Chem 454 – Exam 1 – February 9, 2011

1] (20 points) Draw a Jablonski diagram illustrating the processes of

- absorption
- fluorescence
- phosphorescence
- intersystem crossing
- internal conversion

2] (5 points) In reference to that Jablonski diagram what is external conversion? To which signal is it most detrimental?

3] (5 points) Write down the expected response of a Ca^{2+} ion selective electrode.

4] (10 points) In concise language describe the concepts of accuracy and of precision. How are they different? The statistical term, standard deviation is most associated with which, accuracy or precision?

5] (5 points) Calculate the 95% confidence interval for an experimental result of 32.93 ppb +/- 0.11 ppb with five experimental runs.

$$\mu = \bar{x} \pm \frac{t\sigma}{\sqrt{n}} \quad (1)$$

df	50%	90	95	98	99	99.5	99.99
3	0.765	2.353	3.182	4.541	5.841	7.453	12.92
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959

6] (10 points) With a graph clearly indicate the concepts of

a. detection limit (what is that value?)
b. sensitivity
c. background
d. linear range

7] (10 points) Given the following calculate the standard reduction potential for

$PbSO_4(s) + 2e^- = Pb(s) + SO_4^{2-}(aq)$ $E^0 = ?$

$Pb^{2+}(aq) + 2e^- = Pb(s)$ $E^0 = -0.126$ V

$PbSO_4(s) = Pb^{2+}(aq) + SO_4^{2-}(aq)$ $K_{sp} = 6.3e\text{-}7$

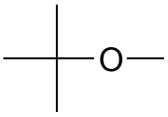
8] (10 points) An analysis for arsenic (as As_2O_3) was conducted by anodic stripping voltammetry. The sample itself gave a current of 10.8 μA. Another sample with a spike of 11.7 ppm of As(III) and gave a current of 17.2 μA. What is the concentration of As(III) in the sample?

Chem 454 – Exam 2 – March 8, 2011

10 points each, 70 points total

1] Draw an energy diagram (Jablonski-type) describing the Raman effect. Include Stokes, anti-Stokes, and Rayleigh scatterings.

2] Using one of the various techniques described since Exam 1 which would be best for the analysis of MTBE in gasoline? Consider that MTBE is a few percent by volume in gasoline. Justify your answer.



MTBE, methyl tert-butyl ether

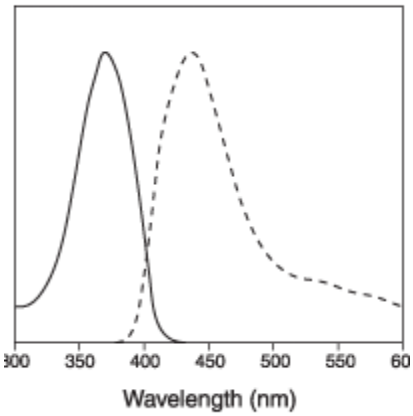
3] How does the graphite furnace AA spectrometer achieve a lower limit of detection than the flame AA spectrometer? What is a major problem normally associated with GFAA?

4] Of the techniques discussed since Exam 1 which would least influenced by matrix effects? Why?

5] What is an HCL? Draw a schematic and describe how it works, its output, and its application.

6] What are flicker, 60 Hz, and shot noises? How do they appear in a signal vs. frequency spectrum? Why is 60 Hz considered environmental noise? How can it be addressed?

7] Below is a fluorescence spectrum for a molecular stain bound to DNA. Which part of this spectrum is an excitation spectrum? Which is an emission? Why are they different?



