MACHAKOS UNIVERSITY

University Examinations 2022/2023

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

THIRD YEAR FIRST SEMSTER EXAMINATION FOR

BACHELOR OF SCIENCE (ANALYTICAL CHEMISTRY)

SAN 301: ORGANIC SPECTROSCOPY

DATE: **TIME:**

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 = 6.625×10^{-34} JS

E= hv

c = 3×10^{8} ms^{-1}

m = 10^{9} nm

µm = 10^{3} nm

QUESTION ONE COMPULSORY (30 MARKS)

(a) Spectroscopic techniques are based on the interaction of matter with electromagnetic spectrum of various energies, which is divided into various regions. Name the **five**

regions of the electromagnetic spectrum and explain how matter (compounds) interacts with each of these regions which you have named. (5 marks)

(b) The quantitative absorption of electromagnetic radiation by matter is governed by the Beer Lambert law.

i. Derive the Beer Lambert equation, explaining each term in the equation. (2 marks)

ii. The absorbance of a solution 1.2×10^{-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) The UV-VIS spectroscopy involves electronic transitions from ground state to excited state involving molecular orbitals.

i. Draw a suitable labelled energy level diagram indicating the ground state (molecular orbitals) and excited state (molecular orbitals). (2 marks)

ii. Indicate with arrows the allowed transitions which occur between the ground state and the excited state. (2 marks)

iii. From the transitions observed in (ii) above which transition whose absorption of radiation occurs in the visible region of the UV-VIS region of the spectrum? (2 marks)

iv. State the transitions in (ii) above whose absorption of radiation occurs in the far UV region of the UV-VIS region of the spectrum. (2 marks)

(d) Briefly explain the following terms as applied to UV-VIS spectroscopy.

i. Bathochromic shift. (1½ marks)

ii. Hypsochromic shift. (1½ marks)

iii. Auxochromes. (1½ marks)

iv. Chromophores. (1½ marks)

(e) A molecule of any substance has total energy of electrons, vibrations and rotations of a molecule. On the basis of the forgoing information, illustrate with a suitable labelled energy level diagram showing the electronic, vibrational and rotational energy levels on the same vertical scale. (7 marks)

QUESTION TWO (20 MARKS)

(a) The allowed quantized vibrational energy level in a vibrational motion of a molecule is given by E = (n+ ½) hv, where h and v are Planck´s constant and frequency,

respectively, and n = 0,1,2,3……. The energy absorbed by a vibrating molecule is ΔE = hv. From the above information, explain clearly explain clearly,

i. Fundamental vibrational bands (peaks). (2 marks)

ii. Overtones. (2 marks)

iii. Explain why absorption of energy by a stretching bond occurs at higher energy than a bending

iv. bond of the same molecule in IR region. (1 mark)

(b) A molecule absorbing in the IR region, which is from 4000 cm^{-1} to 400 cm^{-1} is defined by the equation: **$\bar{\upsilon} = 1/2\pi c(K/\mu)^{1/2}$. Where $\mu = m_1m_2/m_1+m_2$.**

i. Define K and explain how it affects the value of $\bar{\upsilon}$. (2 marks)

ii. Define μ and explain its effect on the value of $\bar{\upsilon}$. (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 Spectro-photometers (FTIR) are used to generate IR spectra of compounds. Outline the 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)

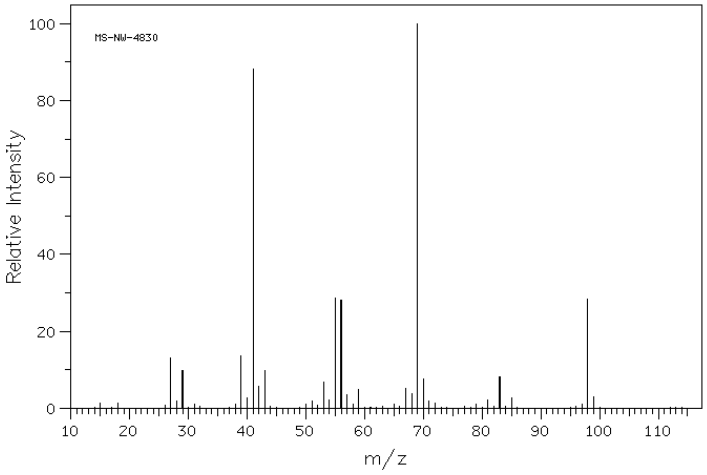
QUESTION THREE (20 MARKS)

