MACHAKOS UNIVERSITY

University Examinations 2023/2024 academic year

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

THIRD YEAR FIRST SEMESTER EXAMINATIONS FOR

BACHELOR OF SCIENCE (ANALYTICAL CHEMISTRY)

SAN 301: ORGANIC SPECTROSCOPY

DATE: **TIME:**

USEFUL DATA

$h = 6.63 \times 10^{-34}$ Js

$c = 2.998 \times 10^{8}$ ms^{-1}

$1m = 10^{6}$ µm

$1m = 10^{10}$ Å

µm = 10^{3} nm

INSTRUCTIONS

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

SECTION A

QUESTION ONE (30 MARKS)

a) Most of spectroscopic techniques are a result of interaction of matter with the various regions of the electromagnetic radiation, which are based on the wavelength and energy (frequency) of the radiation.

i. Name the six major regions of the electromagnetic spectrum**.** **(3 marks)**

ii. State clearly the type of transitions any molecule will undergo that is capable of absorbing in a particular region of these seven major regions of electromagnetic spectrum. **(3 marks)**

b) The 3s ——— 3p transition in sodium is observed at 5893 Å.

i. Determine this wavelength in nanometers? **1½ marks**

ii. Determine the frequency of the absorbed photon**?** **2 marks**

iii. Calculate the energy in joules of absorbed photon**?** **1½ marks**

c) The radiation absorbed by an analyte in the spectroscopic methods is governed by the Beer Lambert law.

i. Derive the equation for the Beer Lambert law defining the terms in the equation. **(2½ marks)**

ii. A solution containing 3.80 µg/µg of A (MW = 220) has a transmittance of 39.8% in 1.50 cm cell at 600 nm. Calculate the molar absorptivity of A. **(7 ½ marks)**

(d). The 340 nm peak in benzophenone is seen to shift to longer wavelengths when placed in a more polar solvent.

(i). Indicate the predictions can you make about the type of transitions responsible for the peak?
(Hint: Consider the possible transitions associated with a molecule in the UV-VIS region of the electromagnetic spectrum). **7 marks**

(ii). Indicate the changes can you make to the structure of a molecule to shift hypsochromically in its absorption in the UV-Vis region of the electromagnetic spectrum? **2 marks**

QUESTION TWO (20 MARKS)

a) Infrared (IR) spectroscopy is a suitable technique for elucidation of structures of molecules.

i. Indicate the requirement for a molecule to be IR active? **2 marks**

ii. Explain how the two types of bands, the fundamental and overtones, are generated in IR

iii. spectroscopy for a molecule that is IR active. **5 marks**

iv. The two factors which affect the energy changes resulting from transitions of the molecule during stretching are the bond strength and the masses of the atoms of the diatomic molecule. Explain how the two factors affect the position (frequency) at which the molecule absorbs in the IR region. **4 marks**

Fig- 2-1 IR Spectrum 23-Mar-2021 15.pdf

b) The Fig: 2.1 above represents a spectrum taken as a KBr pellet and belongs to a compound with the formula C_2H_6O. There are two possible isomers for the formula C_2H_6O, ethanol (CH_3CH_2-OH) and dimethyl ether (CH_3-O-CH_3). Determine the identity of the compound using the table of IR spectral values (Fig. 2.2) below. **4 marks**

Fig- 2-2- Summary of IR values.pdf

c) Determine the reduced mass for each pair of atoms for the following compounds

(i). CO **2½ marks**

(ii). CH **2½ marks**

(C = 12.011; O = 16.00; C =1. 0079).

QUESTION THREE (20 MARKS)

a) The commonly used nuclei for NMR spectroscopy are the ^{1}H and ^{13}C. While C is found in most organic molecules together with H, ^{1}H NMR spectroscopy is preferred to the nucleus of ^{13}C.

i. Explain why ^{1}H-NMR is preferred to ^{13}C-NMR spectroscopy in the structural determination of Organic compounds. **3 marks**

ii. State advantages the ^{13}C-NMR spectroscopy has over the ^{1}H- NMR spectroscopy? **3 marks**

iii. The frequency of the Radiofrequency region of the electromagnetic spectrum is used in the generation of either ^{1}H or ^{13}C NMR signals of organic compounds. Explain in details, how the frequency in the radiofrequency region of the electromagnetic spectrum contributes to the generation of NMR signals. **3 marks**

b) (i). Explain the chemical shift as applied to NMR spectroscopy? **2 marks**

(ii). Explain why all proton magnetic resonance signals are not found at the same frequency? After

all they all arise from the magnetic properties of the same nucleus, namely H. **3 marks**

