MACHAKOS UNIVERSITY

University Examinations 2020/2021

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PYSICAL SCIENCES

FIRST YEAR FIRST SEMESTER EXAMINATION FOR

MASTER OF SCIENCE (CHEMISTRY)

SCH 801: ADVANCED INSTRUMENTAL ANALYSIS

DATE: 14/05/2021 **TIME: 8:30 - 11:30 AM**

INSTRUCTIONS:

- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks).
- Answer any **two** questions from section **B** (each 15 marks).

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

SECTION A (COMPULSORY)

QUESTION ONE (30 MARKS)

a) Most of the 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)What is this wavelength in nanometers? (1½ marks)

ii)What is the frequency of the absorbed photon? (2 marks)

iii)What is 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) State 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) What 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) What 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)

SECTION B: ANSWER ANY TWO QUESTIONS

QUESTION TWO (15 MARKS)

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

(i) What is the requirement for a molecule to be IR active? (1 mark)

(ii) Explain how the two types of bands, the fundamental and overtones, are generated in IR spectroscopy for a molecule that is IR active. (4 marks)

(iii) The two factors which affect the energy changes resulting from the 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)

b) The Fig: 2.1 below represents IR spectrum for a compound with the molecular 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 IR spectral values provided in **Table 2.2** attached in the last page. (2 marks)

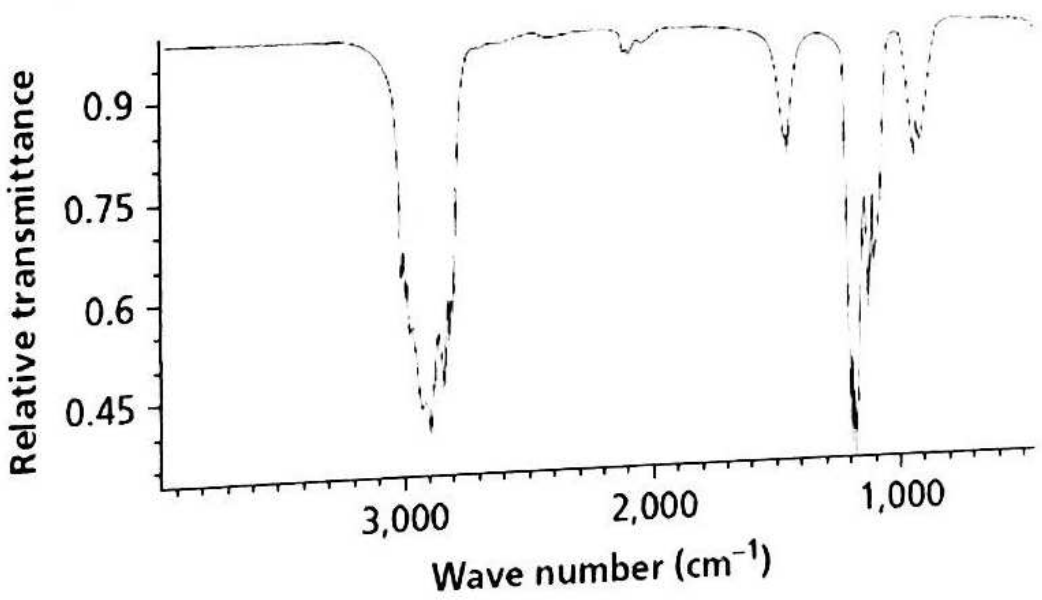


Figure 2.1

c) Determine the reduced mass for each of the following compounds
   i) CO (2 marks)
   ii) CH (2 marks)
   (C = 12.011; O = 16.00; C =1. 0079).

QUESTION THREE (15 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 ^{13}C.

   i) Explain why ^{1}H NMR is preferred to ^{13}C NMR spectroscopy in the structural determination of Organic compounds. (2 marks)

   ii) What advantages does the ^{13}C NMR spectroscopy have over the ^{1}H NMR spectroscopy? (2 marks)

   iii) The frequency of the Radiowaves 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 radiowaves region of the electromagnetic spectrum contributes in the generation of NMR signals. (2½ marks)

b) i) Define chemical shift as applied to NMR spectroscopy? (2 marks)

   ii) Explain why not all proton magnetic resonance signals are found at the same frequency. After all they all arise from the magnetic properties of the same nucleus, namely H. (2 ½ 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?

a. CH_4,
b. CH_3CH_3,
c. $CH_3CH_2CH_3$,
d. $H_2C=CH_2$,
e. $H_2C=CHBr$ (2 ½ marks)

(iv) What spin-spin coupling patterns do you expect for each distinct set of H nuclei in the following molecules:

a. CH_3CHCl_2,
b. $CH_3CHClCH_3$ and
c. $CH_3OCH_2CH_3$? (1 ½ marks)

QUESTION FOUR (15 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. (1½ marks)

ii) Explain what is the base peak and the molecular peak observed in mass spectra. (2 marks)

