

CHUKA



UNIVERSITY

## UNIVERSITY EXAMINATIONS

## EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF

## CHEM 437: ORGANIC SPECTROSCOPY

STREAMS:

TIME: 2 HOURS

DAY/DATE: TUESDAY 09/04/2019

8.30 A.M. – 10.30 A.M.

## INSTRUCTIONS:

- Answer question ONE and any other TWO questions.

## QUESTION ONE (30 MARKS)

1. (a) (i) Compound A and B absorb in the ultraviolet region. Compound A exhibits an absorption maxima at 267 nm ( $a=157$ ) and a trailing shoulder at 312 nm ( $a=12.6$ ). Compound B has an absorption maximum at 312 nm ( $a=186$ ) and does not absorb at 267 nm. A solution containing the two compounds exhibits absorbance (using a 1 cm – cell) of 0.726 and 0.544 at 267 and 312 nm respectively. Calculate the concentrations of compound A and B in mg/l. (3 marks)

(ii) A mine (weak base) from salts with picric acid (trinitrophenol), and all amine picrates exhibit an absorption maximum at 359 nm with a molar absorptivity of  $1.25 \times 10^4$ . 0.2 g sample of aniline,  $C_6H_5NH_2$  is dissolved in 500 ml of water. A 25.0 ml liquor is reacted with picric acid in a 250 ml. volumetric flask and diluted to 100 ml and the absorbance read at 359 nm in a 1 cm cell. If the absorbance is 0.425. Calculate the percent purity of the aniline. (3  $\frac{1}{2}$  marks)

(b) (i) Account for the following observation “The number of the fundamental vibrational frequencies of acetylene observed are less than the

expected theoretical values.”

(5 marks)

(ii) The harmonic vibrational frequency of HCl in wavenumber is  $2989.6 \text{ cm}^{-1}$

(I) Calculate the energies of the first two vibrational levels in Joules.

(2  $\frac{1}{2}$ )

marks)

(II) Determine the wavelength for a transition from the  $v=0$  to the  $v=1$  level is the transition in the infrared region of the spectrum?

electromagnetic

(2  $\frac{1}{2}$  marks)

(c) (i) State five rules used to interpret bonding from fracture patterns of organic molecules. (3  $\frac{1}{2}$ )

marks)

(ii) The mass spectrum of butyrophenone (n-butylphenylketone,  $C_6H_5COCH_2CH_2CH_2CH_3$ ) shows peaks at M/Z 162, 120, 105 and

85.

Interpret these

(iii) In compound Gc-MS analyses fatty acid analyses fatty acid methyl esters can be identified by the presence of a peak at M/Z 74: Explain this observation.

(1 mark)

(d) (i) Explain how secondary magnetic fields associated with the molecule affect the chemical shift in NMR. (2

marks)

(ii) Discuss the two types of shielding phenomena which modify resonance peaks in an NMR spectrum. (2

marks)

(iii) Give the similarities between proton NMR and carbon-13 NMR spectroscopy. (1

mark)

- (iv) State three short-comings of carbon-13 NMR spectra. (1  $\frac{1}{2}$

marks)

- (v) State how many peaks would you expect to see in the carbon-13 spectrum of 2-methylbutane. ( $\frac{1}{2}$

Mark)

### QUESTION TWO (20 MARKS)

2. (a) (i) In the determination of acetone in biological fluids the following calibration curve and unknown data obtained are given in the table below.

Standard	Absorbance
Mg acetone 100ml	
Reagent blank	0.053
2.0	0.097
4.0	0.143
6.0	0.190
8.0	0.221
10.0	0.238
Normal blood	0.119
Ketonic blood	0.222
Normal urine	0.150
Ketonic urine (diluted)	0.230

All the absorbance measurements were against a water blank. Determine the ketone concentration in each of the four unknowns and assuming a 1:25 (initial: final) dilution was used. Calculate the ketone concentration in the undiluted urine. (7 marks)

- (ii) Account for the difference in absorption spectrum of a molecule which contains hydrogen covalently bound to oxygen or nitrogen in a non-polar solvent (figure 1) and in a polar solvent (figure 2)

Fig 1

Absorption of a molecule in a  
Non polar solvent (hexane)

Fig 2

Absorption spectrum for the  
molecule in a polar solvent (ethanol)  
(4

marks)

(b) Explain how the ultraviolet spectrum can be used to decide between the following organic compounds:

(i) (2 marks)

(ii) (3 marks)

(iii) (2 marks)

(iv)

(2 marks)

Table 1: woodward's rules for Diene

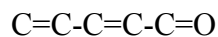
Parent heteroannular diene (a)	214 nm
Absorption of parent diene system C=C-C=C	217 nm
Parent homoannular diene (b)	253 nm
<u>Add to each substituent</u>	
Double bond extending conjugation to diene system	30 nm
Diene system within a ring	36 nm
Exocyclic nature of double bond in conjugated system	5 nm
Each alkyl substituent or ring residue	5 nm
Auxochrome	
O – acyl	0 nm
O – alkyl	6 nm
S – alkyl	30 nm
N – alkyl	60 nm
Cl, Br	5 nm

