MACHAKOS UNIVERSITY

University Examinations 2021/2022

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

THIRD YEAR SUPPLEMENTARY/SPECIAL EXAMINATION FOR

BACHELOR OF SCIENCE (ANALYTICAL CHEMISTRY)

SAN 301: ORGANIC SPECTROSCOPY

DATE: 18/3/2022 **TIME: 2:00 – 4:00 PM**

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 you may require

$c = 3x10^{8}$ m/s
$h = 6.626x10^{-34}$JS
$m = 10^{6}$ µm
µm = 10^{3} nm
E = hv

QUESTION ONE (30 MARKS)

a) The absorption in UV-Visible region of the electromagnetic region is due to the electronic transitions (Molecular transitions). With the help of a well labelled electronic energy level diagram, show the various allowed transitions between the ground state and excited energy levels. (4 marks)

b) Explain what chromophores and auxochromes clearly distinguishing them (3 marks)

c) Explain and distinguish between the terms bathochromic and hypsochromic shifts. (3 marks)

d) (i) Explain with the help of equations what Beer Lambert Law is about. (4 marks)

(ii) Explain where the law applies. (2 marks)

e) Determine the frequency and energy of photons with wavelengths of the following:

(i). 1700 μm (7 marks)

ii). 195 nm (7 marks

QUESTION TWO (20 MARKS)

a) Infrared spectroscopy is one of the spectroscopic tools charged with the structural determination of organic compounds.

(i) Explain fully the conditions required a molecule to be IR active. (3 marks)

ii) Explain clearly how the two factors, the bond strength of the molecular bond and the mass of the molecule affects the position of energy absorption in the IR region (Use a suitable and relevant equation to explain your answer). (3 marks)

b) Explain the following terms

(i). Overtones of the IR bands. (3 marks)

(ii). The fundamental bands in the IR spectra (3 marks)

(iii). The difference between the finger print and functional group groups absorption bands. (8 marks)

QUESTION THREE (20 MARKS)

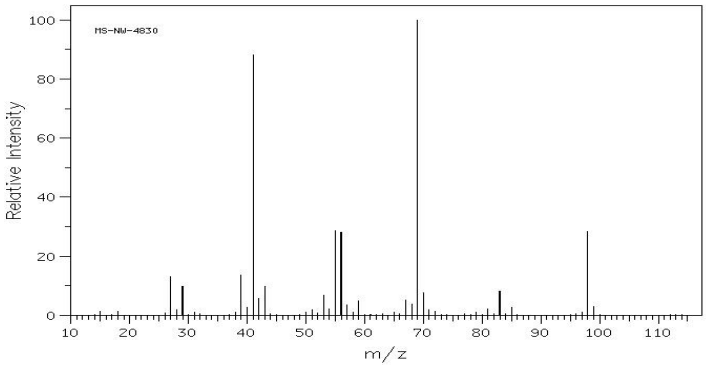
a) Mass spectrometry (MS) is a powerful analytical technique widely used by chemists, biologists, medical researchers, and environmental and forensic scientists, among others.

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)

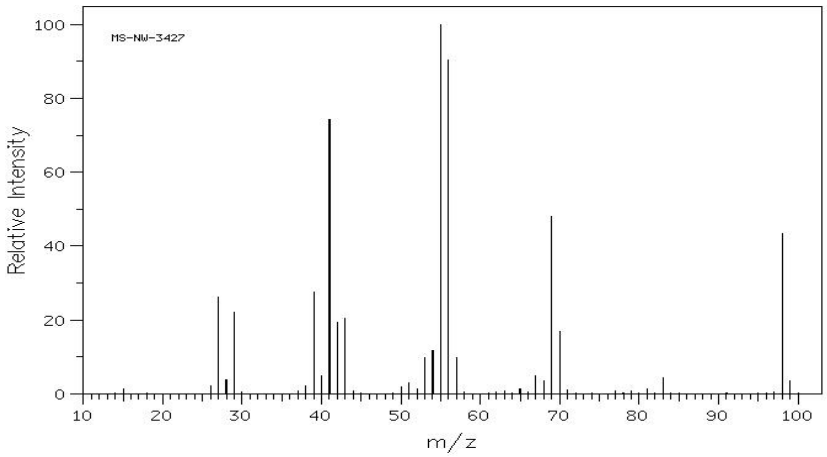
ii) Explain main differences between the two methods and explain why they are considered to be complementary to each other. (4 marks)

b) The following spectra A and B are for 2-methyl-2-hexene and 2-heptene, not necessarily in that order. Decide which spectrum belongs to the correct molecule. Explain your answers. (6 marks)

Spectrum A



Spectrum B



QUESTION FOUR (20 MARKS)

a)

(i). Explain in details how the spinning nucleus in applied external magnetic field of strength of H_o interacts with the resonance frequency in the radio region of electromagnetic spectrum to NMR peaks. (4 marks)

(ii). Explain how nuclei of atoms of various elements are assigned the spin value I which determines if a nucleus of an atom is NMR active. (4 marks)

b) The frequency V_o, which is the resonance frequency at which the spinning nucleus absorbs in the

radio region is given by the equation $V_o = \mu/hI (B_o)$ where μ is the magnetic moment of the spinning nucleus.

(i) From the equation above, explain why different nuclei of atoms of different elements have different values of V_o. (3 marks)

(ii) Explain what is chemical shift and how chemical shift values are assigned to a compound. (3 marks)

(iii) Explain clearly why ^{1}H NMR instrument is more sensitive than the ^{13}C NMR instrument. (2 marks)

(iv) What advantages does ^{13}C NMR Instrument have over the ^{1}H NMR instruments? (2 marks)

QUESTION FIVE (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 the 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 the interference leading to the inaccuracy in the determination of an analyte by AAS in a sample. (3 marks)

c) Describe how the hollow cathode lamp generates the radiation required to excite the gaseous atoms electronically for atomic absorption spectrometry. (3 marks)

d) 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 P 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)