



MAASAI MARA UNIVERSITY

**REGULAR EXAMINATIONS
2022/2023 ACADEMIC YEAR
THIRD YEAR SECOND SEMESTER**

**SCHOOL OF PURE, APPLIED AND HEALTH
SCIENCES
BACHELOR OF SCIENCE (BSc.)**

COURSE CODE: CHE 3225

**UNIT NAME: ANALYTICAL TECHNIQUES IN
STRUCTURAL DETERMINATION**

DATE: 21ST APRIL 2023

TIME: 1100 – 1300HRS

INSTRUCTIONS TO CANDIDATES

1. Answer question ONE and any other TWO
2. All rules and regulations regarding University examinations apply

This paper consists of 6 printed pages. Please turn over:

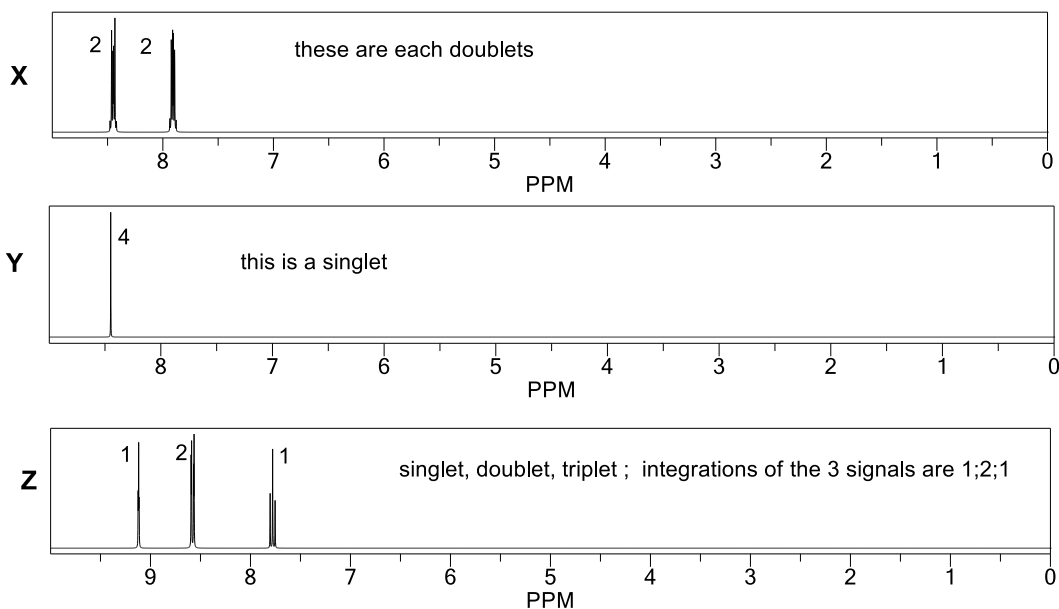
SECTION A

Question One (20 marks)

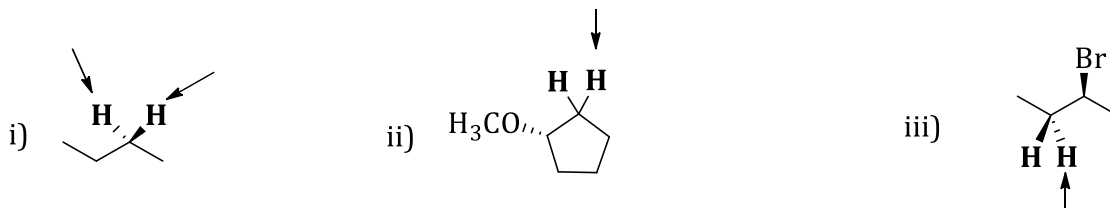
a) Give brief definitions of the following spectroscopic terms and where applicable elucidate using examples. (4 marks)

- i. Shielding
- ii. Base peak
- iii. Multiplicity
- iv. Diastereotopic hydrogens

b) The 3 ^1H NMR spectra below are for the three **dicyanobenzene** isomers. Draw the correct compound that corresponds to each of the given spectra X, Y and Z. Give a brief explanation on how you deduced and matched each structure to spectrum. (6 marks)



c) Consider the following organic molecules. Indicate whether the hydrogens (pointed with arrows) are homotopic, enantiotopic or diastereotopic. Do these hydrogens have same or different chemical shifts? Briefly explain. (3 marks)

