



# MACHAKOS UNIVERSITY

University Examinations for 2021/2022 Academic Year

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

THIRD YEAR FIRST SEMESTER EXAMINATION FOR

BACHELOR OF SCIENCE IN ANALYTICAL CHEMISTRY

SAN 301: ORGANIC SPECTROSCOPY

DATE: 29/8/2022

TIME: 8.30-10.30 AM

---

## INSTRUCTIONS:

- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks).
- Answer any **two** questions from section **B** (each 20 marks).

## Useful information

Planck constant =  $6.625 \times 10^{-34}$  JS

$c = 3 \times 10^8$  ms<sup>-1</sup>

$m = 10^9$  nm

$\mu\text{m} = 10^3$  nm

### QUESTION ONE (30 MARKS)

- a) Spectroscopic techniques are based on the interaction of matter with electromagnetic spectrum of various energies, which is divided into various regions. Briefly explain what interaction occurs between the molecules and the following specific regions in the electromagnetic spectrum resulting in the absorption of the radiation. (4 marks)
- The UV-Vis region
  - The IR region
  - The Microwave region
  - Radio waves region.
- b) The quantitative absorption of electromagnetic radiation by matter is governed by the Beer-Lambert law.
- Derive the Beer Lambert equation, explaining each term in the equation. (2 marks)
  - The absorbance of a solution of  $1.2 \times 10^{-4}$  M is found to be 0.23 in a path length of 3.0 cm. Determine the molar absorption of the solution. (2 marks)
- c) Briefly explain the following terms as applied to UV-Vis spectroscopy.
- Bathochromic shift. (1½ marks)
  - Hypsochromic shift. (1½ marks)
  - Lambda max. ( $\lambda_{\text{max}}$ ) (1½ marks)
  - Molar (absorption) Extinction coefficient ( $\epsilon$ ) (1½ marks)
- d) The UV-Vis and IR spectrophotometers are used to measure both the position at which the molecule absorbs and also the radiation absorbed quantitatively according to Beer Lambert law.
- Name the respective sources of radiation for the UV-Vis and IR spectrophotometers, respectively. (4 marks)
  - Describe the role of the monochromatic systems for the two respective spectrophotometers. (2 marks)

- iii. Describe the types of cell samples used in the two respective spectrophotometers. (2 marks)
- iv. Describe the differences between the detectors used in the two respective spectrophotometers. (4 marks)
- e) Explain clearly how the two spectroscopic methods, UV-VIS and IR can be used to complement each other in the structural determination of compounds. (4 marks)

### QUESTION TWO (20 MARKS)

- a) The allowed quantized vibrational energy level in a vibrational motion of a molecule is given by  $E = (n + \frac{1}{2}) h\nu$ , where  $h$  and  $\nu$  are Planck's constant and frequency, respectively, and  $n = 0, 1, 2, 3, \dots$ . The energy absorbed by a vibrating molecule is  $\Delta E = h\nu$ .
  - i. From the above information, explain clearly what are fundamental vibrational bands (peaks). (2 marks)
  - ii. Explain what are overtones. (2 marks)
  - iii. Explain why absorption of energy by a stretching bond occurs at higher energy than a bending bond of the same molecule in IR region. (1 mark)
- b) The position where a molecule absorbs in the IR region, which is from  $4000 \text{ cm}^{-1}$  to  $600 \text{ cm}^{-1}$  is defined by the equation:  $\tilde{\nu} = 1/2\pi c(\kappa/\mu)^{1/2}$ . Where  $\mu = m_1m_2/m_1+m_2$ .
  - i. Define  $\kappa$  and explain how it affects the value of  $\tilde{\nu}$ . (2 marks)
  - ii. Define  $\mu$  and explain its effect on the value of  $\tilde{\nu}$ . (2 marks)
  - iii. Explain what affects the intensity of IR absorption fundamental bands. (2 marks)
- c) Two types of IR spectrophotometers the dispersive and the Fourier transform IR Spectrophotometers (FTIR) are used to generate IR spectra of compounds. Give major differences between the two instruments in terms of,
  - i. The components of the respective instruments (4 marks)

- ii. Modes of operation of the two instruments including the sensitivity and speed.