Note

- (a) Diene system not involved in a ring structure.  
 (b) Diene system within ring structure

Table 2: Rules for  $\alpha, \beta$  unsaturated ketones and aldehyde absorption

$\delta - 1 \beta \alpha$



-Value assigned to parent	$\alpha, \beta$ - unsaturated six ring or acyclic ketone	215 nm
-Value assigned to parent	$\alpha, \beta$ -unsaturated five ring ketone	202 nm
-Value assigned to parent	$\alpha, \beta$ -unsaturated aldehyde	207 nm

Increment added for	Shift to longer $\lambda_{\text{max}}$ (nm)	Increment added for	Shift to longer $\lambda_{\text{max}}$
Each exocyclic double bond	5	s-alkyl	
-Diene within a ring	39	$\beta$	85
-Double bond extending the conjugation	30	Cl	15
<u>Each alkyl substituent</u>		$\beta$	12
$\alpha$	10	Br	
$\beta$	12	$\alpha$	25
Y and higher	18	$\beta$	30
Each		NR2	
OH		$\beta$	95
$\alpha$	35		
$\beta$	30		
$\delta$	50		
0-acyl			
$\alpha, \beta, \sigma$	6		
0-me			
A	35		
$\beta$	30		
Y	17		
$\delta$	31		

**QUESTION THREE (20 MARKS)**

- (a) The presence of ethylene in samples of ethane was determined by using the absorbance band of ethylene at  $1443\text{ cm}^{-1}$ . A series of standards gave the following data

% of ethylene	0.50	1.00	2.00	3.00
Absorbance	0.120	0.240	0.480	0.719

- (i) Explain how the absorbance of ethylene was determined. (4 marks)
- (ii) Calculate the percentage of ethylene in an unknown sample that had an absorbance of 0.634 when the same cell and instrument were used. (4 marks)
- (b) (i) State the advantages of pressed pellet technique over Nujol technique in IR analysis. (2 marks)
- (ii) How could infrared spectroscopy be used to distinguish the members of the following pairs and how reliable would these distinctions be?
- (I) Natural rubber (cis-polyisoprene) and butyl rubber (polyisobutene) (1 mark)
- (II) The CIS and Trans isomers of 3-hexene. (1 mark)
- (III) 1-hexyne and 3-hexyne? Assume that you do not have access to any authenticated spectra.
- (c) (i) Explain which functional groups are present in the compound on the basis of its IR spectrum given in fig 1. (fig 1 a it's the spectrum of the compound collected as a liquid film between salt plates while fig 1 b shows the IR spectrum of the same compound collected as vapour. Explain also the differences between the two spectrum. (4  $\frac{1}{2}$  marks)
- (ii) How might the following pairs of isomers be distinguished from infrared absorption spectra, assuming you have both spectra for each pair propiophenone,  $\text{PhCOCH}_2\text{CH}_3$  and phenylacetone. (1 mark)
- (iii) The hydrolysis of an ester  $\text{R COO R}$ , in dilute aqueous KOH produces the alcohol and the potassium salt of the carboxylic acid. The progress of the hydrolysis can be followed by infrared spectroscopy. Suggest how this procedure might

be carried out using a prominent infrared feature as a marker. (1  $\frac{1}{2}$  marks)

**QUESTION FOUR (20 MARKS)**

4. (a) (i) Explain various factors which contribute to proton NMR spectra of compounds such as  $RCONH_2$  with protons bonded to the nitrogen atom to be complicated. (6 marks)

(ii) Account for small broad peaks located at 6.3 and 6.6 ppm as shown by HNMR spectra of propionamide given in fig 2. (4  $\frac{1}{2}$  marks)

(b) (i) Figure 3 shows the mass spectrum of a certain organic compound. Deduce the structure of the compound. (7 marks)

(ii) The dominant mass analyzer in proteomics, especially if matrix-associated laser desorption/ionization (MALDI) is used is the time of flight (TOF). However, the dominant mass analyzer in GC-MS and LC-MS remains the quadrupole. Explain what it is about these applications and mass analyzers that make one or the other preferred. (1 mark)

(iii) A singly protonated ion having  $M/Z = 375.9$  is initially accelerated by an electric potential of 5,000 V. After it is accelerated, it enters a homogeneous magnetic field with a strength of 4 T, applied perpendicular to the path of the ion's travel. Calculate the resultant radius of curvature for this ion in the magnetic field

$$\{IV=1 \quad JC^{-1}, 1J=1 Kg m^2 s^{-2}, 1C=IAS, e=1.602 \times 10^{-19} C$$

$$1u=1 amu=1.6605 \times 10^{-27} kg,$$

$$1T=1 Kg C^{-1} S^{-1}=1 Kg A^{-1} s^{-2}, v(velocity)=m s^{-1} \}$$


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