

Chem 384 – Bioanalytical Chemistry  
Interim 2009  
Problem Set #1  
Due Monday, Jan. 12

All problems from “Bioanalytical Chemistry” by Mikkelsen and Cortón

1. Chap. 1 - #1
2. Chap. 3 - #5
3. Chap. 9 - #1
4. Chap. 9 - #2
5. Chap. 10 -#1
6. Chap. 10 -#2
7. Chap. 10 -#4
8. Chap. 11 -#2
9. Chap. 11 -#4
10. Chap. 11 -#6
11. Chap. 11 -#7
12. Chap. 14 -#2
13. Chap. 14 -#4

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Interim 2009  
Problem Set #2  
Due Wednesday, Jan. 14

Problems from “Bioanalytical Chemistry” by Mikkelsen and Cortón

1. Chap. 6 - #2
2. Chap. 6 - #4
3. Chap. 9 - #3
4. Chap. 9 - #4
5. Chap. 9 - #5
6. Chap. 12 - #1
7. Chap. 12 - #2
8. Chap. 12 - #6
  
9. A solution in a particular capillary has an electroosmotic mobility of  $2.3 \times 10^{-8} \text{ m}^2/(\text{V}\cdot\text{s})$  at pH 3.0 and  $9.5 \times 10^{-8} \text{ m}^2/(\text{V}\cdot\text{s})$  at pH 10.0.
  - a. How long will it take a neutral analyte to travel 65 cm from the injector to the detector window if 25 kV are applied across the 75 cm long capillary at pH 3.0?
  - b. At pH 10?
  - c. An analyte anion has an electrophoretic mobility of  $-1.9 \times 10^{-8} \text{ m}^2/(\text{V}\cdot\text{s})$ . How long will it take for this analyte to reach the detector at pH 3.0?
  - d. An analyte cation has an electrophoretic mobility of  $1.2 \times 10^{-8} \text{ m}^2/(\text{V}\cdot\text{s})$ . How separated (measured in time) will these two analytes be if a pH 3.0 solution is used with the same instrumental parameters listed above
  
10. The water soluble vitamins niacinamide (a neutral compound), riboflavin (a neutral compound), niacin (an anion), and thiamine (a cation) were separated by micellar electrokinetic chromatography in pH 8.0 buffer with 50 mM SDS. The migration times were 8.1 min, 13.0 min, 14.3 min, and 21.9 min respectively. What would the order have been in the absence of SDS? Which compound is most soluble in the micelles?

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Problem Set #3  
Due Wednesday, Jan. 21

Problems from “Bioanalytical Chemistry” by Mikkelsen and Cortón

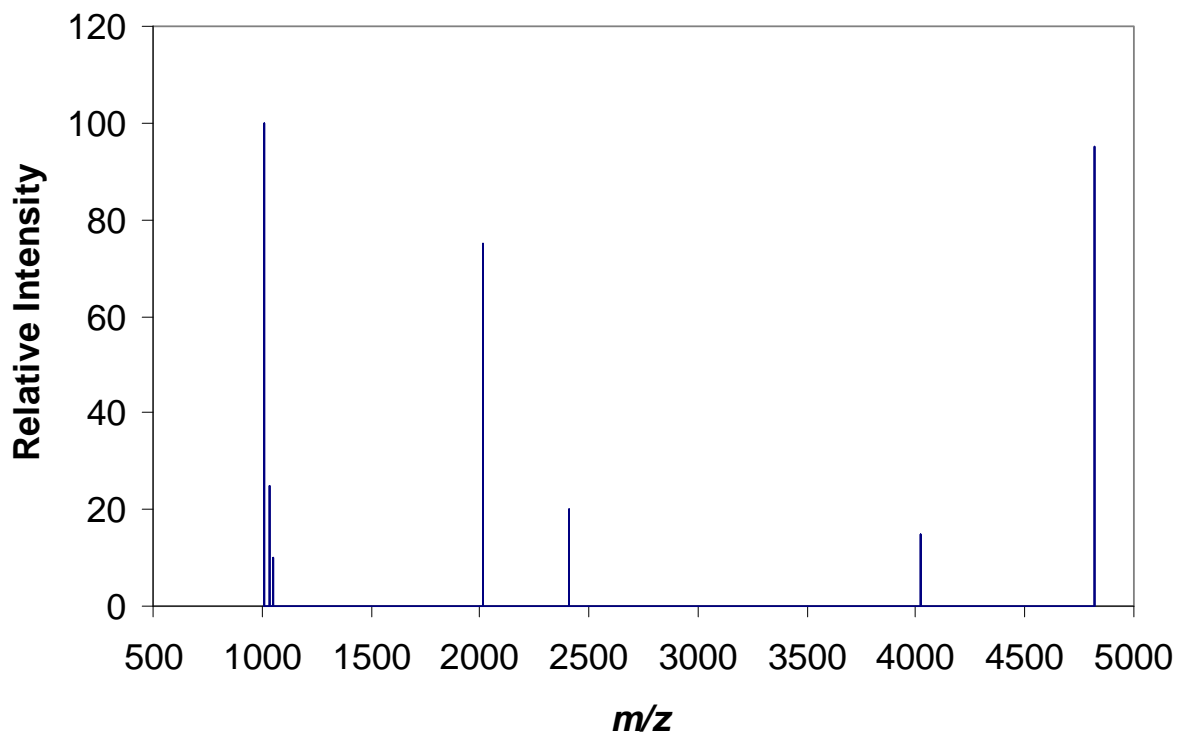
1. Chap. 15 - #1
2. Chap. 15 - #3
3. Chap. 15 - #4
4. Spectrum 1 is a MALDI spectrum of a mixture. The peak list is given below. Identify how many compounds are present in the mixture and list the molecular weight of each compound. Also, indicate the species that each peak represents.

