

Chemistry 312 Final Exam A
August 2000

- Answer one question from section A, three questions from section B, answer one question from section D, answer one question from section E, three questions from section F and one question from section G.
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- When asked for the advantages and disadvantages of a method or instrument be sure to justify your claim. For example:
 - advantage: long linear dynamic range of 5 orders of magnitude.
 - disadvantage: expensive (\$40000-\$100000), because each detector costs \$1000-\$2000 and there is a detector for each element.The more information that you give me the more marks I can give you!!
- If you answer an extra question the lower mark in that section will be thrown out.

Statistics and Atomic Spectroscopy

SECTION A (Answer ONE question, 5%)

1a) Two students have obtained the following mean values for the same sample using a well established method. Is there a statistically important difference between these two means at the 99% confidence level?

Student 1: mean = 78.8 $\mu\text{mol/L}$, 5 measurements

Student 2: mean = 83.5 $\mu\text{mol/L}$, 6 measurements

The well established standard deviation of the method = 4.0 $\mu\text{mol/L}$

2a) Why are mirrors preferred for focusing light into monochromators?

3a) Why is ICP-MS the preferred method of determining rare earth elements such as Cerium?

SECTION B (Answer THREE questions, 30%)

- 1b) Derive the Beer-Lambert law for absorption. Use a drawing to clarify the terms that you are using.
- 2b) You have been asked to help a co-worker develop a method of analyzing seawater for a variety of trace elements using ICP-MS. Your partner is having difficulty obtaining accurate results using simple aqueous standards. He finds that most of the ion intensities are lower than expected. Suggest reasons for the difficulty, and how to solve the problem.
- 3b) You have been asked to help a co-worker develop a method of analyzing seawater for trace elements using flame atomic emission. Your co-worker is having difficulty obtaining accurate results using simple aqueous standards. She finds that atomic emission lines are more intense whereas ionic emission lines are less sensitive. Suggest why she is observing the unexpected line intensities, having difficulty quantitating the trace elements and how to solve the problem.
- 4b) Why are electrodeless discharge lamps preferred for atomic fluorescence measurements? Why are hollow cathode lamps preferred for atomic absorption measurements? (Hmm, look familiar?)
- 5b) A student has obtained the following measurements: 12.0, 12.1, 11.8, 14.2 Volts. Calculate the concentration of the sample given that the slope of the calibration curve is 42 Volts/ppm and the intercept is 2.4 Volts.
- 6b) Draw and describe a flame atomic absorption instrument that uses a deuterium lamp for background correction. Be sure to include all of the necessary parts. Describe how the absorption measurement is taken.
- 7b) Draw and describe an echelle spectrometer. What are the advantages and disadvantages of this type of spectrometer?

SECTION C (Answer ONE question, 15%)

For the following questions, verify that the calibration curve is “perfectly” straight, you should not have to use the least squares method for determining the calibration curve (its too @#%\$@* long)

1c) The following data was collected in the lab from an experiment.

| Concentration | Signal from internal standard | Signal from analyte |
|---------------|-------------------------------|---------------------|
| 0 | 1.356 | 0.041 |
| 1 | 1.539 | 0.908 |
| 2 | 0.881 | 1.013 |
| 5 | 1.906 | 5.394 |
| unknown #1 | 1.383 | 1.978 |
| unknown #1 | 1.102 | 1.638 |
| unknown #1 | 1.356 | 1.863 |

Determine the concentration of the unknown (from the three measurements) at the 99% confidence level.

2c) The following is data from a standard additions experiment. Calculate the concentration of the unknown at the 95% confidence level. The concentration of the standard is 200 $\mu\text{g/ml}$.

| Volume of std (ml) | Volume of sample (ml) | Total volume (ml) | Signal |
|--------------------|-----------------------|-------------------|-------------------------|
| 0 | 20 | 50 | 201.6 208.9 188.8 |
| 10 | 20 | 50 | 453.6 |
| 20 | 20 | 50 | 705.6 |
| 30 | 20 | 50 | 957.6 |

Chromatography

SECTION D (Answer ONE question, 5%)

1d) Explain why fused silica is used for open tubular gas chromatography columns?

