temperature programming) such that each compound elutes with a reasonable k' (this *dynamically* adjusts α so that all compounds can be resolved).

k. (10 pts) While Ms. Atograffer is off at lunch, you decide to do a last-minute analysis of an environmental sample suspected of containing chlorinated hydrocarbon residues. What common detector should you use in order to give the best sensitivity and selectivity for these compounds?

The Electron Capture Detector (ECD) would be ideal for this application as it has the desired detectability and selectivity.

Detection Limits: DL obtained with the ECD are in the range of 10^{-9} - 10^{-12} g, enabling ultratrace (ppb) level determinations to be performed.

Selectivity: The ECD is selective to compounds with a high affinity for electrons, so it is specific to the chlorinated hydrocarbon compounds that are being analyzed and will not produce signals for many of the other potentially interfering compounds in the samples being tested.

QUICKIES (10 points each) - No more than 2 sentences!

a. A gas chromatographic separation of a mixture of polar compounds was performed on a column having a stationary phase of didecylphthalate, a solvent of intermediate polarity. If a nonpolar solvent such as a silicone oil had been used as the stationary phase instead, would the retention times for the compounds in the mixture be larger or smaller? Why?

Smaller retention times would result: the polar compounds in the sample will have **LESS** affinity for the nonpolar stationary phase, reducing the time spent in the stationary phase, so the compounds will elute in less time (spending more time in the mobile phase).

b. Why do open tubular columns produce gas chromatograms with significantly better resolution than do packed GC columns?

OT columns have plate heights that are similar to those found with packed columns, BUT because they do not have any packing to restrict the flow of the mobile phase, OT columns can be up to 100x longer than packed columns. This 100-fold increase in theoretical plates greatly improves the resolution obtainable with OT columns.

c. Briefly explain how a *Fourier Filter* would be employed in order to remove an interference noise component of a signal that occurs at a well-defined frequency (f_0). (i.e., How does it work?)

First, we use a Fourier Transform to convert the signal from the *time domain* to the *frequency domain*, which allows us to view the signal components based on their frequency properties. There should be a peak at the frequency of the interference noise (f_0) - we can then multiply the frequency domain signal by a function that zeros out the interferent peak at f_0 . Now that the noise has been removed, we can do an *Inverse* Fourier Transform and convert the cleaned up frequency domain signal back to a time domain signal that will no longer have the interference noise component.