

CHUKA



UNIVERSITY

## UNIVERSITY EXAMINATIONS

## EXAMINATION FOR BACHELOR OF SCIENCE (CHEMISTRY)

CHEM 405: ANALYTICAL CHEMISTRY II

STREAMS: BSc

TIME: 2 HOURS

DAY/DATE: MONDAY 27/09/2021

2.30 P.M. – 1.30 P.M.

## INSTRUCTIONS

- Answer question one and any two questions
- Do not write on the question paper

## QUESTION ONE (30 MARKS)

1. A) Explain the following as used in the spectroscopy

- |                         |           |
|-------------------------|-----------|
| (i) Detection limit     | (½ marks) |
| (ii) Thermal noise      | (1 mark)  |
| (iii) Short noise       | (½ marks) |
| (iv) Flicker noise      | (1 marks) |
| (v) Environmental noise | (2 marks) |

b) i) Suggest ways of reducing various fundamental noise. (3½ marks)

ii) The detection limit of an analytical instrument is quoted as 0.0005 absorbance.

Determine the transmittance of the instrument at this detection limit. (1 marks)

iii) Red light and blue light are having wavelengths of 0.0007mm and 0.0004mm respectively in a vacuum. Calculate the wave length  $\lambda$  blue and  $\lambda$  red and wave number  $\bar{\nu}$  blue and  $\bar{\nu}$  red for red and blue light in glass {speed of light in vacuum =  $3 \times 10^{10}$  cm/sec,  $n_{\text{vacuum}} = 1.0$ ,  $n_{\text{glass}} = 1.52$ } (4 marks)

iv) Calculate the energy in Joule  $\text{Mol}^{-1}$  of Photons of wavelength  $3000 \text{ \AA}$  { $h = 6.62 \times 10^{-34}$  Js,  $c = 3 \times 10^8 \text{ m s}^{-1}$ ,  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ ,  $1 \text{ \AA} = 10^{-10} \text{ m}$ } (2 marks)

v) Suppose that the screen is at a distance of 2.0m and the slit spacing is 0.3mm. What is the wavelength of radiation if the fourth band is located 15.4mm from the central band.

(1 mark)

vi) Calculate percentage of reflection losses when radiation passes through glass ( $n_2 = 1.52$ ) at normal water ( $n_1 = 1.332$ )

(1½ marks)

c i) A sample in a 1.0cm cell transmits 80% light at a certain wavelength, if the absorptivity of this substance at this wavelength is 0.26. Calculate its concentration.

(2

marks)

ii) The concentration of yeast t-RNA in an aqueous solution is 10M. The absorbance is found to be 0.209 when this solution is placed in a 1.00cm cuvette and 258nm radiations are passed through it.

I. Calculate the specific absorptivity, including units of yeast t-RNA. (1 mark)

II. What will be the absorbance if the solution is 5M? (1 mark)

III. What will be the absorbance if the path length of the original solution is increased to 5.0cm? (1 mark)

iii) Calculate the concentration of methyltestosterone in an ethanolic solution of which the absorbance in cm cell at its  $\lambda_{\max}$ , 241nm, was found to be 0.8910. The  $A_{1\text{cm}}^{1\%}$  in the B.P monograph of methyltestosterone is given as 540 at 241nm.

iv) Calculate the concentration in  $\text{Mgml}^{-1}$  of a solution of tryptophan (molecular weight 204.2) in 0.1M hydrochloric acid, giving an absorbance at its  $\lambda_{\max}$ , of 0.613

d i) What do the x and y axis in an XRD pattern represent. (1½ marks)

ii) What information does the XRD pattern of a crystal provide? (½ marks)

iii) Explain why peaks of different heights are observed in the XRD. (2 marks)

### QUESTION TWO (20 MARKS)

2. a) i) Outline the advantages and disadvantages of x-ray Fluorescence method. (4 marks)

ii) Explain the following:

- I. Luminescence (½ marks)
- II. Fluorescence (½ marks)
- III. Phosphorescence (½ marks)

iii) Calculate the x-ray fluorescence emission which appears as a strong peak at  $2\theta = 46.82^\circ$  on being diffracted by the analyzer crystal having a “d” spacing of  $2.24 \text{ \AA}$   
(1 mark)

b i) Explain why tetramethylsilane (TMS) was chosen as a reference in NMR studies.  
(2½ marks)

ii) Describe how NMR spectrometer performance are characterized. (2½ marks)

C i) Outline factors affecting Thermogravimetric curve. (6 marks)

ii) Discuss the application of polarimetry techniques in food industry.

### QUESTION THREE (20 MARKS)

3. a) i) Discuss chemical deviation as one of the limitations of Lambert – Beer’s Law. (4 marks)
- ii) A mines (weak base) from salts with picric acid (trinitrophenic) and all a mine picrates exhibit an absorption maximum at 359 nm with a molar absorptivity of  $1.25 \times 10^4$ . 0.200g sample of aniline,  $C_6H_5NH_2$  is dissolved in 500ml of water. A 25.0ml aliquot is reacted with picric acid in a 250ml volumetric flask and diluted to volume. A 10.0ml aliquot of this is diluted to 100ml and the absorbance read at 359nm in a 1cm cell. If the absorbance is 0.425, what is the percent purity of the aniline? (3 marks)
- b) i) State five requirement for effective coupling interaction in IR spectroscopy.  
(2½ marks)
- ii) How many bands due to fundamental vibrations do you expect to observe in the IR spectrum of water. (3 marks)
- iii) List five requirements for the absorption of IR radiation by molecules. (2½ marks)

c i) calculate the approximate wave number and wavelength of the fundamental absorption due to the stretching, vibration of carbonyl groups CO. The force constant =  $1 \times 10^3 \text{ N/M}$   $\{N_A = 6.0 \times 10^{23} \text{ C} = 12, \text{ O} = 16, \text{ C} = 3.0 \times 10^{10} \text{ cm/s}\}$  (2½ marks)

ii) Discuss the various non-fundamental bands which increases the number of bands as compared to that expected from the theoretical number of fundamental vibrations.

(2½

marks)

#### QUESTION FOUR (20 MARKS)

4. a) i) Assign the fundamental absorption bands of the IR spectrum shown in fig 1 and fig 2. (2½ marks)

ii) Describe various sample handling techniques pertaining the sample in solid state.

(6½

marks)

b) Using IR spectroscopy, how will you distinguish the following isomeric compounds.



C i) State the benefits and limitations of electrospray ionization method. (5½ marks)

ii) Outline factors governing fragmentations processes in mass spectrometer.

(1½

marks)

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