2d) Explain why exposed silanol groups on the surface of GC stationary phases can cause peak tailing for some analytes.

3d) A FSOT column is 50 meters long and has an inside diameter of 0.25 mm and a film thickness of 1 micron. What is the ratio of concentration of the analyte is in the stationary phase to that in the mobile phase if k' is 10?

4d) Does increased diffusion in the mobile phase always lead to poorer performance (increased plate height)? Justify.

SECTION E (Answer THREE questions, 30%)

1e) If you wanted to analyze a sample of wine for the presence of sulfur containing flavinoids (flavour producing compounds) what type of chromatographic system would be suitable and why? (injector, column, stationary phase, detector mobile phase...)

2e) The following data has been calculated from the chromatogram. The column is 100 cm long and the unretained marker takes 2 minutes to be detected. Calculate the resolution for the peaks (A-B, B-C). How long must the column be in order to have baseline resolution? Assume the plate height, flow rate, selectivity and retention factor (capacity factor) will remain constant. If you use a shortcut equation in calculating the resolution, justify. (This should be old hat by now!)

| Compound | Plate number | Retention factor |
|----------|--------------|------------------|
| A | 2450 | 6.4 |
| B | 2500 | 7.8 |
| C | 2850 | 8.8 |

3) Draw and describe a flame ionization detector. What are its advantages and disadvantages (remember to quantify/justify your statements)?

4) HPLC is much less efficient than GC (10000 to 60000 plates/column compared to 50000 to 500000 plates/FSOT column). Why is GC not used for all analyses? (there are several reasons)

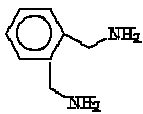
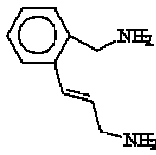
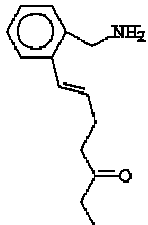
5) Draw and describe a refractive index detector. How does this detector function? What are its advantages and disadvantages (remember to quantify/justify your statements)?

6) Explain how ion-exchange chromatography can give peaks (like partition chromatography) even though the analyte ions are NOT partitioning with the stationary phase. (you should use some chemical equilibria equations)

SECTION F (Answer ONE question, 15%)

1f) A HPLC separation has been run with a 25% acetonitrile 75% water mobile phase. The unretained marker elutes in 1.3 minutes and the following retention times were recorded for the following analytes.

- i- Calculate an appropriate acetonitrile/water mixture to elute the analytes in a reasonable amount of time. Justify your choice for a reasonable amount of time. A quick look in the solvent cabinet reveals the following: Toluene ($P'=4.0$), Acetonitrile ($P'=5.8$), Water ($P'=10.2$), Ethanol ($P'=4.3$), Cyclohexane ($P'=0.04$) and Methanol ($P'=5.1$).
- ii- It is apparent that the first and second analytes will not be well resolved. Suggest how would you correct your solvent mixture to improve resolution (no need for calculations)?

| Analyte & Retention time |
|---|
|  <p>Analyte #1 $t_r = 11$ min</p> |
|  <p>Analyte #2 $t_r = 12$ min</p> |
|  <p>Analyte #3 $t_r = 26$ min</p> |

2f) Given the following parameters: the stationary phase is the same for both columns. The diffusion coefficient in the mobile phase is 3.3×10^{-4} cm²/s, in the stationary phase the diffusion coefficient is 2.6×10^{-6} cm²/s. The mobile phase flow rate is 1.2 cm/s, the obstructive factor is 0.6, the tortuosity factor is 0.8 and the film thickness is 0.1 microns. Assume that both the stationary phase mass transfer function and the mobile phase mass transfer function are equal to 0.3. What sort of increase in efficiency (plates/m) would be expected if the diameter of the particles is reduced from 10 microns to 5 microns?