

STIA – Assignment – Final_21

Note: Answers should be *truly brief and to the point*.

Problem 1. How many types of nuclear spin orientations are observed when a proton is placed in a magnetic field? Which spin orientation state has higher energy? [2+1]

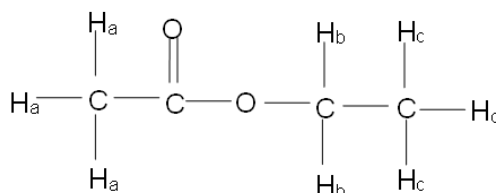
Problem 2. A nucleus has a spin quantum number of $3/2$. How many magnetic energy states does this nucleus have? What is the magnetic quantum number of each? [1+1]

Problem 3. The difference in the number of nuclei lined up against each other at equilibrium is given by, $\Delta N \approx h\gamma B_0 N_0 / 2\pi kT$. Prove it. [3]

Problem 4. The compounds with the following molecular formulas show only one ^1H NMR signal each. Draw their structural formulas. [2+2]

(a) C_8H_{18} (b) $\text{C}_2\text{H}_6\text{O}$

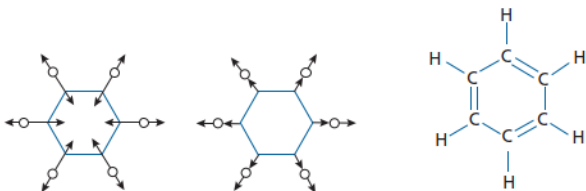
Problem 5. The structural formula of ethyl ethanoate ($\text{CH}_3\text{COOCH}_2\text{CH}_3$) is shown below. The letters a, b, & c beside H indicate the types of protons. Based on this information, fill up the Table given below for the ^1H NMR spectrum of this compound. [3×3]



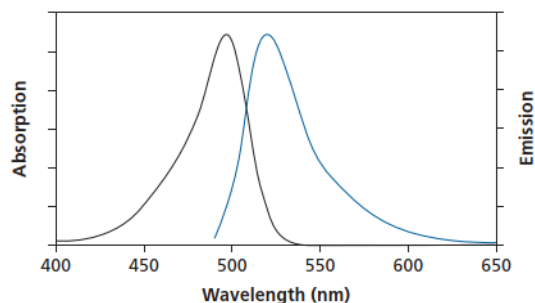
Proton	integration	δ / ppm	splitting
H_a			
H_b			
H_c			

Problem 6. Which would you expect to have the largest Raman frequency, carbon–carbon single bonds, double bonds, or triple bonds? [2]

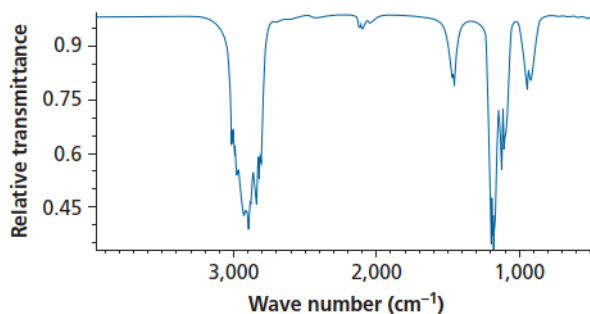
Problem 7. Two normal modes for benzene (C_6H_6) are shown. The first occurs at $3,061\text{ cm}^{-1}$ (called the C–H stretch, where the hydrogen and carbon move in opposite directions) and the second at 992 cm^{-1} (called the ring stretch, where the hydrogen and carbons move in the same direction). Would you expect these vibrations to be Raman active? Would you expect them to be IR active? [2+2]



Problem 8. The excitation (black) and emission (blue) spectra for rhodamine 110 are shown here. You have access to an argon ion laser operating at 488 nm and a Nd:YAG laser operating at 532 nm with your Raman instrument. **Which** laser would you recommend using for rhodamine 110 and **why**? [2+4]



Problem 9. The spectrum seen here was taken as a KBr pellet and belongs to a compound with the formula $\text{C}_2\text{H}_6\text{O}$. Determine the identity of the compound. Justify your answer. [8]



Problem 10. While IR spectroscopic measurement, arrangement is done to avoid the interference arising from moisture and carbon dioxide but nothing is done to remove nitrogen. However, nitrogen content is much higher than that of moisture and carbon dioxide in air. Explain why?

[3]

Problem 11. How can you explain that the anti-Stokes lines of carbon tetrachloride have the following order of intensity: $219 > 314 > 459 \text{ cm}^{-1}$?