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

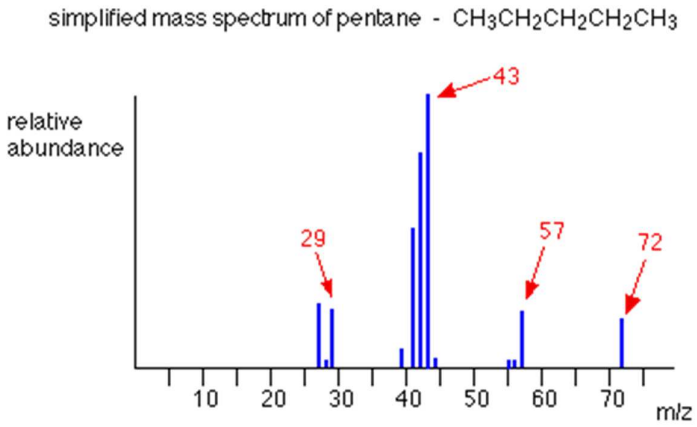


Figure 4.1

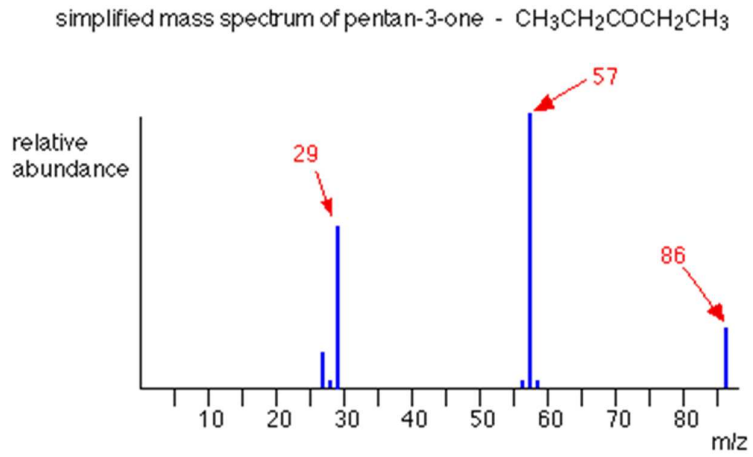
i) Explain giving reasons what method is used to generate this spectrum. (1 mark)

iii) Identify the m/z of the molecular peak. (½ mark)

iii) Identify the m/z value of the base peak. (½ mark)

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



(i). Identify the fragments whose m/z values are 86, 57 and 29 (1 ½ marks)

(ii). Identify both the molecular and base peaks. (½ mark)

(iii). Work out the fragmentation patterns. (1½ marks)

QUESTION FIVE (15 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. (3 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. (1½ marks)

b) Describe how the hollow cathode lamp generates the radiation required to excite the gaseous atoms electronically for atomic absorption spectrometry. (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 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. (5½ marks)

Fig 2

Summary of IR values

wavenumber	functional group	description
3500-3300	alcohol, COH or amine, CNR_2	alcohol is strong, broad amine is usually weak/medium, broad, 2 peaks = 1° amine (RNH_2), 1 peak = 2° amine (RR'NH)
3400-2400	acid, COOH	very broad, also will have C=O at ca. 1700
3300	alkyne (terminal)	sharp, ≡C-H stretch, also will have 2150 peak
3050	alkene or aromatic	=C-H stretch, usually weak
2950	alkane	-C-H stretch, usually weak
2750	aldehyde, CHO	=C-H stretch, also ~1700 peaks
2250	nitrile	C≡N stretch, medium to strong
2150	alkyne	C≡C stretch, usually weak
1810, 1760	anhydride, $(CO)_2O$	C=O stretch, -30 if conj.
1800	acid chloride, COCl	C=O stretch, -30 if conj.
1735	ester, COOR	C=O str, -25 if conj at C=O, +30 if conj at O
1725	aldehyde, CHO	C=O str, also 2750 peak, -30 if conj.
1715	ketone, CO	C=O str, **no** 2750 peak, -30 if conj.
1710	acid, COOH	C=O str, also v. broad 3400-2400 -OH, -30 if conj.
1690	amide, $CONR_2$	C=O str, also 3300 peak unless 3°, -30 if conj.
1650	alkene	C=C stretch
1250	alkane	C-C stretch
1220	O-Aryl	O-C str, confirmatory only
1150	O-*tert*-C, 3° (RR'R"C-O)	O-C str, confirmatory only
1100	O-*sec*-C, 2° (RR'HC-O)	O-C str, confirmatory only
1050	O-*prim*-C, 1° (RH_2C-O)	O-C str, confirmatory only
990, 910	mono alkene, $RCH=CH_2$	=C-H bend, usually strong, **two peaks**
970-960	*trans*-RCH=CHR	=C-H bend, usually strong
900	1,1-disubst. alkene, $R_2C=CH_2$	=C-H bend, usually strong
880, 780, 690	*meta*-disubst. Ar ring	=C-H bend, **three peaks**
~825±25	*para*-disubst. Ar ring	=C-H bend, **one peak**
~750±25	*ortho*-disubst. Ar ring	=C-H bend, **one peak**
~700	*cis*-RCH=CHR	=C-H bend, weak to medium, position varies
700, 690	mono-subst. Ar ring	=C-H bend, **two peaks**