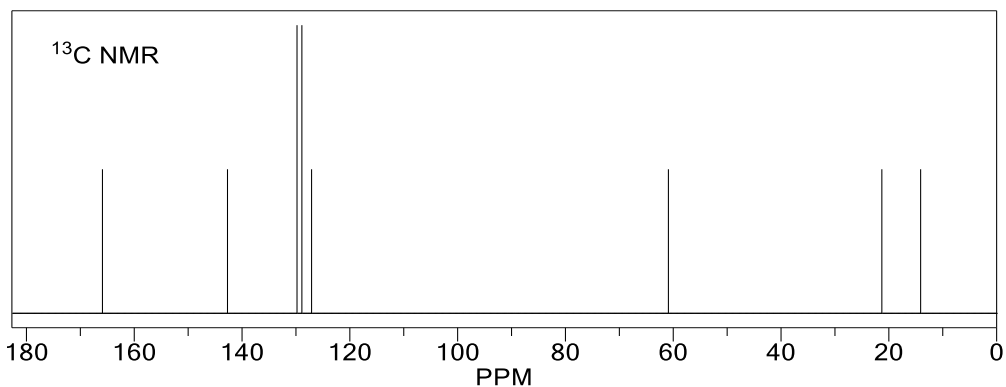
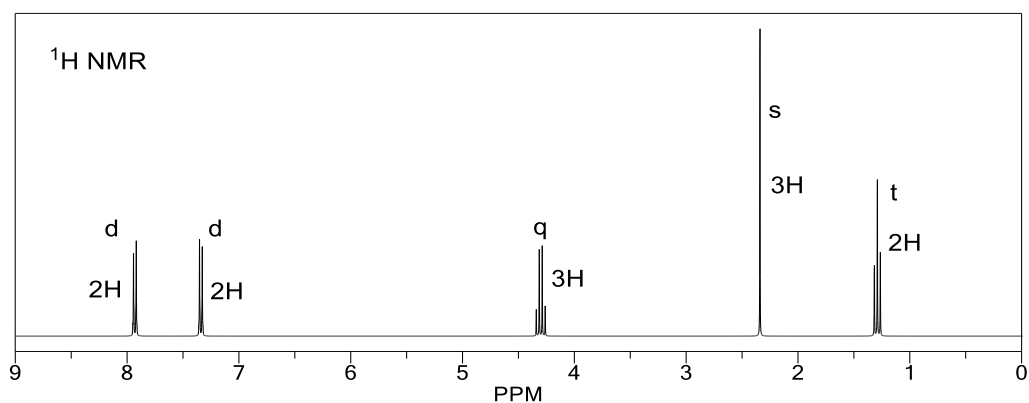


- d) List the main components of an Atomic Absorption Spectroscopy (AAS) and give a brief explanation of their functions. (3 marks)
- e) The following ^1H NMR absorptions were obtained on a spectrometer operating at 200 MHz from the TMS standard. Convert the absorptions to δ units. (2 marks)
- 0.956 kHz
 - 1.504×10^{-3} MHz
- f) Draw the structure of a type of pentane that has only a single singlet peak in its ^1H NMR spectrum and provide its correct IUPAC name. (2 marks)

SECTION B

Question Two (15 marks)

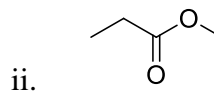
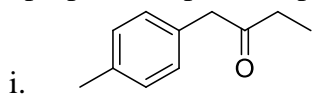
- a) ^1H NMR and ^{13}C NMR spectra for an aromatic compound with formula $\text{C}_{10}\text{H}_{12}\text{O}_2$ are given below. Deduce the chemical structure that corresponds to this compound. Partial credit will be awarded if you solve pieces of the final structure and show your reasoning. (4 marks)



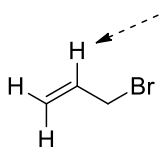
- b) Propanone and 2-propen-1-ol are constitutional isomers. Show how to distinguish between them by IR spectroscopy. (2 marks)
- c) 2,2-dimethylpentane shows an intense peak in the mass spectrum at $m/z = 57$. Propose a likely structure for this fragmented ion. (3 marks)
- d) The spectroscopic techniques MS, IR, and NMR are said to be complementary in structure determination. What structural information does each of these techniques provide? (3 marks)
- e) Propose a structure for $C_7H_{14}O$, that has the following ^{13}C NMR spectral data;
 Broad decoupled ^{13}C NMR: 29.3, 30.1, 31.2, 58.0, and 208.7 δ ;
 DEPT-135: positive peak at 29.3, 30.1 and negative peak at 58.0 δ . (3 marks)