(5 marks)

### QUESTION THREE (20 MARKS)

- a) The mass spectroscopic technique utilizes electron and chemical ionization methods in the generation of fragment ions from molecular compounds in the gas phase before analysis by a mass spectrometer.
- Explain how the two methods generate ions from the molecular compounds. (6 marks)
  - State clearly three major differences between the two methods. (4 marks)
  - Explain how the mass spectrum of a compound is presented, showing what is on the vertical and horizontal axes. (3 marks)
  - Explain and differentiate between the molecular ion peak and the base peak in the mass Spectrum. (3 marks)
  - Name two factors which determine the intensity of peaks in the mass spectrum and explain how they affect the intensity of the peaks. (4 marks)

### QUESTION FOUR (20 MARKS)

- a) The figures (i) and (ii) below are mass spectra of isomers  $\text{CH}_3\text{-CH(CH}_3\text{)-CH}_2\text{-CH}_3$  (2-methyl butane) and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  (pentane). The mass spectra do not necessarily represent the compounds in the order they appear. Use the figures to answer the questions below.

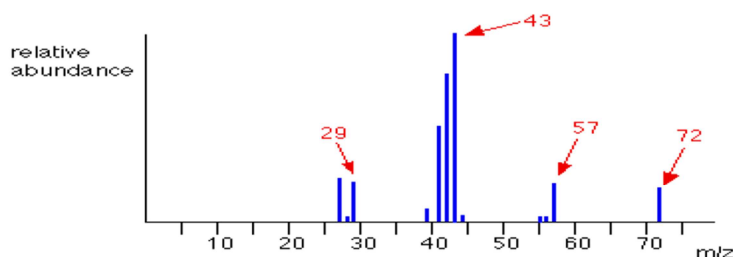
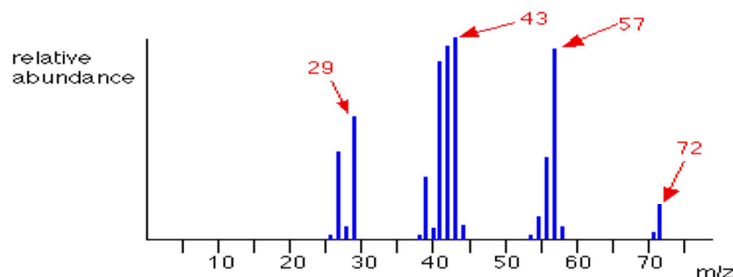
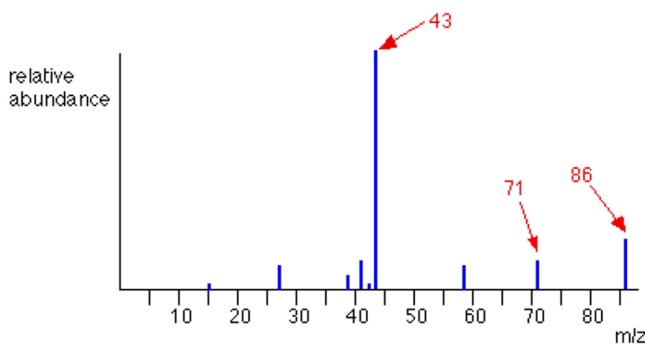


Figure (i)