Chem 454 – Exam 3 – April 27, 2011

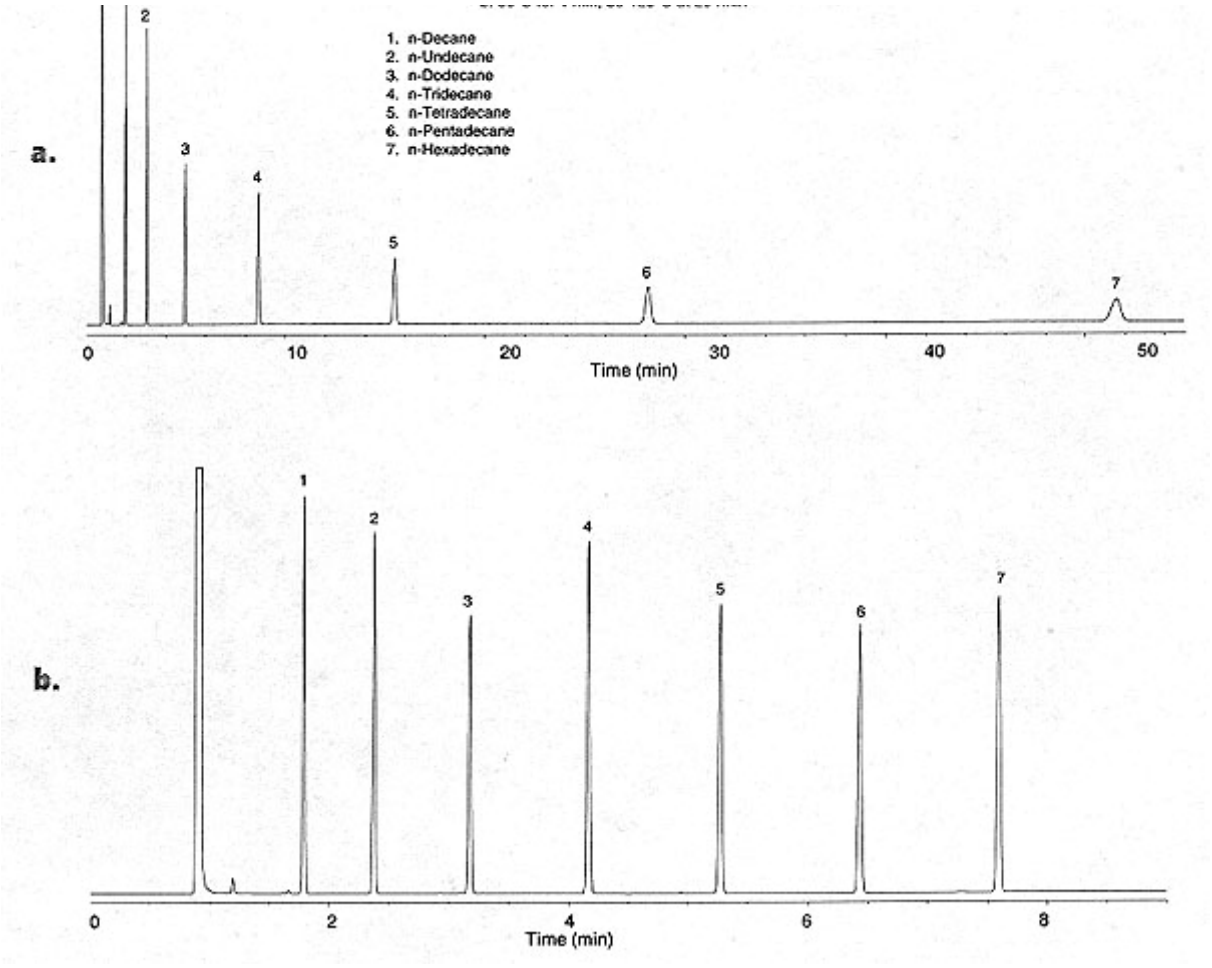
7 question, 5 points each.

1] Below are gas chromatograms for 7 solutes.

a. Which of the two would you expect to be a temperature programmed chromatogram? Which is isothermal? Explain why.

b. Sketch a reasonable temperature program for question 1a, clearly label the axes.

b. Explain the elution order, why does the pattern of solute 1-7 not change in the two chromatograms?



Undecane: $C_{11}H_{24}$, Dodecane: $C_{12}H_{26}$, tridecane: $C_{13}H_{28}$, tetradecane: $C_{14}H_{30}$, Pentadecane: $C_{15}H_{32}$, Hexadecane: $C_{16}H_{34}$

2] When designing a binary (CH_3CN:H_2O) mobile phase for gradient elution on using a C-18 stationary phase would it be best to increase or decrease the proportion of water during elution? Why?

3] A GC analysis was conducted on a sample with analyte X. The table below describes the analysis:

Run	X (concentration, peak area, t_r)	IS (concentration, peak area, t_r)
1	112 ppm, 11,202, 6.77 minutes	77.0 ppm, 5,998, 3.44 minutes
2	Unknown, 13,772, 6.67 minutes	77.0 ppm, 6,122, 3.45 minutes

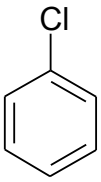
IS is the internal standard. What is the concentration of X in Run 2? Watch Significant Figures.

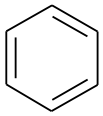
4] Using the van Deemter Equation, H = A + B/u + Cu explain why the number of theoretical plates for CE is much greater than for HPLC systems.

5] Predict the elution order of the following solutes in reversed phase HPLC.

a] 

b] 

c] 

d] 

6] a. What is APCI?

b. How is it related to electrospray?

c. Is it a hard or soft ionization technique?

d. What is the difference between hard and soft ionization?

7] Sketch a schematic of an FID. What sorts of analytes are detectable with an FID? Which separation system is it associated with the FID?

Chem 454 Instrumental Analysis Spring 2011

American Chemical Society Instrumental Analysis Exam Form 2009

X – National Percentile; Y – Frequency

UI Average – 82nd Percentile