MACHAKOS UNIVERSITY

University Examinations 2018/2019

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

APRIL SESSION EXAMINATION FOR

MASTER OF SCIENCE (CHEMISTRY)

SCH 801: ADVANCED INSTRUMENTAL ANALYSIS

DATE: 13/8/2019 **TIME: 8:30-11:30AM**

INSTRUCTIONS:

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

QUESTION ONE COMPULSORY (30 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 spinning nucleus. (2 marks)

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

ii) Identify the peaks at 0ppm, 1.8ppm, 3.2ppm and 7.25ppm. (6 marks)

iii) Explain why the peaks at 1.8 and 3.2 ppm are split into a quadruplet and triplet, respectively. (6 marks)

QUESTION TWO (15 MARKS)

a) Mass spectrommetry (MS) is considered as the most outstanding among analytical methods and is applied widely in many fields.

i) Give **four** characteristics of the MS technique that makes it most outstanding among analytical methods. (1 mark)

ii) Out line briefly what happens whenever a compound collides with an electron in the gas phase in the initial stage of the MS technique. (2 marks)

iv) Define what is m/z ratio in MS. (1 mark)

iv) In the mass spectrum what is molecular ion? (1 mark)

v) What is the base peak in the mass spectrum? (1 mark)

b) There are two methods of generating ions from compounds in the MS technique, the electron ionization and the chemical ionization

i) Explain the major difference between the two methods of ionization. (1 mark)

ii) Name and explain the behaviour of the three reagent gases used in chemical Ionization. (1 mark)

iii) Using CH_4 as a reagent gas in chemical ionization, describe in details with the help of chemical equations how chemicasl ionization generates the ions analyzed in the MS technique. (2 marks)

c) The figures below are mass spectra of diketopiperazine produced by electron ionization (EI) in the upper figure and by chemical ionization (CI) with methane as a reagent in the lower figure. From the figures;

i) What is the molecular mass of the compound? (1 mark)

ii) What major difference do you see between the upper and lower spectra? (1 mark)

iii) Identify the molecular peak in the two spectra (2 marks)

iii) Identify both peaks QM^+ and Q+29. (1 mark)

QUESTION THREE (15 MARKS)

a) A molecule of any substance has internal energy which is the sum of the energy of its electrons made of up of electronic, vibrational and rotational energies;

i) Show on the same vertical scale how these three types of energies are distributed according to different energy levels. (1 mark)

ii) With the help of an energy level diagram, show how electronic energy transitions occur between the ground states and excited electronic states (involving molecular orbitals) in molecules. (1 ½ marks)

iii) Explain fully (three different causes) why absorption of radiation by a molecule in the UV-Visible results in a spectrum made of bands instead of sharp lines (peaks). (1 ½ marks)

b) The position and intensity of absorption in the UV-Vis region is determined by the molecular structure of compounds. Explain the terms λ_{max} and molar extinction coefficient (ξ) as relates to the statement above. (3 marks)

c) Explain the following terms;

i) Chromphores (1 mark)

ii) Bachochromic shift (1 mark)

iv) Auxochromes (1 mark)

v) Hypochromic shift (1 mark)

d) State the Lambert law and give an equation governing the absorbance of radiation by a UV-Vis molecule. (4 marks)

QUESTION FIVE (15 MARKS)

a) Infrared spectroscopy is a powerful tool in the structural elucidation of compounds

i) Explain the requirement for a molecule to be Infrared active. (3 marks)

ii) Explain what factors determine the position at which an Infrared active molecule will absorb in the Infrared region. (4 marks)

iii) Theoretically the CO_2 molecule which is linear is expected to produce four peaks in the Infrared spectrum but in reality, only two peaks are observed. Explain this disparity. (4 marks)

iv) Explain the three peaks observed in the Infrared spectrum of H_2O molecule as it is theoretically predicted. (4 marks)

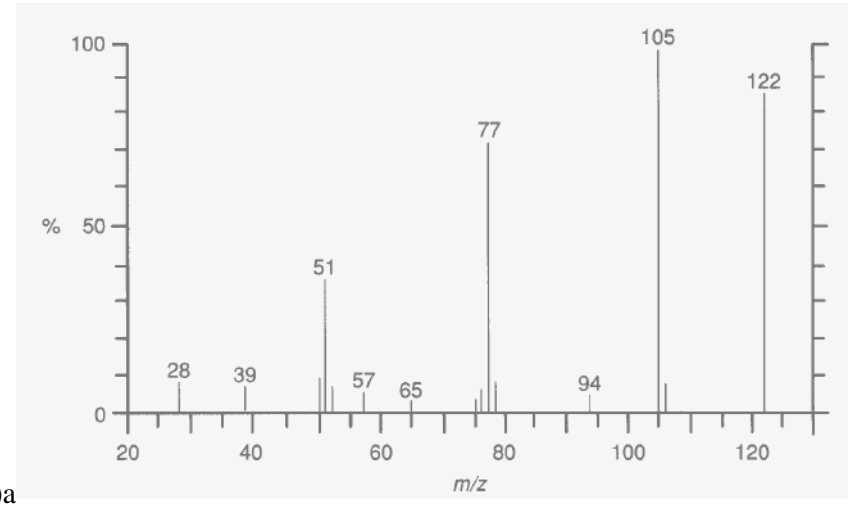
QUESTION FIVE (15 MARKS)

a) The figures (i)a and (ii)b below are the mass spectra of benzoic acid and methyl benzoate, respectively.