<u><i>m/z</i></u>	<u>Ion Count</u>
1012	100
1034	25
1050	10
2013	75
2410	20
4025	15
4819	95

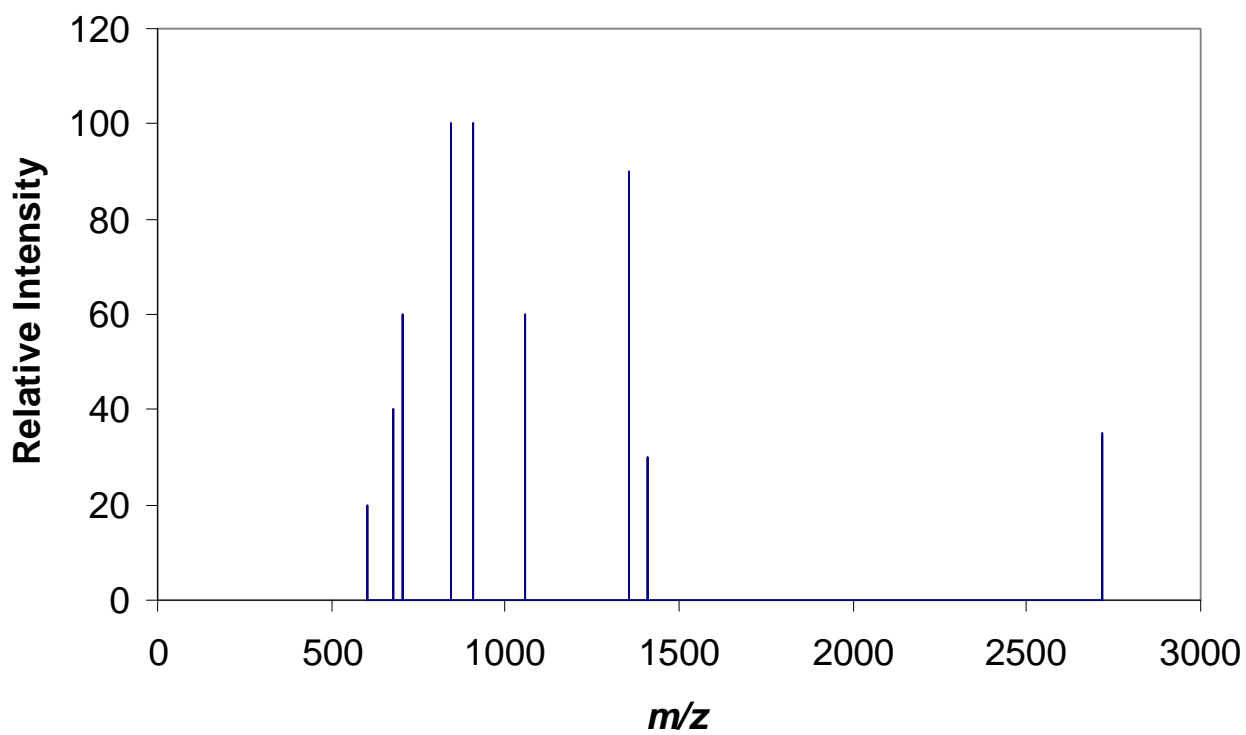
5. Spectrum 2 is an ESI spectrum of a mixture. The peak list is given below. Identify how many compounds are present in the mixture and list the molecular weight of each compound. Also, indicate the species that each peak represents including the charge.

<u><i>m/z</i></u>	<u>Ion Count</u>
603.6	20
679.5	40
704.0	60
844.6	100
905.7	100
1055.5	60
1358.0	90
1407.0	30
2715.0	35

# Spectrum 1: MALDI Experiment



## Spectrum 2: ESI Experiment



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Problem Set #4  
Due Monday, Jan. 26

1. The following ions were observed in a MALDI spectrum of a tryptic digest from an unknown protein. The molecular weight of the protein is approximately 20,000 Da as determined from SDS-PAGE. Using a database, determine the identity of the protein. Assume all peaks are monoisotopic and singly charged. Please attach a copy of the database printout.