Question Three (15 marks)

- a) Sketch 1H NMR spectra for the following compounds. Estimate the chemical shifts and show the proper multiplets for peaks that exhibit spin-spin coupling. (4 marks)

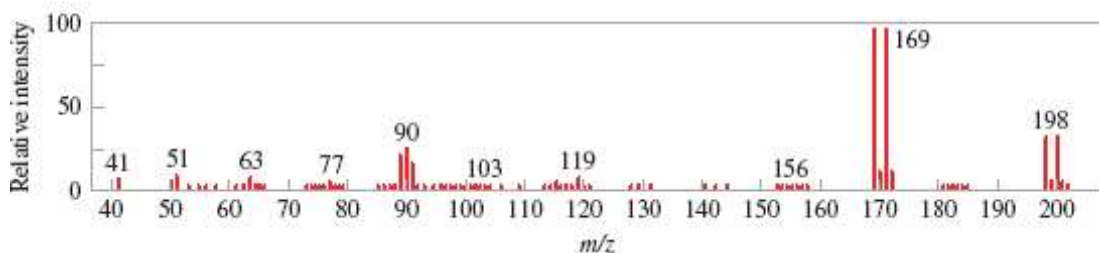
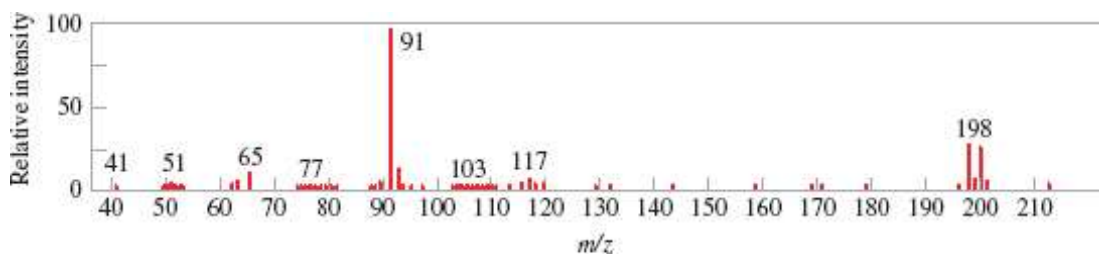


- b) Predict the splitting pattern that you would see for the proton marked with an arrow. (1 mark)

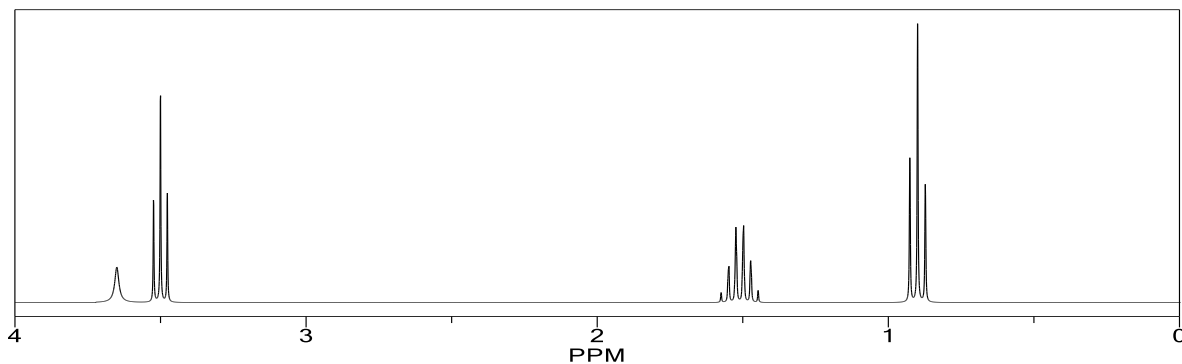


- c) Briefly explain the general principles of Fourier transform infrared (FTIR) spectroscopy. (3 marks)
- d) What information can we learn from a routine DEPT experiment regarding hydrogen or carbon nuclides that we cannot learn from a routine ^{13}C NMR? (1 mark)
- e) The 1H NMR signal for dimethylsulphoxide- d_6 (C_2D_6SO) appears at 1336 Hz when recorded on a 400-MHz NMR spectrometer. Calculate the chemical shift in ppm? (2 marks)