[3]

Problem 12. (a) Name two instrumental methods that can be used for elemental qualitative analysis.

(b) Name the instrumental methods that are used for elemental quantitative analysis.

(c) Name three instrumental methods that can be used for molecular organic functional group identification.

(d) What instrumental methods provide molecular structural information, that is, indicate which functional groups are next to each other in an organic molecule?

(e) What instrumental analysis methods are best (in terms of limit of detection) for *quantitative* analysis of (i) pure compounds (ii) simple mixtures, and (iii) complex mixtures? [2+2+3+1+3]

Problem 13. What is meant by “molecular ion”? What is the importance of identifying it to an analyst?

[1+1]

Problem 14. Calculate the resolution required to resolve peaks for

(a) $\text{C}_3\text{H}_7\text{N}_3^+$ ($M = 85.0641$) and $\text{C}_5\text{H}_9\text{O}^+$ ($A_t = 85.0653$).

(b) androst-4-en-3,17,-dione (M^+) at $m/z = 286.1930$ and an impurity at 286.1240 . [2+2]

Problem 15. Mention one advantage of the fragmentation produced with electron impact ionization.

[1]

Problem 16. (a) Which type of ionization source (hard or soft) is more useful for molecular mass determination? (b) Which for compound identification? (c) Which for structure elucidation?

Give your reasoning with your answer.

[2+2+2]

Problem 17. You have the following samples for MS study. Suggest suitable method of ionization for MS for each of the following samples. Briefly give your reasoning. [2+2+2]

(a) Dioxin, a byproduct of the bleaching of paper by chlorine.

(b) Horseradish peroxidase.

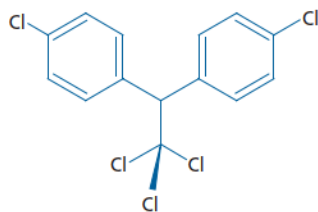
(c) Steel shavings.

Problem 18. Calculate the ratio of the $(M + 1)^+$ to M^+ peak heights for footballene (fullerene) (formula: C_{60}), knowing that carbon has two isotopes ^{12}C : 12 amu (98.9%) and ^{13}C : 13 amu (1.1%). [3]

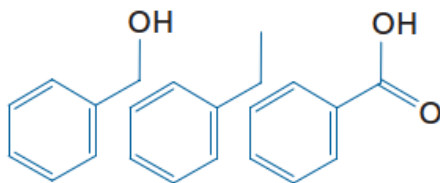
Problem 19. Calculate the ratio of the $(M + 2)^+$ to M^+ and the $(M + 4)^+$ to M^+ peak heights for (a) $C_{10}H_6Br_2$ and (b) C_3H_7ClBr . [2,2+2,2]

Given: For 100 ^{79}Br atoms there are 98 ^{81}Br atoms. For every 100 ^{35}Cl atoms there are 32.5 ^{37}Cl atoms.

Problem 20. The mass spectrometric analysis of the common pesticide DDT ($C_{14}H_9Cl_5$) resulted in a base peak of $m/z = 352$, with the only other major peaks being 317, 235, and 165. Postulate about the type of ionization (EI or CI), the most logical mode of ionization (negative or positive mode); the ionization reaction responsible for the base peak; and the $m/z = 317$ peak. [2+2]



Problem 21. Based solely on molecular polarity, predict the most likely order of elution for the following set of three compounds in a normal phase chromatographic experiment. [3]



Problem 22. Predict the elution order of (n-Octane, n-octanol, and naphthalene) for a normal-phase (NP) and a reversed-phase (RP) separation. [3×2]

Problem 23. (a) What type (polar/nonpolar) of stationary phases should one recommend for the analytical separation of polar analytes? Why? [2]

(b) If an analyte is strongly polar, whether a strongly polar/nonpolar or a weakly polar/nonpolar stationary phase should one use for a reasonable separation? Why? [2]

