**CHUKA** **UNIVERSITY**

# UNIVERSITY EXAMINATIONS

## FOURTH YEAR EXAMINATION FOR THE AWARD OF
## DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

**CHEM 437: ORGANIC SPECTROSCOPY**

**STREAMS:**

**TIME: 2 HOURS**

**DAY/DATE : WEDNESDAY 22 /09/ 2021**                 **8.30 AM – 10.30 AM**

**INSTRUCTIONS TO CANDIDATES:**
- Answer Question One and any other Two Questions.
- DO NOT WRITE ANYTHING on the question paper.

**QUESTION ONE (30 MARKS)**

1.      a)      Calculate the wavelength of the absorption maximum of the following compounds

b.  (i)  Assign the structure shown to the respective isomer on the basis of this
information; the α- Isomer shows a peak at 228 nm ( $\in$ =14,000) while the
β –  Isomer has a band at 296 nm ( $\in$ =11,000).

[5 Marks]

(ii)  Justify the following statement

The compound                              (structure 1) will absorb at longer wavelength compared
to                              (structure II)                              [$1\frac{1}{2}$ Marks]

c. (i)  The molar absorptivity of the B1 (III) thiorea complex is 9.3 x$10^3$ L cm -1 mol$^{-1}$ at
470nm. What concentration of this complex would be needed to produce a solution with

a  transmittance of 6.85% when measured in a 1.0 cm cell at this wavelength.[$\frac{1}{2}$ Mark]

(ii)  Determine the following frequency in hertz

(I)  The calcium emission line at 422.7nm                              [$1\frac{1}{2}$ Marks]

(II)  An infrared absorption peak at 3.00 *HM*                              [1 Mark]

(III)  The line in the x-ray emission spectrum of potassium at 3.742 A$^0$                              [1 Mark]

(IV)  The microwave beam with a wavelength of 250 cm.                              [$\frac{1}{2}$ Mark]

$[1\text{m} = 10^6 HM = 10^9\text{nm} = 10^2\text{cm} = 10^{10}\text{A}^0$

$h = 6.62608 \times 10^{-34}$ JS, $C = 3.0 \times 10^8$ m/s

(d) A 2.83 x 10-4 M solution of potassium permanganate has a molar absorbance of 0.510 when measurement in 1.00 cm cell at 520 nm. Calculate

(i)     The molar absorptivity for $kmn0_4$ at this wavelength                    [$^1/_2$ Mark]

(ii)    The absorptivity when the concentration is expressed in PPM (k=39.098, Mn =54.938 , 0

        =15.999                                                                [$1^1/_2$ Mark]

(iii)   The concentration of permanganate in a solution that has an absorbance of 0.697 when
        measured in 1.5 cm cell at 520nm.                                     [$^1/_2$ Mark]

(iv)    The transmittance of the solution in (d (iii))                        [1 Mark]

(v)     The absorbance of a solution that has twice the transmittance of the solution in (d(iii)

                                                                             [1 Mark]

## QUESTION TWO (20 MARKS)

2a.     (i)     Describe the principle of Mclafferty Rearrangements using suitable examples.

                                                                             [4 Marks]

        (ii)    Outline the mode of fragmentation during mass spectrometric study of the
                        following compounds leading to the peaks at indicated m/z

(I)     Methylbut anoate at m/e 74 and 79.                                   [1 Mark]

(II)    Benzyl methyl ether at $m/e$ 91 and 65                               [2 Marks]

        (iii)   How will you distinguish 3-methylcyclonexene and 4-methyl-cyclonexene and 4-
                        methyl-cyclonexene using mass spectroscopy.                    [1
Mark]

        (iv)    An organic compound gave a peak at m/z 122 (w) and another peak of nearly
                        equal intensity at m/z 124 in its mass spectrum.  What is the likely
molecular                        formula of the compound?
        [$2^1/_2$ Marks]

b (i)   In the mass spectrum of an unsaturated hydrocarbon, the molecular ion peak has relative intensity 70.0, the m+1 peak 4.7 and the base peak a relative intensity of 100.  How many carbon atoms are there in the hydrocarbon per molecule.          [1 Mark]

 (ii)   State various types of ions produced in a mass spectrometer.          [2$\frac{1}{2}$ Marks]

(iii)   An unknown substance has a molecular ion peak at m/z =107, with a relative intensity of 100.  The relative intensity of the M+1 Peak is 8.00 and the relative intensity of the m+2 peak    is 0.30.  What is the   molecular formula for this unknown.          [3 Marks]

(iv)   The mass spectral data of an unknown liquid are given below.  What is the molecular formula of this unknown?

   m/z          intensity

   78          23.6 ($m^r$)

   79          0.79

   80          7.55

   81          0.25

                                                                        [3 Marks]

**QUESTION THEEE (20 MARKS)**

3.      a)      Discuss real deviation from lambert – Beer's law.          [5 Marks]

        b)      Write short notes on the following in relation to sample handling
                        techniques in infrared spectroscopy.

        i)      Vapour Phase                                              [1$\frac{1}{2}$ Marks]

        ii)     Liquid film                                               [1 Mark]

        iii)    Solution                                                  [4$\frac{1}{2}$ Mark]


c.      (i)     Why does hydrogen bonding lower the absorption frequency.[4 Marks]

        (ii)    Distinguish between Inter and intra molecular hydrogen bondings.

                                                                        [4 Marks]

**QUESTION FOUR (20 MARKS)**

4a.    (i)    Assign the bands of the IR Spectrum given fig 1                    [21/2 Marks]

       (ii)    Consider the reaction between 1, 4- dinitro -1, 3- cyclohex adine with styrene to
                give a product compare the spectra of the initial compound and product in
fig 2

       (iii)    Assign the fundamental bands of the IR spectrum given in Fig.3     [$2^1/_2$ Marks]

       (iv)    Compare the spectra shown in Fig.4 to Fig.6 and make a qualitative evaluation of
                the effect of substituents at the α –positions with respect to the –No2
ground.  On                    the positions of the absorption bands of the nitro group and of the
double bond.
        [$6^1/_2$ Marks]

       b.    The IR Spectrum of CO shows a vibrational absorption band centered at 2170cm-
1

       (i)    What is the force constant for the CO band?                    [$2^1/_2$ Marks]

       (ii)    At what wave number would the corresponding peak for $^{14}CO$ occur

              C=12, 0 =16, Na = 6.02214 x $10^{23}$

              Mol-1, C=2.99792558 x$10^8$ m/s                    [2 Marks]

       c.    Explain the parameters given below in relation to high resolution NMR spectra.

(i) Chemical shifts [$^1/_2$ Mark]

(ii) Spin-spin coupling constants [$1^1/_2$ Marks]

(iii) Integrated intensities [$^1/_2$ Mark]

(iv) Line widths and shifts as function of parameters like temperature or concentrations. [1 Mark]