(a) Mass spectrometry (MS) is a powerful analytical technique widely used by chemists, biologists, medical researchers, environmental and forensic scientists, among others.

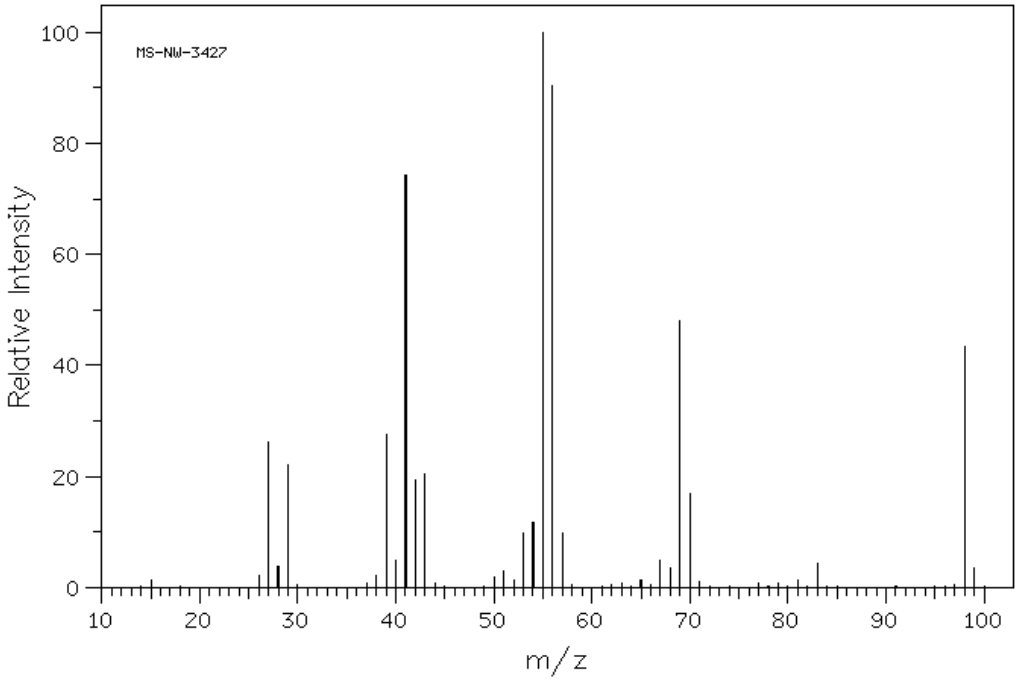
i. Describe how the two methods, Electron and Chemical ionisation methods are used in the gas phase to generate ion fragments for generation of mass spectra of compounds. (10 marks)

ii. Explain main differences between the two methods and explain why they are considered to be complementary to each other. (4 marks)

(b) The following spectra **A** and **B** are for 2-methyl-2-hexene and 2-heptene, not necessarily in that order. Determine which spectrum belongs to the listed molecules. Explain your answer. (6 marks)



Spectrum A



Spectrum B

QUESTION FOUR (20 MARKS)

(a) Atomic spectroscopy entails the interaction of radiation with atoms of elements generated from compounds. Atomic spectroscopy is classified into atomic absorption spectroscopy (AAS), Atomic emission spectroscopy (AES) and Atomic fluorescence spectroscopy (AFS).

