W1-2-60-1-6

JOMO KENYATTA UNIVERSITY OF AGRICULTURE AND TECHNOLOGY
UNIVERSITY EXAMINATIONS 2024/2025

END OF SEMESTER EXAMINATION FOR THE DEGREE OF MASTER OF SCIENCE IN MEDICINAL PHYTOCHEMISTRY

TPS 3104: SPECTROSCOPIC METHODS

DATE: DECEMBER 2024 **TIME: 3 HOURS**

Instructions: Answer any FOUR of the SIX questions

Useful information: - Speed of light, $c = 2.998 \times 10^{10}$ cm/sec, Mass of carbon, C = 12.0, mass of hydrogen, H = 1.0, Avogadro's number = 6.023×10^{23}, pi, $\pi = 3.14$)

QUESTION ONE

a) Write short notes on: (5 marks)
   (i.) Spectroscopy
   (ii.) Nuclear magnetic resonance (NMR) spectrum
   (iii.) Chemical shift
   (iv.) Molar absorptivity (ε, in units of $M^{-1}cm^{-1}$)
   (v.) Chromophore

b) Explain how electromagnetic radiations are produced. (2 marks)

c) Distinguish the terms frequency and wavenumber. (2 marks)

d) Using a schematic diagram, show the orientation of the source and the detector when measuring fluorescence and phosphorescence: (4 marks)

e) The infrared spectrum of l-hexyne shows a sharp absorption peak near 2100 cm^{-1} due to stretching of its triple bond. However, 3-hexyne shows no absorption in that region. Explain. (4 marks)

f) NMR spectra can be used to provide valuable information about the structure of a molecule. Explain any two (2) features of a molecule's proton NMR spectrum that can be used in determining its structure. (4 marks)

g) An infrared spectrum is divided into two areas. Explain. (4 marks)

QUESTION TWO

a) Most Infrared (IR) spectrophotometers are double-beam instruments. Draw a well labeled schematic block diagram of a double-beam infrared spectrophotometer and explain its main parts. (10 marks)

b) In an actual IR spectrum, the theoretical number of fundamental bands are seldom obtained because there are certain factors which decrease, whereas certain factors increase the number of bands. State five (5) such factors that decrease the theoretical number of fundamental bands. (5 marks)

c) A hydrocarbon containing 10% hydrogen shows the following bands in its IR spectrum: (i) 3295 cm^{-1} (ii) 2130 cm^{-1} (iii) 625 cm^{-1}. Deduce the structure of the hydrocarbon. (5 marks)

d) Photoluminescence is divided into two categories: fluorescence and phosphorescence. Explain how fluorescence and phosphorescence spectra are produced. (5marks)

QUESTION THREE

a.) With an illustration, describe how electron impact (EI) ionization mass spectrometry occurs. (10 marks)

b.) Outline the steps that summarize how proton nuclear magnetic resonance (^{1}H NMR) spectroscopy is applied in elucidating the structure of unknown compounds. (5 marks)

c.) Describe Beer–Lambert law. Explain all the parameters in this law. (5 marks)

d.) A carbon hydrogen (C-H) bond has a force constant of 5 x 10^5dynes/cm. Calculate the stretching frequency of the C-H bond. (Mass of carbon = 12.0, mass of hydrogen = 1.0, Avogadro's constant = 6.023 x 10^{23}, speed of light = 3.0 x 10^{10}cm/sec). (5 marks)

QUESTION FOUR

a) State the wavelength range for UV light and visible light. (2 marks)

b) Calculate the wavelength in angstrom of an electromagnetic radiation having frequency 7 x 10^{14} Hz. (c = 3 x 10^8 m/s; 1Å = 10^{-10} m or 10^{-8} cm) (3 marks)

c) A compound with the molecular formula $C_4H_4O_2$ has a strong sharp absorbance near 3300 cm^{-1}, absorbances in the 2800–3000 cm^{-1} region, and a sharp absorbance peak near 2200 cm^{-1}. It also has a strong broad absorbance in the 2500–3600 cm^{-1} region and a strong peak in the 1710–1780 cm^{-1} region. Propose a possible structure for the compound. (10 marks)

d) Sketch a predicted proton NMR spectrum for ethanol, showing signals in the expected chemical shift ranges (based on Table 1 provided below) and with the appropriate number of peaks in each. (10 marks)

Table 1. Approximate Proton Chemical Shifts.

Type of Proton	Chemical Shift (δ, ppm)	Type of Proton	Chemical Shift (δ, ppm)
1° Alkyl, RCH_3	0.8–1.2	Alkyl bromide, RCH_2Br	3.4–3.6
2° Alkyl, RCH_2R	1.2–1.5	Alkyl chloride, RCH_2Cl	3.6–3.8
3° Alkyl, R_3CH	1.4–1.8	Vinylic, $R_2C{=}CH_2$	4.6–5.0
Allylic, $R_2C{=}\underset{\displaystyle R}{\underset{\vert}{C}}{-}CH_3$	1.6–1.9	Vinylic, $R_2C{=}\underset{\displaystyle R}{\underset{\vert}{CH}}$	5.2–5.7
Ketone, $R\overset{\displaystyle O}{\overset{\Vert}{C}}CH_3$	2.1–2.6	Aromatic, ArH	6.0–8.5
Benzylic, $ArCH_3$	2.2–2.5	Aldehyde, $R\overset{\displaystyle O}{\overset{\Vert}{C}}H$	9.5–10.5
Acetylenic, $RC{\equiv}CH$	2.5–3.1	Alcohol hydroxyl, ROH	0.5–6.0[a]
Alkyl iodide, RCH_2I	3.1–3.3	Amino, $R{-}NH_2$	1.0–5.0[a]
Ether, $ROCH_2R$	3.3–3.9	Phenolic, ArOH	4.5–7.7[a]
Alcohol, $HOCH_2R$	3.3–4.0	Carboxylic, $R\overset{\displaystyle O}{\overset{\Vert}{C}}OH$	10–13[a]

[a]The chemical shifts of these protons vary in different solvents and with temperature and concentration.

QUESTION FIVE

a) Discuss Atomic Emission Spectroscopy. (15 marks)
b) Discuss the electronic transitions involving metal ions. (5 marks)
c) Explain the source of UV/Vis absorption for inorganic metal–ligand complexes (5 marks)

QUESTION SIX

a) Discuss Liquid Chromatograpy-Mass Spectroscopy (LC-MS) based on instrumentationand application (15 marks)
b) Discuss Gas-Chromatograpy-Mass Spectroscopy (GC-MS) based on instrumentationand application (10 marks)