- f) 1-bromo-4-propylbenzene and (3-bromopropyl)benzene are constitutional isomers. These two isomers give distinguishable mass spectra shown below. Match the correct isomer to its corresponding mass spectrum. Show your reasoning! (2 marks)



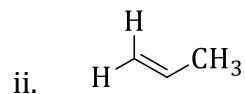
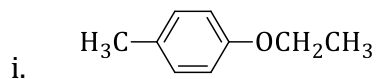
- g) Carboxylic acid **A** is treated with LiAlH_4 to give a saturated product, compound **B**. The $^1\text{H NMR}$ of the unknown **B** is shown below. Compounds **A** and **B** are known to contain at least one chlorine atom. Using the info provided, determine the structures of **A** and **B**. (2 marks)



Question Four (15 marks)

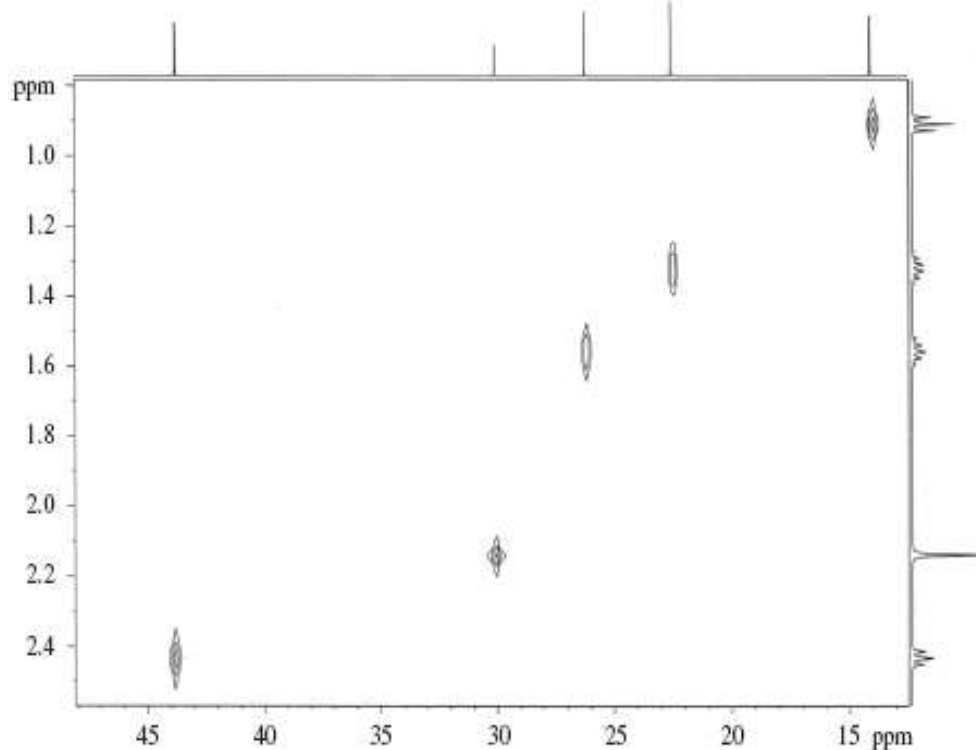
- a) In 2D NMR experiments, what is the general difference between correlation spectroscopy (COSY) and Heteronuclear Multiple Quantum Correlation (HSQC)? (2 marks)
- b) 2,2-dimethylpentane shows an intense peak in the mass spectrum at $m/z = 57$. Propose a likely structure for this fragmented ion. (2 marks)

- c) Determine the number of ^1H NMR signals and splitting pattern in each of the following compounds. (Label each unique carbon with letters A, B, C.....) (4 marks)



- d) If β -carotene, the pigment responsible for the orange colour of carrots, has $\lambda_{\text{max}}=325$, ($\epsilon=1.38 \times 10^5 \text{ L}/(\text{mol}\cdot\text{cm})$), what is the β -carotene concentration in a sample whose absorbance at 325 nm is $A=0.370$ in a cell with a path length of 10 mm? (2 marks)

- e) The HETCOR spectrum provided below was obtained for unknown ketone. Predict the structure of the unknown ketone. Justify your reasoning! (2 marks)



- f) Propose a structure that is consistent with the given spectroscopic data: (3 marks)

MS: $m/z = 114, 71$

IR: 2975, 1710 cm^{-1}

^1H NMR: $\delta =$ 2.32 (*t*, 4H)
1.64 (*m*, 4H)
0.87 (*t*, 6H)

//END