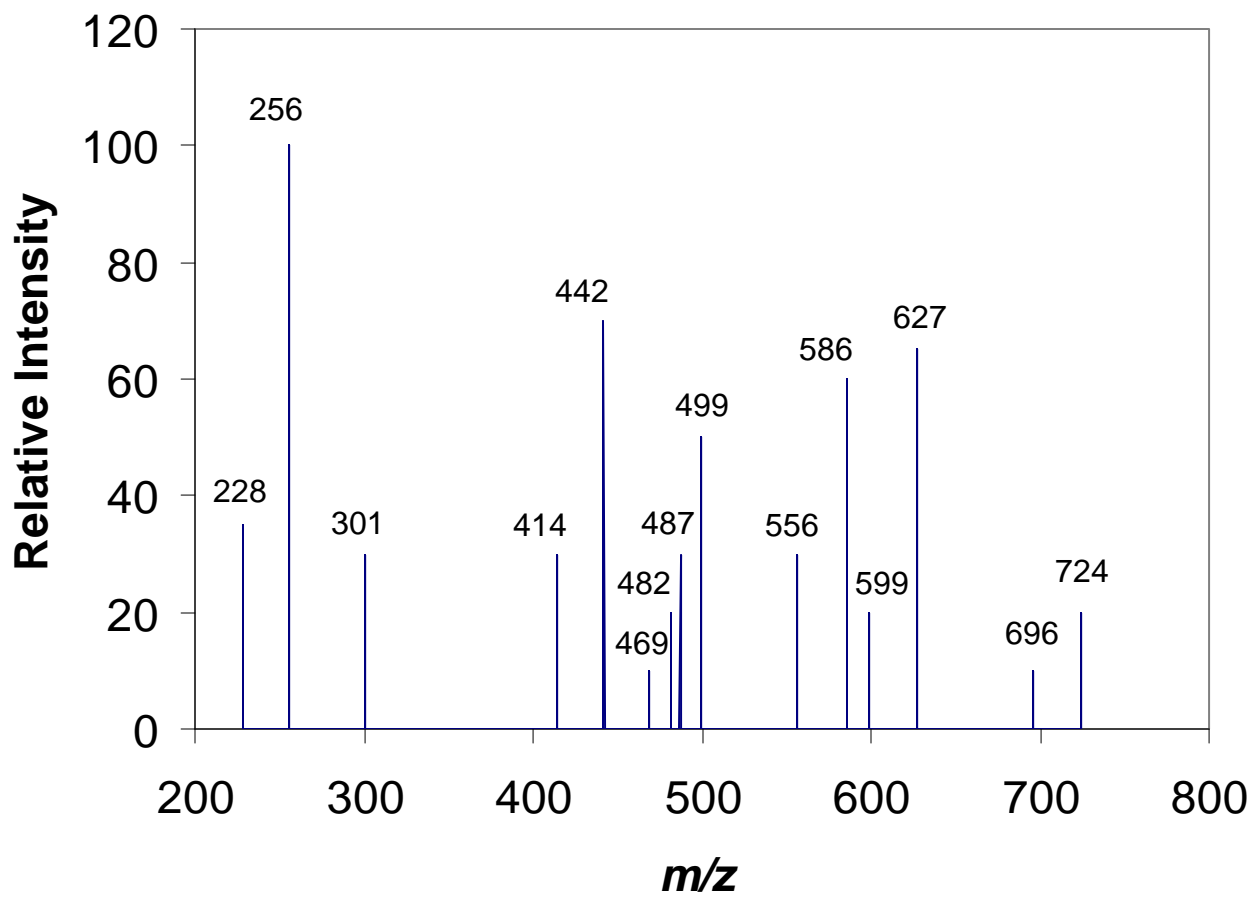
*m/z*  
544.35  
578.27  
796.39  
1039.53  
1313.77  
1452.74  
1545.72  
1556.90  
2021.00  
2242.06  
3121.44

2. Explain how a neutral-loss experiment is performed. What type of instrument is required for such an experiment? List one example of an application where neutral-loss would be used.
3. List the molecular weight, the 'a' ions, 'b' ions, and 'y' ions that would result from a CID experiment on the following peptide:

Y-F-L-R-S

4. The  $(M+H)^+$  peak of a peptide was observed at  $m/z$  742. The  $(M+H)^+$  peak was selected and fragmented using CID to give the MS/MS spectrum shown in Figure 1. Determine the sequence of the peptide. Also, list the peak assignments for all peaks.

# CID of $m/z$ 742



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Interim 2009  
Problem Set #5  
Due Thursday, Jan. 28

Problems from “Bioanalytical Chemistry” by Mikkelsen and Cortón

1. Chap. 13 - #1
2. Chap. 13 - #2
3. Chap. 13 - #5
4. Chap. 13 - #6
5. Data were collected for two proteins in water at 25 °C:

<u>Protein</u>	<u>Sedimentation coefficient (S)</u>	<u>Diffusion coefficient (cm<sup>2</sup>/sec)</u>	<u>Partial specific volume (cm<sup>3</sup>/g)</u>
Concanavalin	6.40	$5.10 \times 10^{-7}$	0.730
Myosin	6.43	$1.10 \times 10^{-7}$	0.730

Calculate the molecular weight for each protein.

6. List one chemical species that would interfere with an oxygen-sensing probe and briefly explain why this species would interfere.