i. Describe briefly what each of this technique entails in the analysis of elements in a sample. (6 marks)

ii. Describe the role of the flame in atomic spectrometry. (2 marks)

iii. Give three processes in the burner flame considered to contribute to interference leading to the inaccuracy in the determination of an analyte by AAS in a sample. (3 marks)

(b) In atomic absorption Spectroscopy describe how the hollow cathode lamp generates radiation required to excite gaseous atoms electronically. (3 marks)

(c) Phosphorous in urine is determined by treating a sample with Mo (VI) and reducing the resulting phosphomolybdo complex with aminonaphtholsulfonic acid to give the characteristic molybdenum blue color that absorbs at 690 nm. Suppose a patient excretes 1270 mL of urine in 24 hours. A 1.00-mL aliquot of the urine is transferred to a 50-mL volumetric flask and treated with the molybdate reagent and aminonaphtholsulfonic acid. After diluting to volume, its absorbance is measured as 0.625 in a 1.00-cm cell. A series of standard phosphate solutions that contain 1.00, 2.00, 3.00, and 4.00 ppm are prepared and analyzed in the same manner as the urine sample giving absorbance values of 0.205, 0.410, 0.615, and 0.820, respectively. Calculate the total grams of P that the patient excreted during the 24-hour sampling period. **(6 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** is an NMR spectrum of ethyl iodide (CH_3CH_2I) dissolved in deuterochloroform ($CDCl_3$

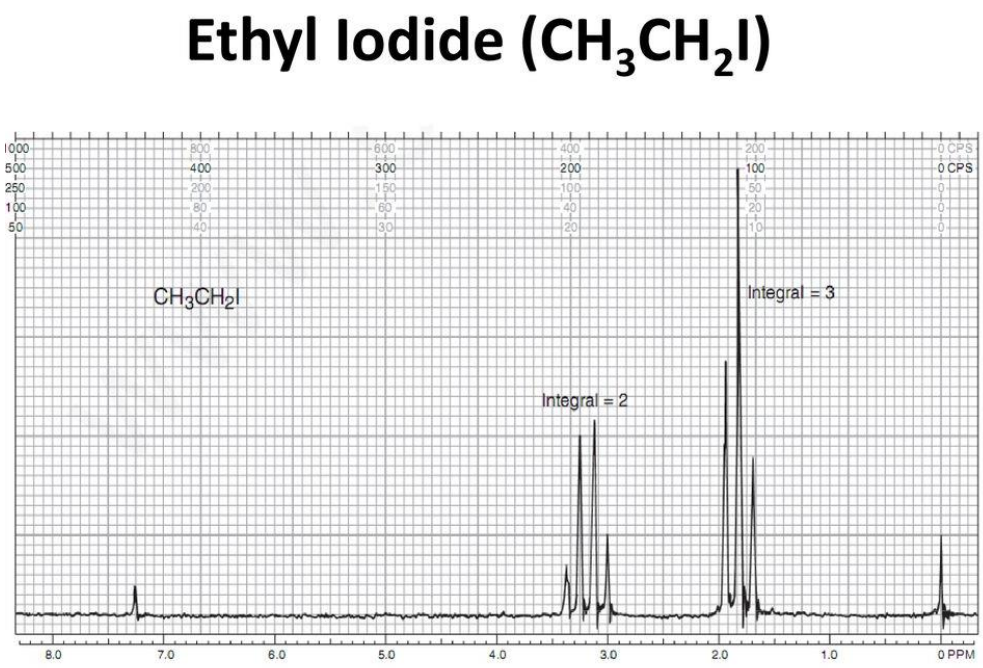


Figure 5

i. Explain why deuterochloroform is used instead of chloroform to dissolve ethyl iodide**.** (2 marks)

ii. Identify the peaks at 0 ppm, 1.8 ppm, 3.2 ppm and 7.25 ppm. (3 marks)

iii. Explain why the peaks at 1.8 and 3.2 ppm are split into a quadruplet and triplet, respectively. (2 marks)