(iii). How many different chemical shifts do you expect for H nuclei in the following molecules? Where there is more than one chemical shift expected what will be the relative intensities of the different signals? CH_4, CH_3CH_3, $CH_3CH_2CH_3$, $H_2C{=}CH_2$, $H_2C{=}CHBr$. **3 marks**

(iv). Determine the spin-spin coupling patterns for each distinct set of H nuclei in the following molecules: CH_3CHCl_2, $CH_3CHClCH_3$ and $CH_3OCH_2CH_3$? **3 marks**

QUESTION FOUR (20 MARKS)

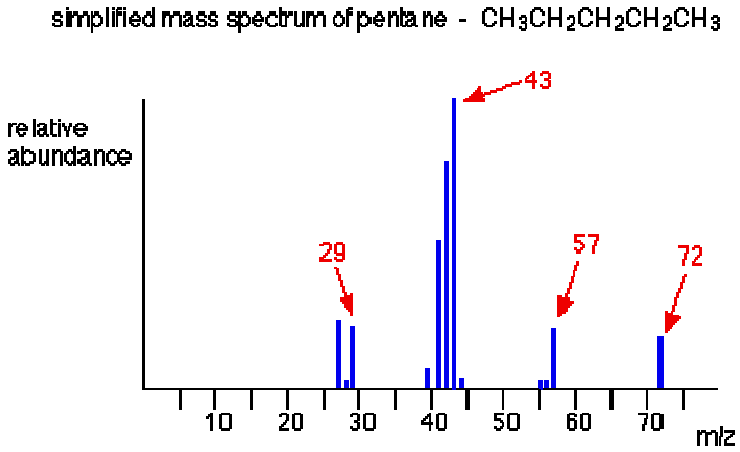
a) In mass spectroscopy, a compound is ionized in the gas phase by either high energy election impact ionization (EI) or by chemical ionization (CI).

i. Discuss in details how the two methods lead to formation of mass spectrum of a compound which is the peak abundance versus the m/z ratio of the fragment. **4 marks**

ii. Explain major differences in the two methods in the generation of the mass spectrum**.** **2 marks**

iii. Explain what is the base peak and the molecular peak observed in mass spectra. **2 marks**

Figure 4.1



b) The figure 4.1 above represents the mass spectrum of the alkane pentane.

i. With reasons explain what method is used to generate this spectrum. **1 mark**

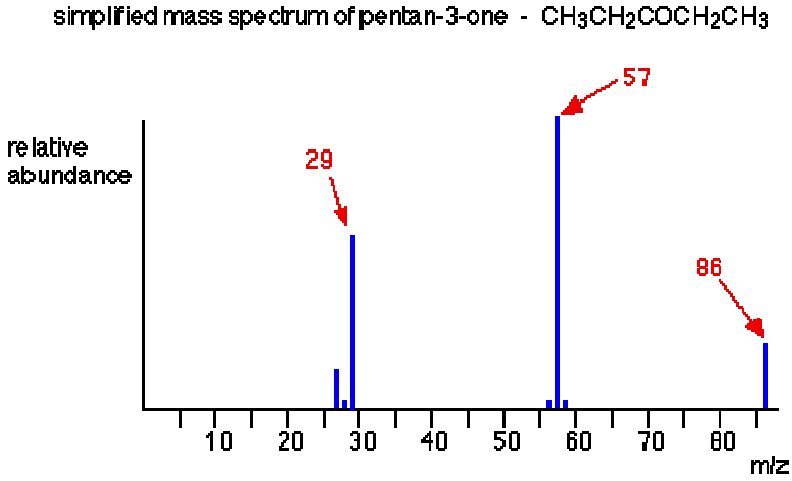
ii. Identify the m/z of the molecular peak. **1½ mark**

iii. Identify the m/z value of the base peak. **1½ mark**

iv. (iv). Show the fragmentation pattern and identify all the fragments with the m/z values shown on the spectrum**.** **2 marks**

c) Figure 4.2 below is the mass spectrum of pentan-3-one

Figure 4.2



i. (i). Identify the fragments whose m/z values are 86, 57 and 29 **2 marks**

ii. (ii). Identify both the molecular and base peaks. **2 marks**

iii. (iii). Work out the fragmentation patterns**.** **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**.** **3 marks**

ii. Explain with the help of an equation the size of the magnetic moment generated by a

iii. spinning nucleus. **2 marks**

iv. Explain what happens when the spinning nucleus interacts with external magnetic field**.** **2 marks**

v. 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). **2 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**.** **2 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) The figure attached is an NMR spectrum of ethyl iodide (CH_3CH_2I) dissolved in deuterochloroform ($CDCl_3$).

i. Explain why deuterochloroform is used instead of chloroform itself to dissolve ethyl iodide. **1 mark**

ii. Identify the peaks at 0ppm, 1.8ppm, 3.2ppm and 7.25ppm. **2 marks**

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