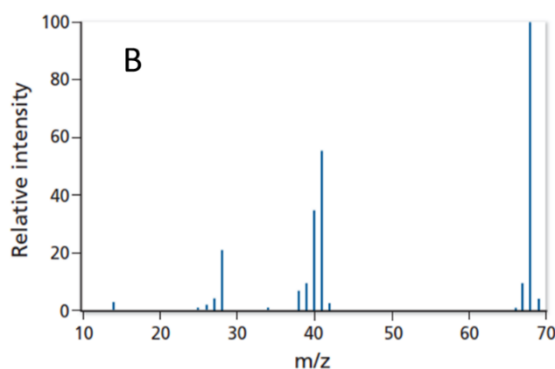
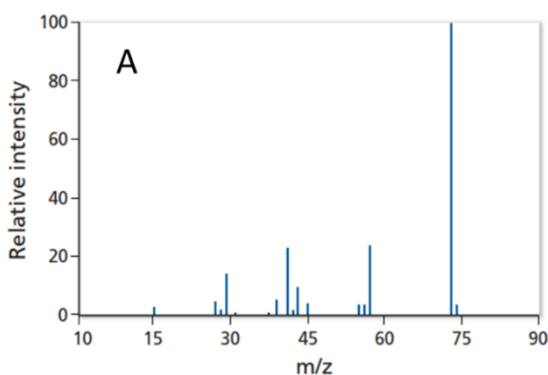
Problem 24. In preparing a hexane-acetone gradient for an alumina HPLC column, is it desirable to increase or decrease the proportion of hexane as the column is eluted and why? [2]

Problem 25. What is the order of elution of the following compounds from a normal-phase packed HPLC column? Justify your answer. Compounds are: Geometric isomers: o-, m-, and p-nitroaniline. [3]

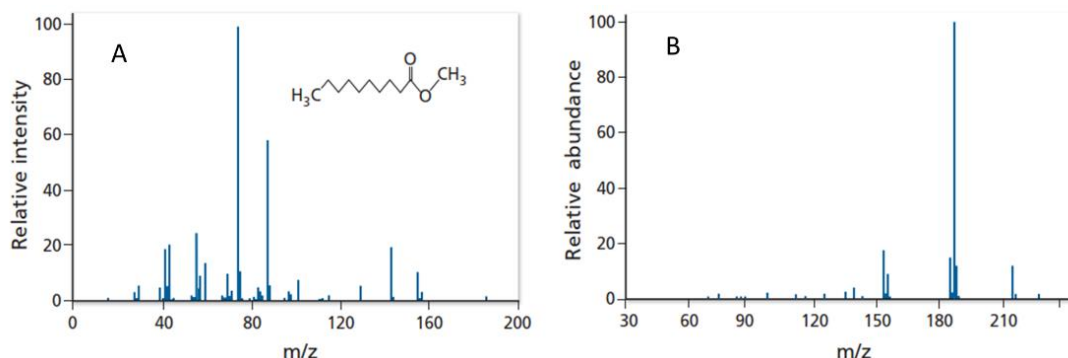
Problem 26. You have learnt several types of liquid phase chromatographic (LC) separation procedures. Suggest one (or more) suitable LC separation method(s) for the following analyte mixtures: [8×2]

- (a) A mixture of alkaline earth metal halides
- (b) Peptides from a tryptic digest
- (c) A partially racemized, optically active, drug molecule having phenolic groups
- (d) Isolation of a single antibody protein from a preparation of disrupted cells
- (e) A mixture of hydrocarbon ethers
- (f) A mixture of polysaccharide polymers (e.g., starches or sugars)
- (g) A mixture of fullerenes
- (h) A preparative extract of a mixture of spice essences from leaves

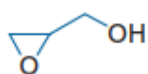
Problem 27. Electron impact ionization was used to obtain the following mass spectra A & B. One of them corresponds to imidazole and the other one to methyl tert-butyl ether. Match these compounds to A and B. Justify your answer. [2,2]



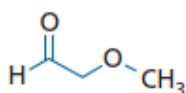
Problem 28. The following mass spectra (A & B) of the methyl ester of decanoic acid ($C_{11}H_{22}O_2$, 186.3 g/mol) were obtained using chemical ionization and electron ionization. Which MS was most likely obtained with chemical ionization? How did you reach that conclusion?



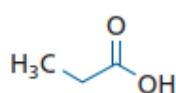
Problem 29. From the mass spectral and elemental analysis data, you have determined the formula of an unknown compound from a petroleum distillate to be $C_3H_6O_2$. You have limited the possibilities to the four different structures shown. Each has the formula $C_3H_6O_2$.



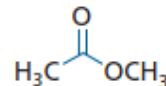
A: Glycidol



B: Methoxyacetaldehyde



C: Propionic acid



D: Methyl acetate

- Describe how an IR spectrum would aid in narrowing down your choices. Be specific.
- Use the 1H -NMR spectrum of your unknown shown to determine which isomer you have.