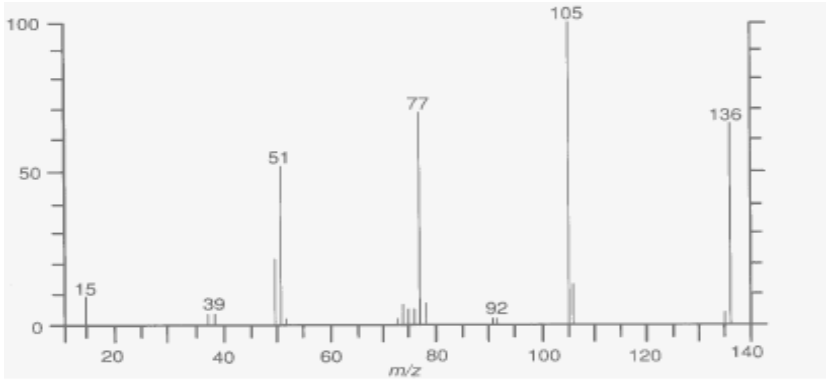
i) Write the chemical formualae of the compounds**.** (2 marks)

ii) Identify the ions responsible for the major peaks in each spectrum. (6 marks)

(i)a



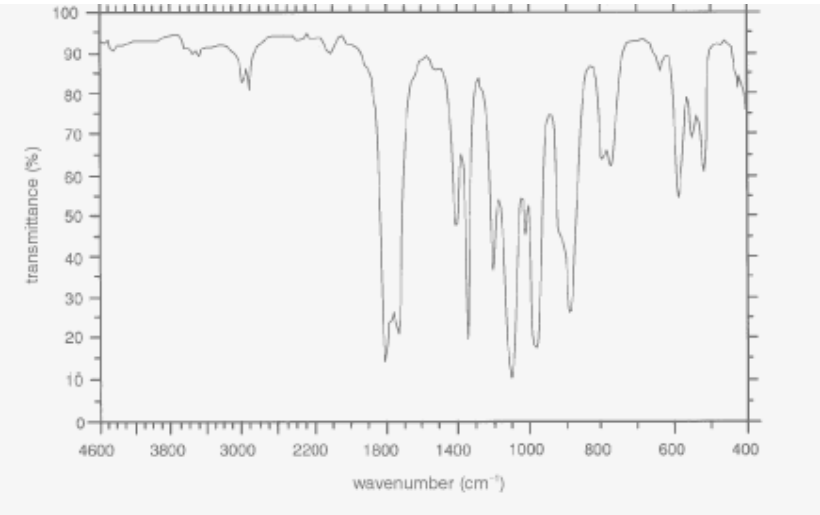
(ii)b

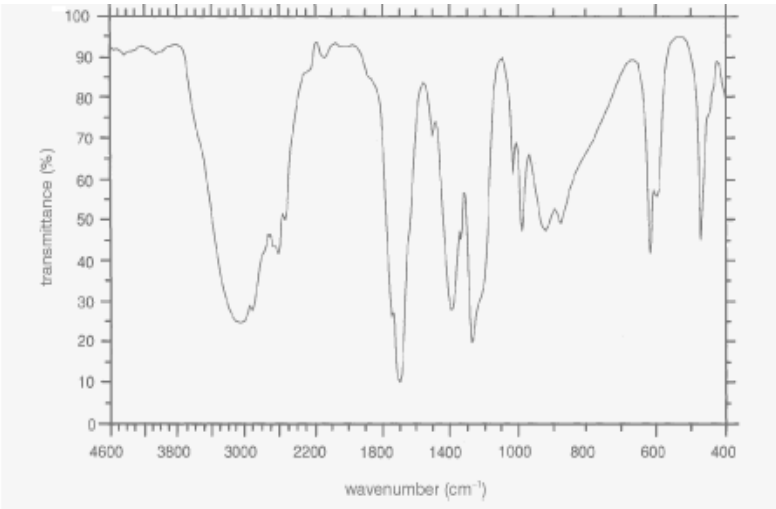


b) The IR spectra below are of ethanoic acid CH_3COOH and ethanoic anhydride $(CH_3CO)_2O$, respectively.

i) Draw the full structural formulae for both compounds. (2 marks)

ii) Determine, giving reasons, which spectrum is due to which compound. (5 marks)


transmittance (%)
100
90
80
70
60
50
40
30
20
10
0
4600
3800
3000
2200
1800
1400
1000
800
600
400
wavenumber (cm⁻¹)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600
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wavenumber (cm⁻¹)