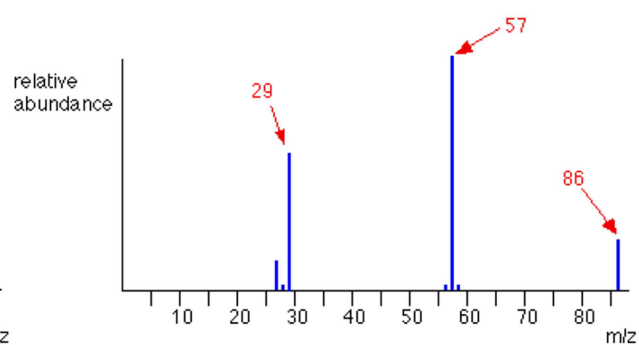


**Figure (ii).**

- i. Identify all the four peaks in the respective figures by giving the structures of the fragment ions. (2 marks)
  - ii. Identify the base peak and explain what a base peak is. (2 marks)
  - iii. Identify the molecular (parent) ion peaks. (2 marks)
- b) The peak at  $m/z$  57 in figure (ii) has higher relative abundance (higher intensity) than the peak  $m/z$  57 in figure (i).
- i. Based on the above observation, explain why the peak at  $m/z$  57 in figure (ii) is stronger than the corresponding one in figure (i). (2 marks)
  - ii. Although the fragment ions for the  $m/z$  57 peaks in the respective figures are the same but are structurally different. Propose the structural formulae of the fragments in the respective figures based on their respective intensities (relative abundancies). (2 marks)
  - iii. Based on the answers given in parts b (i) and (ii), identify which compound is represented by which mass spectrum [ figures (i) and (ii)]. (2 marks)
- c) The following **figures (iii)** and **(iv)** represent pentanone, which is either pentan-2-one ( $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$ ) or pentan-3-one ( $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$ ), not necessarily in the order mentioned.



**Figure (iii)**



**Figure (iv)**

Based on the information given above on the figures (iii) and (iv),

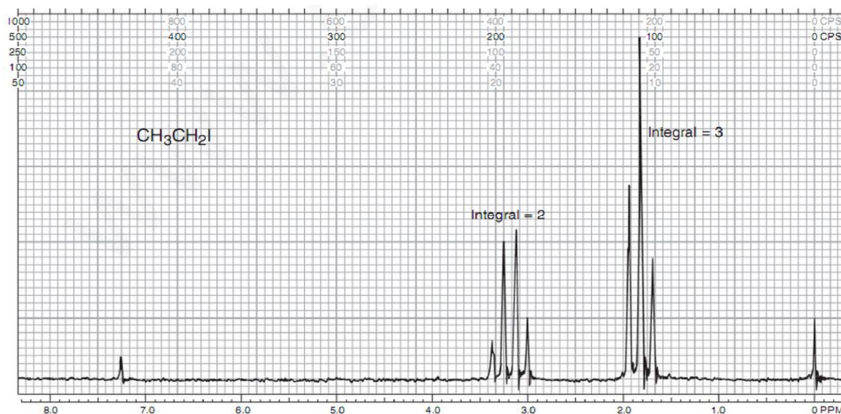
- i. Identify the peaks at  $m/z$  86, 71 and 43, respectively in figure (iii). (2 marks)
- ii. Suggest the name of the compound and its fragmentation pattern whose mass spectrum is represented by figure (iii). (2 marks)
- iii. Identify the peaks at  $m/z$  86, 57 and 29 in figure (iv). (2 marks)
- iv. Suggest the name of the compound and its fragmentation pattern whose mass spectrum is represented by figure (iv). (2 marks)

### QUESTION FIVE (20 MARKS)

- a) Nuclei of atoms of different elements are classified as having spin or no spin. The spin values of nuclei of different elements are therefore, classified as 0, integral values or half-integral values.
  - i. State the three rules governing assignment of spin values to different nuclei of elements. (1½ marks)
  - ii. Explain with the help of an equation the size of the magnetic moment generated by a spinning nucleus. (1½ marks)
  - iii. Explain what happens when the spinning nucleus interacts with external magnetic field. (1½ marks)

- iv. Explain how this interaction leads to the spinning nucleus being able to interact with the energy of the radiofrequency leading to the Nuclear Magnetic resonance spectroscopy (NMR). (1½ marks)
- b) i. Explain the term chemical shift as used in NMR spectroscopy. (2 marks)
- ii. Explain the term spin-spin coupling in NMR spectroscopy. (3 marks)
- iii. Explain why Tetra-Methyl Silane (TMS) is used as a reference standard in NMR Spectroscopy measurement of chemical shifts of compounds. (2 marks)
- c) Figure 5 below attached is an NMR spectrum of ethyl iodide ( $\text{CH}_3\text{CH}_2\text{I}$ ) dissolved in deuteriochloroform ( $\text{CDCl}_3$ ).

### Ethyl Iodide ( $\text{CH}_3\text{CH}_2\text{I}$ )



**Figure 5**

- i. Explain why deuteriochloroform is used instead of chloroform itself to dissolve ethyl iodide. (2 marks)
- ii. Identify the peaks at 0ppm, 1.8ppm, 3.2ppm and 7.25ppm (3 marks)
- iii. Explain why the peaks at 1.8 and 3.2 ppm are split into a quadruplet and triplet, respectively. (2 marks)